Supplementary Information (SI) for Physical Chemistry Chemical Physics.

An All-Atom Force Field for MD Simulations on Organosulfur and Organohalogen Active Pharmaceutical Ingredients Developed from Experimental Sublimation Enthalpies and Single Crystal X-Ray Diffraction Data

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1. General

The uncertainties quoted were assigned following previous recommendations.[1] The standard errors of the mean (u) were computed as:

$$u = \sqrt{\frac{\sum_{i}^{n}(x_i - <x>)^2}{n(n-1)}}$$ (S* MERGEFORMAT 1)

where $<x>$ is the average value of the measured quantity, obtained from n independently determined x_i values.

The uncertainties quoted for the standard molar enthalpies of fusion, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}^{\mathrm{o}}$, correspond to expanded uncertainties for a 95% confidence level, $U = 2u$. Those assigned to the standard molar enthalpies of sublimation and vaporization, $\Delta_{\mathrm{sub/vap}}H_{\mathrm{m}}^{\mathrm{o}}$, represent combined expanded uncertainties for a 95% confidence level ($U_{\mathrm{c}} = 2u_{\mathrm{c}}$), including the uncertainties of the electrical calibration, ε, and the main experiment:

$$u_{\mathrm{c}} = M \cdot \Delta h \sqrt{\left(\frac{u_{\Delta h}}{\Delta h}\right)^2 + \left(\frac{u_{\varepsilon}}{\varepsilon}\right)^2}$$ (S* MERGEFORMAT 2)

where Δh represents a specific enthalpy of sublimation or vaporization.

The molar masses, M, determined using the conventional atomic weights recommended by the IUPAC Commission in 2013,[2] were used to calculate the molar quantities. For SN $M(C_6H_8N_2O_2S)$ = 172.202 g mol^{-1}, for SP $M(C_{11}H_{11}N_3O_2S)$ = 249.288 g mol^{-1}, for CZ $(C_7H_4ClNO_2)$ = 169.564 g mol^{-1}, for CI $M(C_9H_5ClNO)$ = 305.499 g mol^{-1}, and for TR $M(C_{12}H_7Cl_3O_2)$ = 289.536 g mol^{-1}.

2. ^{1}H-NMR Results

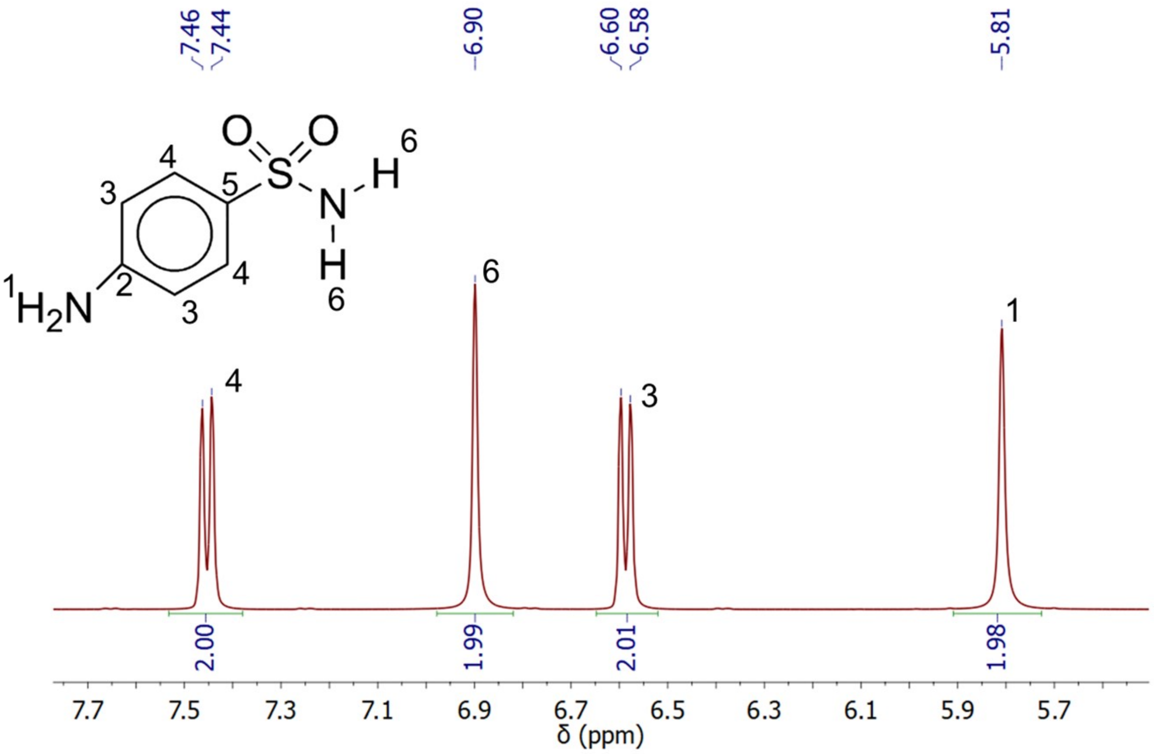


Figure S1. ^{1}H-NMR spectrum of sulfanilamide (SN) in DMSO-d_6 at 293 K.

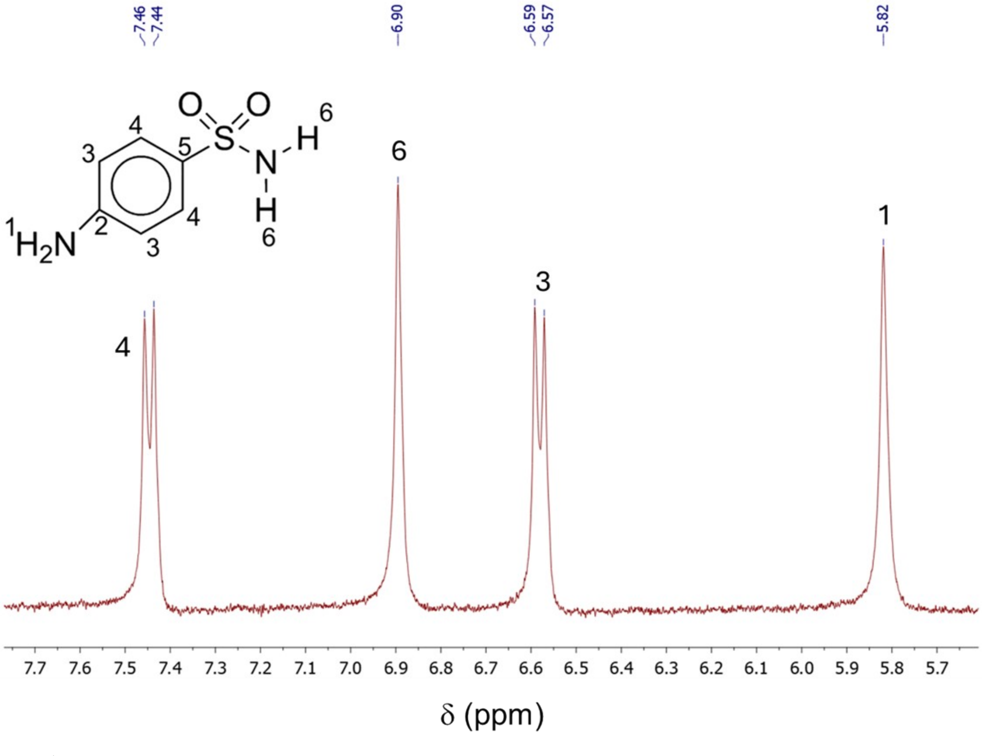


Figure S2. ^{1}H-NMR spectrum of a DMSO-d_6 solution of sublimed sulfanilamide (SN) at 293 K.

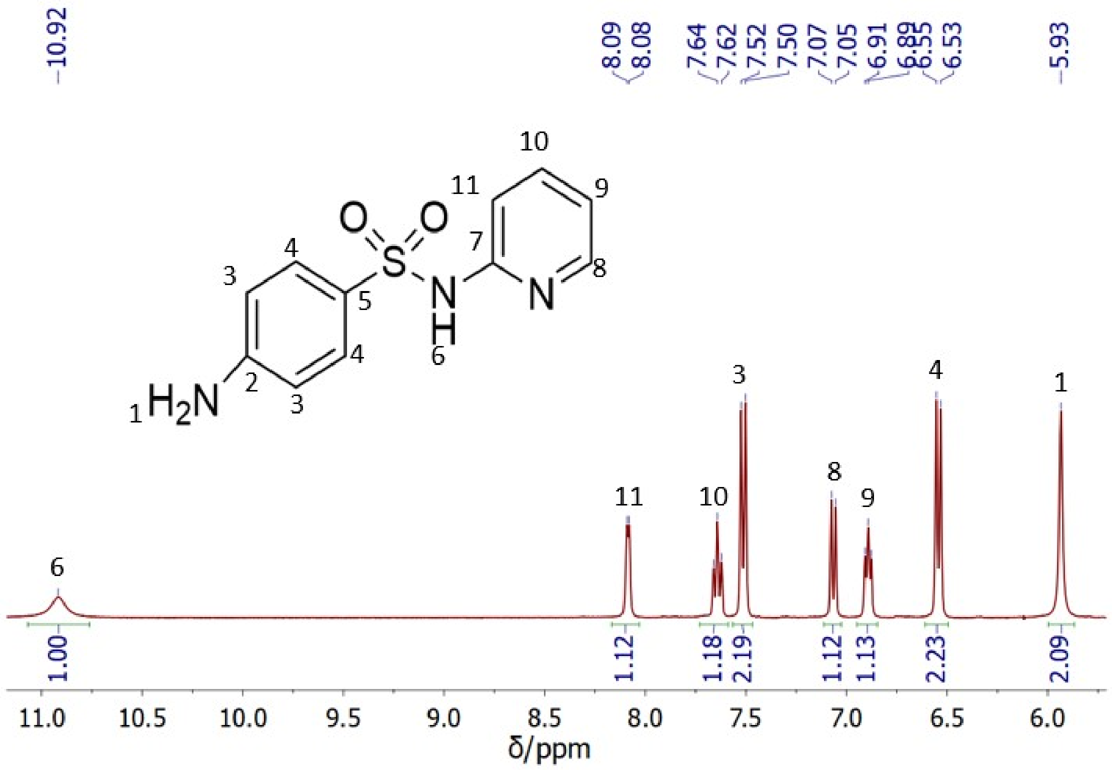


Figure S3. ^{1}H-NMR spectrum of sulfapyridine (SP) in DMSO-d_6 at 293 K.

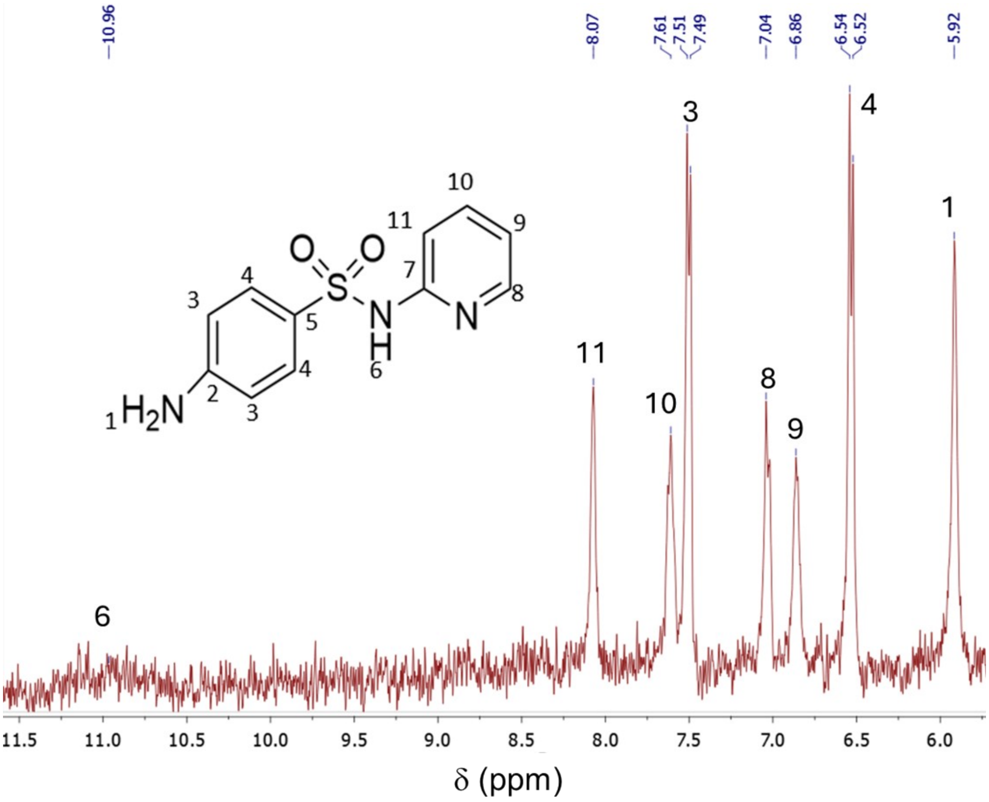


Figure S4. ^{1}H-NMR spectrum of a DMSO-d_6 solution of sublimed sulfapyridine (SP) at 293 K.

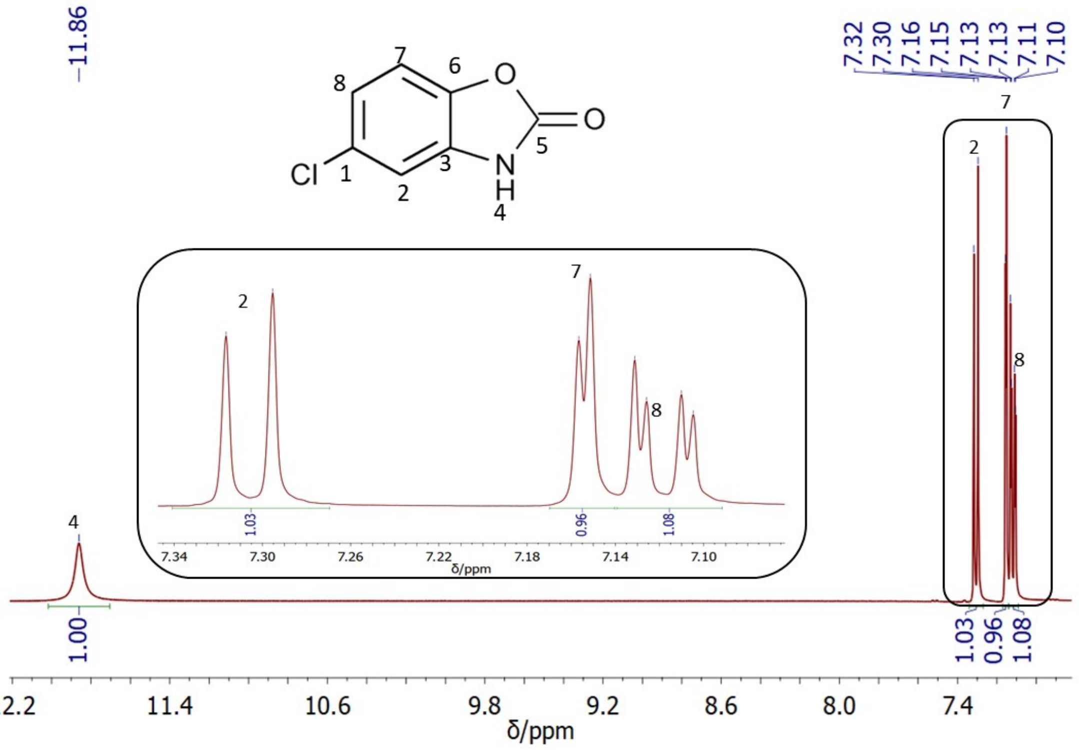


Figure S5. ^{1}H-NMR spectrum of chlorzoxazone (CZ) in DMSO-d_6 at 293 K.

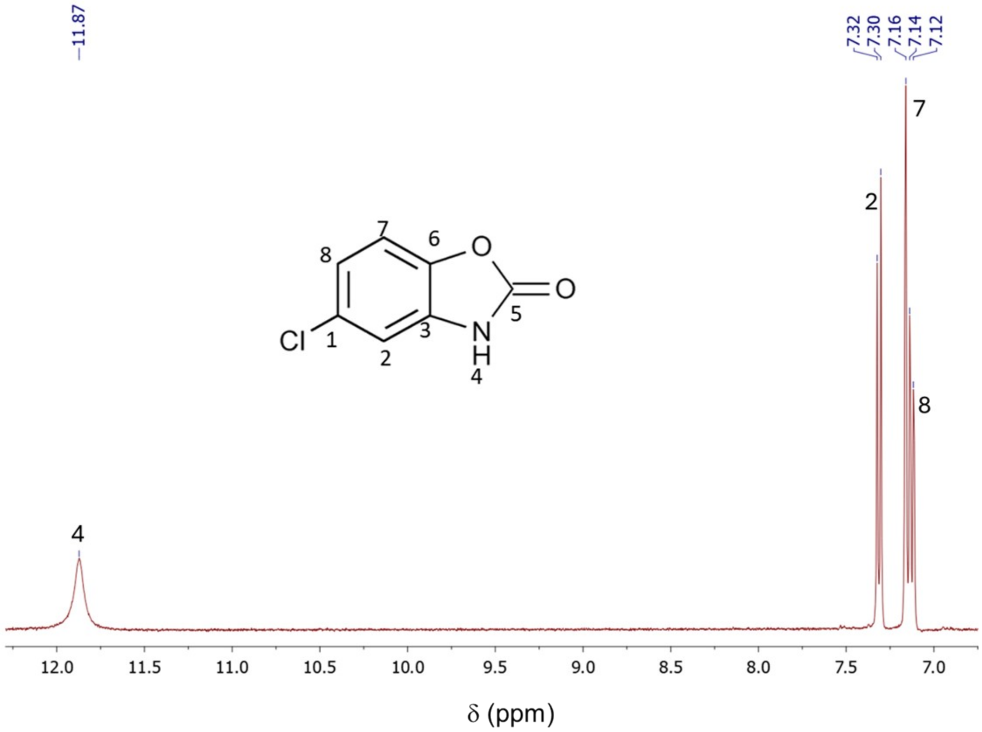


Figure S6. ^{1}H-NMR spectrum of a DMSO-d_6 solution of sublimed chlorzoxazone (CZ) at 293 K.

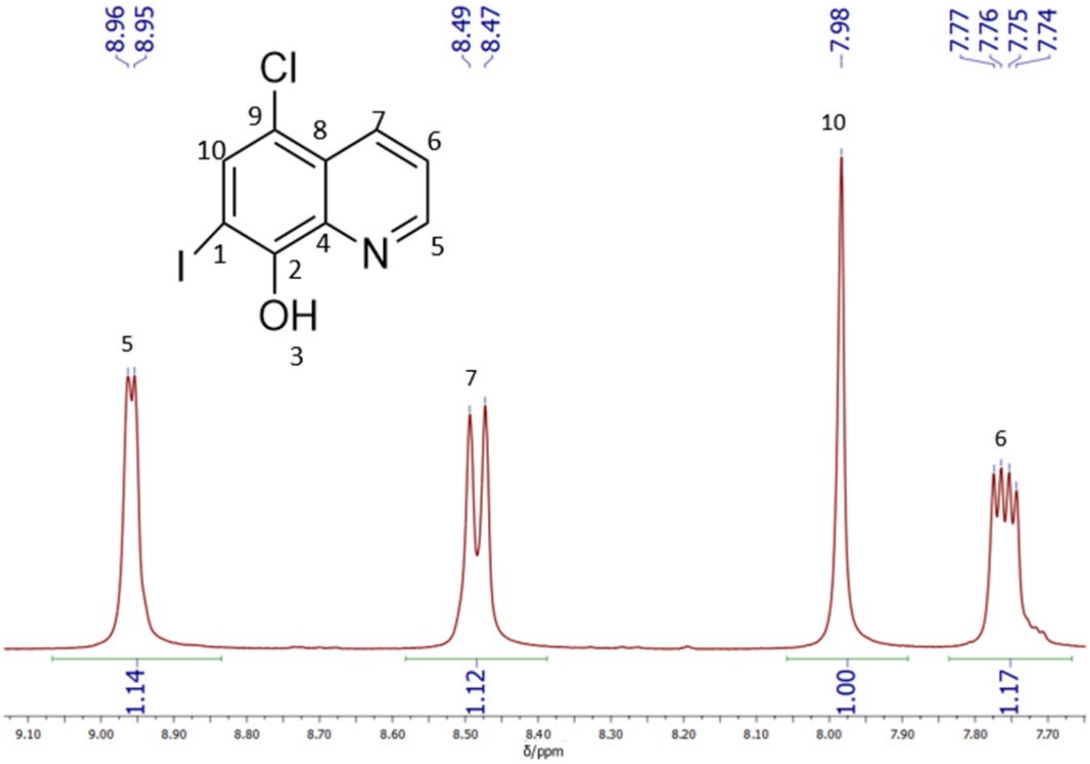


Figure S7. ^{1}H-NMR spectrum obtained for clioquinol (CI) in DMSO-d_6 at 293 K.

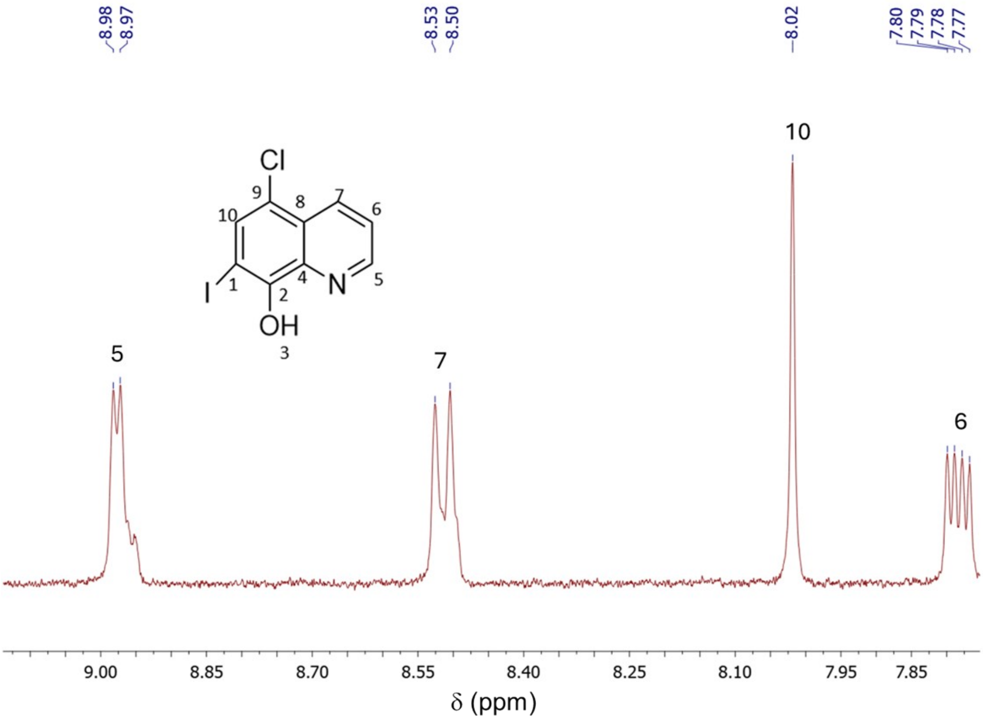


Figure S8. ^{1}H-NMR spectrum of a DMSO-d_6 solution of sublimed clioquinol (CI) at 293 K.

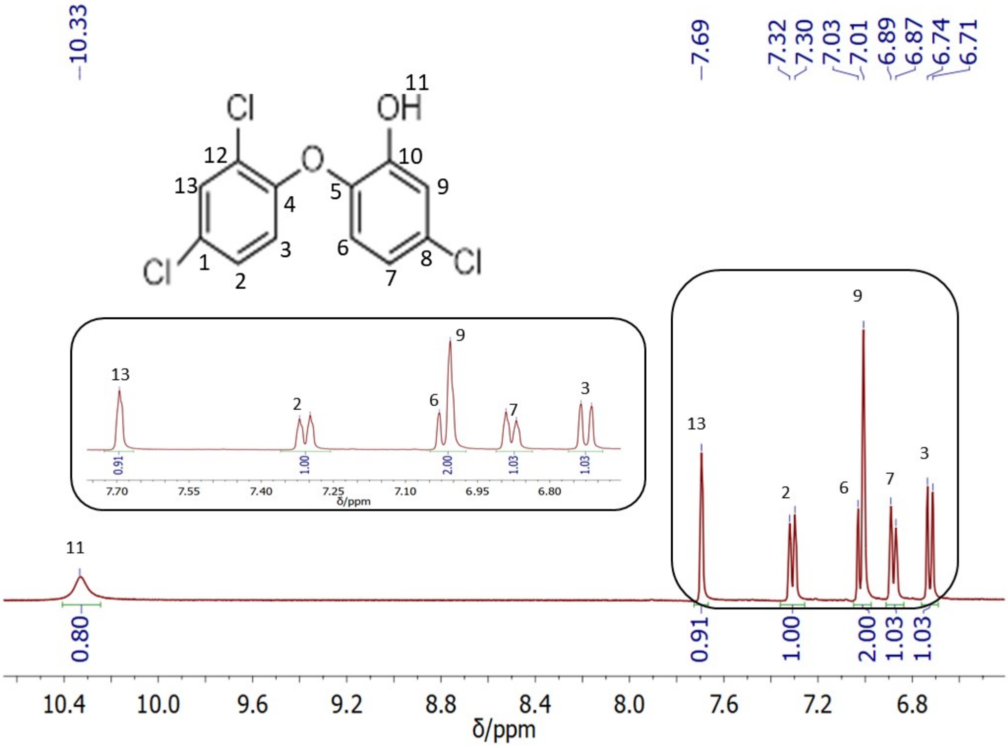


Figure S9. ^{1}H-NMR spectrum obtained for triclosan (TR) in DMSO-d_6 at 293 K.

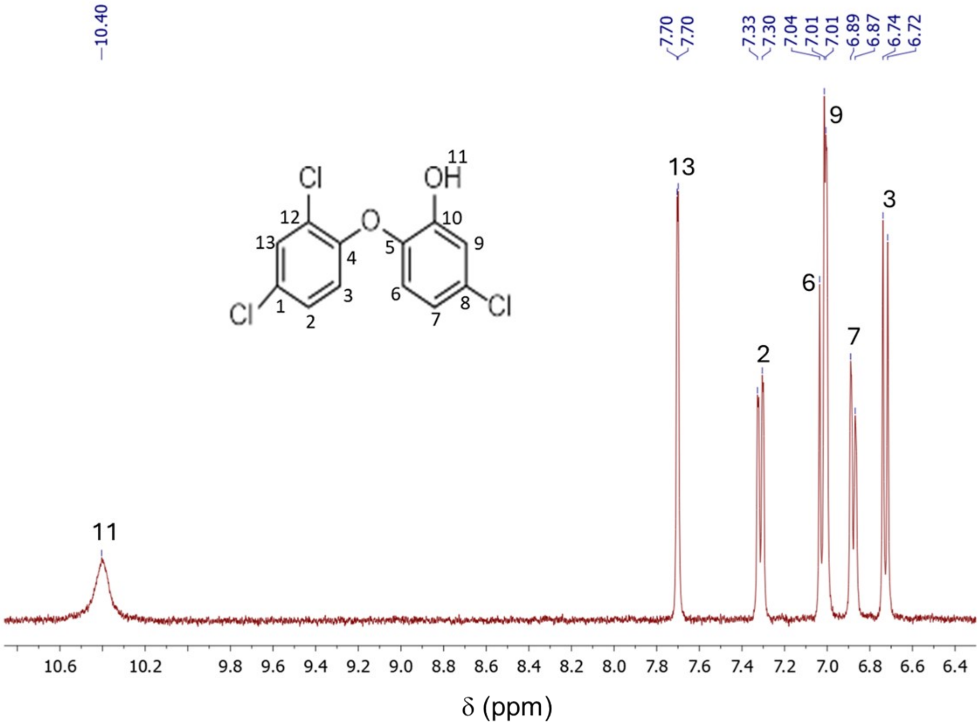


Figure S10. ^{1}H-NMR spectrum of a DMSO-d_6 solution of sublimed triclosan (TR) at 293 K.

3. X-ray Powder Diffraction

Table S1. Indexation of the powder X-ray diffraction pattern of sulfanilamide to the monoclinic space group $P2_1/c$, with unit cell parameters $a \pm u$ = 899.4±0.9 pm, $b \pm u$ = 902.3±0.4 pm, $c \pm u$ = 1005.2±0.1 pm, $\beta \pm u$ = 111.55±0.10 °, and density ρ = 1507.4±5.1 kg m^{-3}.[a] h, k, l are the Miller indices, 2θ(obs) is the angle corresponding to the maximum of the peaks in the experimental diffraction pattern, and $\Delta 2\theta$ is the difference between the experimental and computed diffraction peaks obtained based on the indexed unit cell parameters. (p = 0.1 MPa).[b]

h	k	l	2θ(obs)/°	$\Delta 2\theta$/°
1	0	0	10.555	-0.010
0	1	1	13.610	-0.017
1	1	0	14.395	-0.031
-1	0	2	17.995	-0.013
0	0	2	18.965	-0.001
1	1	1	19.290	-0.015
0	2	0	19.615	-0.047
-1	1	2	20.535	-0.003
2	0	0	21.220	-0.001
0	1	2	21.385	-0.002
0	2	1	21.860	0.004
-2	1	1	22.150	0.015
-2	0	2	22.740	0.021
2	1	0	23.435	0.015
1	0	2	24.955	-0.018
1	2	1	25.835	-0.001
-1	2	2	26.795	0.010
2	1	1	28.140	-0.001
-1	1	3	28.400	0.007
2	2	0	29.085	-0.002
-2	2	2	30.205	-0.014
-2	1	3	30.430	-0.002
-3	1	1	31.480	-0.017
1	2	2	32.000	0.017
2	2	1	33.080	0.016
1	3	1	34.225	0.033

[a] The uncertainties correspond to standard deviations of the mean, u, estimated as described in reference 3, and in the case of ρ referring to combined standard uncertainties, u_c, calculated as recommended in reference 4; [b] $u(p)$= ±5 kPa.

Table S2. Indexation of the powder X-ray diffraction pattern of sulfapyridine to the monoclinic space group *C*2/c, with unit cell parameters $a \pm u$ = 1271.5±3.8 pm, $b \pm u$ = 1166.9±2.7 pm, $c \pm u$ = 1537.3±5.7 pm, $\beta \pm u$ = 93.70±1.00° and density $\rho \pm u$ = 1454.9±15.7 kg m^{-3}. [a] *h*, *k*, *l* are the Miller indices, 2θ (obs) is the angle corresponding to the maximum of the peaks in the experimental diffraction pattern, and $\Delta 2\theta$ is the difference between the experimental and computed diffraction peaks obtained based on the indexed unit cell parameters. (p = 0.1 MPa).[b]

h	*k*	*l*	2θ(obs)/°	$\Delta 2\theta$/°
0	0	2	11.600	0.073
1	1	1	12.115	0.098
2	0	0	13.940	-0.008
0	2	0	15.130	-0.043
1	1	2	15.790	-0.020
0	2	1	16.225	-0.015
-2	0	2	17.500	-0.043
0	2	2	19.140	0.044
-1	1	3	19.800	0.002
1	1	3	20.625	0.043
3	1	0	22.265	-0.075
-3	1	1	22.655	-0.086
3	1	1	23.380	-0.050
2	2	2	24.215	0.046
-1	3	1	24.460	-0.043
-1	1	4	25.010	0.020
1	1	4	25.830	0.000
-2	0	4	26.205	-0.141
1	3	2	26.850	0.033
4	0	0	28.015	-0.093
-1	3	3	29.390	-0.015
-2	2	4	30.595	0.054
4	0	2	31.115	-0.059
-3	3	1	31.395	-0.115
4	2	0	32.010	-0.081
-4	2	1	32.800	0.505
-1	3	4	33.200	-0.011
-2	4	1	34.110	-0.036

[a] The uncertainties correspond to standard deviations of the mean, u, estimated as described in reference 3, and in the case of ρ referring to combined standard uncertainties, u_c, calculated as recommended in reference 4; [b] $u(p)$= ±5 kPa.

Table S3. Indexation of the powder X-ray diffraction pattern of chlorzoxazone to the triclinic space group $P\bar{1}$ with unit cell parameters $a\pm u$ = 381.7±0.4 pm, $b\pm u$ = 902.1±0.8 pm, $c\pm u$ = 1004.8±0.8 pm, $\alpha\pm u$ = 93.38±0.08°, $\beta\pm u$ = 95.50±0.08°, $\gamma\pm u$ = 98.32±0.09°, and density $\rho\pm u$ = 1657.2±5.4 kg m^{-3}.[a] h, k, l are the Miller indices, 2θ(obs) is the angle corresponding to the maximum of the peaks in the experimental diffraction pattern, and $\Delta 2\theta$ is the difference between the experimental and computed diffraction peaks obtained based on the indexed unit cell parameters. (p = 0.1 MPa).[b]

h	k	l	2θ(obs)/°	$\Delta 2\theta$/°
0	0	1	8.920	0.061
0	-1	1	12.865	0.045
0	1	1	13.840	0.037
0	0	2	17.800	0.029
0	2	0	19.950	0.018
0	1	2	21.020	-0.016
0	-2	1	21.250	0.018
-1	0	1	24.435	0.026
-1	1	1	25.255	-0.001
0	-2	2	25.820	0.016
1	-1	1	26.495	0.001
-1	-1	1	27.495	-0.021
0	-1	3	27.815	-0.107
-1	0	2	28.170	-0.003
-1	2	0	28.650	-0.015
0	1	3	29.365	0.026
0	3	0	30.075	-0.017
-1	-1	2	30.700	-0.010
1	0	2	31.275	0.008
0	3	1	32.055	-0.019
0	-2	3	32.400	0.028
1	2	0	33.440	0.001
-1	0	3	34.060	0.013
0	2	3	34.815	-0.012

[a] The uncertainties correspond to standard deviations of the mean, u, estimated as described in reference 3, and in the case of ρ referring to combined standard uncertainties, u_c, calculated as recommended in reference 4; [b] $u(p)$= ±5 kPa.

Table S4. Indexation of the powder X-ray diffraction pattern of clioquinol to the monoclinic space group *P*2/c, with unit cell parameters $a \pm u$ = 1455.4±2.2 pm, $b \pm u$ = 412.7±0.8 pm, $c \pm u$ = 1660.5±2.4 pm, $\beta \pm u$ = 111.63±0.14°, and density $\rho \pm u$ = 2188.5±13.5 kg m^{-3}.[a] *h*, *k*, *l* are the Miller indices, 2θ (obs) is the angle corresponding to the maximum of the peaks in the experimental diffraction pattern, and $\Delta 2\theta$ is the difference between the experimental and computed diffraction peaks obtained based on the indexed unit cell parameters. (p = 0.1 MPa).[b]

h	*k*	*l*	2θ(obs)/°	$\Delta 2\theta$/°
1	0	0	6.590	0.062
0	0	2	11.505	0.049
2	0	0	13.130	0.053
1	0	2	15.170	0.014
-3	0	2	18.745	-0.018
-3	0	0	19.705	0.035
2	0	2	20.390	0.007
-1	0	4	21.460	-0.014
-2	0	4	21.890	-0.002
0	0	4	23.015	-0.013
-3	0	4	24.210	0.025
3	0	2	26.260	-0.027
-4	0	0	26.350	0.021
-4	0	4	27.900	-0.021
-1	1	4	30.580	0.000
-5	0	2	30.680	-0.018
4	0	2	32.520	-0.041
-1	0	6	32.925	-0.003
-3	0	6	33.100	0.003
0	0	6	34.855	0.010

[a] The uncertainties correspond to standard deviations of the mean, u, estimated as described in reference 3, and in the case of ρ referring to combined standard uncertainties, u_c, calculated as recommended in reference 4; [b] $u(p)$= ±5 kPa.

Table S5. Indexation of the powder X-ray diffraction pattern of triclosan to the trigonal space group $P3_1$ with unit cell parameters $a\pm u$ = 1264.4±0.9 pm, $b\pm u$ = 1264.4±0.4 pm, $c\pm u$ = 672.1±1.1 pm, crystal density $\rho\pm u$ = 1550.1±6.4 kg m^{-3}.[a] *h*, *k*, *l* are the Miller indices, 2θ(obs) is the angle corresponding to the maximum of the peaks in the experimental diffraction pattern, and $\Delta 2\theta$ is the difference between the experimental and computed diffraction peaks obtained based on the indexed unit cell parameters. (p = 0.1 MPa).[b]

h	*k*	*l*	2θ(obs)/°	$\Delta 2\theta$/°
0	1	0	8.070	0.002
1	1	0	14.020	0.023
0	1	1	15.430	-0.027
0	2	0	16.165	-0.011
1	1	1	19.245	-0.015
0	2	1	20.945	0.034
1	2	0	21.435	-0.018
0	3	0	24.350	-0.017
1	2	1	25.285	0.033
0	3	1	27.790	-0.002
2	2	0	28.210	0.001
1	3	0	29.370	-0.016
2	2	1	31.245	0.000
1	3	1	32.310	-0.012

[a] The uncertainties correspond to standard deviations of the mean, u, estimated as described in reference 3, and in the case of ρ referring to combined standard uncertainties, u_c, calculated as recommended in reference 4; [b] $u(p)$= ±5 kPa.

4. Differential Scanning Calorimetry (DSC)

The DSC results are given in Figures S11 to S13 and Tables S6 to S11, where: m is the mass of the sample; T_{fus} and T_{max} are the onset and maximum temperatures of the fusion peak, respectively; T_{trs} and $T_{\text{max, trs}}$ are the onset and maximum temperatures of phase transitions, respectively; $\Delta_{\text{trs}}h$ and $\Delta_{\text{trs}}H_{\text{m}}^{\text{o}}$ are the specific and standard molar enthalpy of phase transitions, respectively; and $\Delta_{\text{fus}}h$ and $\Delta_{\text{fus}}H_{\text{m}}^{\text{o}}$ are the specific and standard molar enthalpy of fusion (assigned to T_{fus}), respectively. The errors correspond to the standard error of the mean, u, computed as described above, and those of $\Delta_{\text{fus}}H_{\text{m}}^{\text{o}}$ correspond to the expanded uncertainty for a 95% confidence level ($U = 2u$).

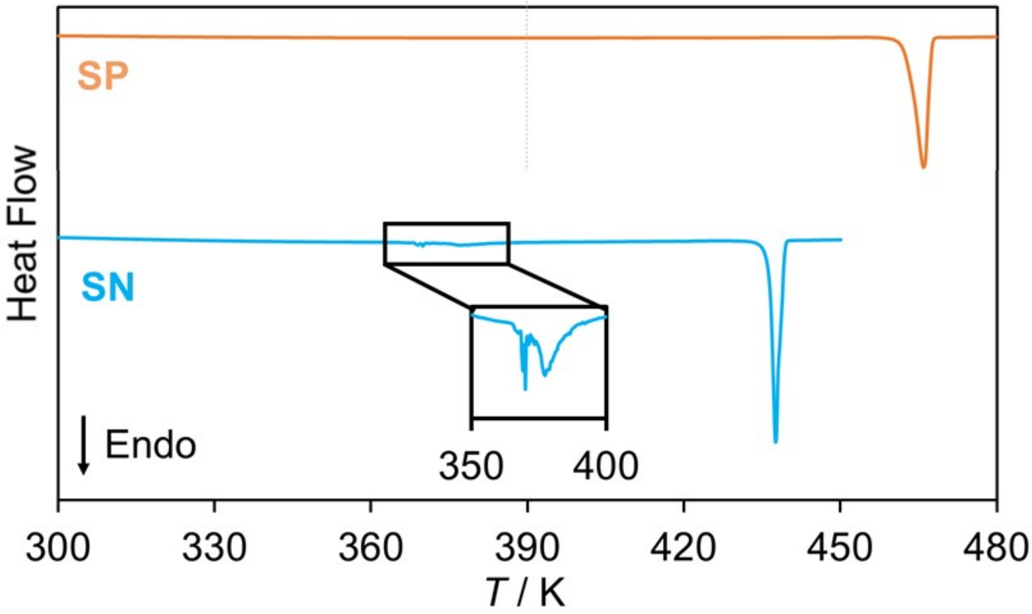


Figure S11. Typical DSC curves obtained at a heating rate of 5 K·min^{-1} for sulfapyridine (SP) and sulfanilamide (SN). The inset shows an enlargement of the heat flow curve of SN in the region of the $\beta \rightarrow \gamma$ phase transition.

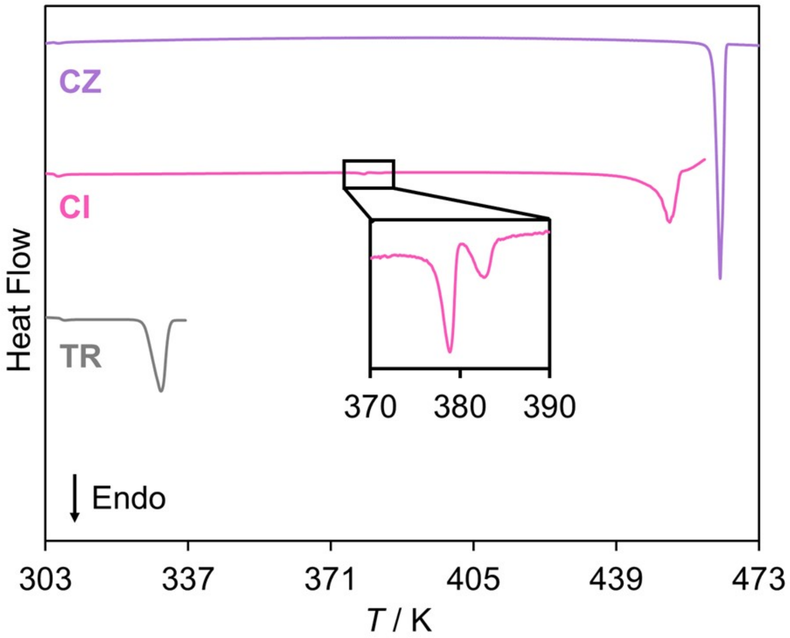


Figure S12. Typical DSC curves obtained at a heating rate of 5 K·min^{-1} for chlorzoxazone (CZ), clioquinol (CI), and triclosan (TR). The inset shows an enlargement of the heat flow curve of CI in the region of the phase transition.

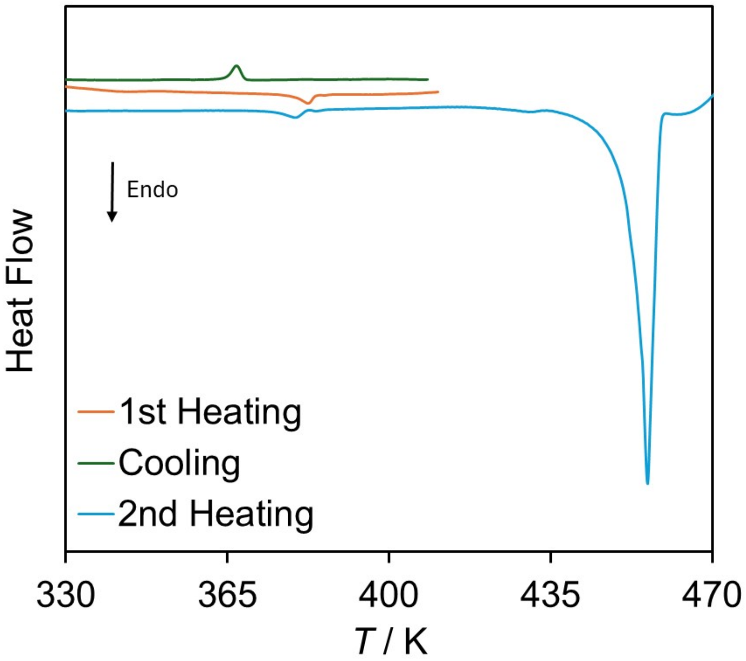


Figure S13. DSC curves obtained at a heating rate of 5 K min^{-1} for a sample of clioquinol (CI) using the following temperature program: (*i*) heating from 320 K to 413 K; (*ii*) cooling from 413 K to 320 K; (*iii*) heating from 320 K to 470 K.

Table S6. DSC results obtained for form β of sulfanilamide (SN) at a heating rate of 5 K min^{-1} (p^{o} = 0.1 MPa).[a]

	$\beta \rightarrow \gamma$ Transition			Fusion		
m /mg	T_{trs} /K	$T_{\mathrm{max,\ trs}}$ /K	$\Delta_{\mathrm{trs}}h$ /J g^{-1}	T_{fus} /K	T_{max} /K	$\Delta_{\mathrm{fus}}h$ /J g^{-1}
5.2683	368.96	379.50	7.74	437.98	439.75	136.52
3.9463	372.11	378.21	6.26	438.23	439.92	136.46
4.2936	369.51	376.67	7.59	438.05	439.59	135.23
3.8805	374.03	375.29	7.86	438.02	439.33	136.04
5.6510	368.74	378.72	9.52	438.12	439.75	138.79

[a] $u(m)$ = ±0.00005 mg; $u(T)$= ±0.1 K; $u(p)$= ±5 kPa. For $\Delta_{\mathrm{trs}}H_{\mathrm{m}}^{\mathrm{o}}$ and $\Delta_{\mathrm{fus}}H_{\mathrm{m}}^{\mathrm{o}}$ the expanded uncertainty of 95% confidence level (U=2u) is indicated. The symbol u denotes standard uncertainty.

$<T_{\mathrm{trs}}>\pm u = 370.7 \pm 1.0$ K
$<T_{\mathrm{max,\ trs}}>\pm u = 377.7 \pm 0.8$ K
$<\Delta_{\mathrm{trs}}h>\pm u = 7.8 \pm 0.5$ J g^{-1}
$<\Delta_{\mathrm{trs}}H_{\mathrm{m}}^{\mathrm{o}}>\pm U = 1.3 \pm 0.2$ kJ mol^{-1}

$<T_{\mathrm{fus}}>\pm u = 438.1 \pm 0.0$ K
$<T_{\mathrm{max}}>\pm u = 439.7 \pm 0.1$ K
$<\Delta_{\mathrm{fus}}h>\pm u = 136.6 \pm 0.6$ J g^{-1}
$<\Delta_{\mathrm{fus}}H_{\mathrm{m}}^{\mathrm{o}}>\pm U = 23.5 \pm 0.2$ kJ mol^{-1}

Table S7. DSC results obtained for sulfapyridine (SP) at a heating rate of 5 K min^{-1} (p^{o} = 0.1 MPa).[a]

m /mg	T_{fus} /K	T_{max} /K	$\Delta_{\mathrm{fus}}h$ /J g^{-1}
4.9342	462.80	466.12	153.11
4.9770	463.11	465.74	153.75
4.0796	463.72	466.00	154.01
4.2424	463.51	465.75	154.83
6.0490	463.61	466.50	153.94

[a] $u(m)$ = ±0.00005 mg; $u(T)$= ±0.1 K; $u(p)$= ±5 kPa. For $\Delta_{\mathrm{fus}}H_{\mathrm{m}}^{\mathrm{o}}$ the expanded uncertainty of 95% confidence level (U=2u) is indicated. The symbol u denotes standard uncertainty.

$<T_{\mathrm{fus}}>\pm u = 463.4 \pm 0.2$ K
$<T_{\mathrm{max}}>\pm u = 466.0 \pm 0.1$ K
$<\Delta_{\mathrm{fus}}h>\pm u = 153.9 \pm 0.3$ J g^{-1}
$<\Delta_{\mathrm{fus}}H_{\mathrm{m}}^{\mathrm{o}}>\pm U = 38.4 \pm 0.1$ kJ mol^{-1}

Table S8. DSC results obtained for chlorzoxazone (CZ) at a heating rate of 5 K min^{-1} (p^{o} = 0.1 MPa).[a]

m /mg	T_{fus} /K	T_{max} /K	$\Delta_{\text{fus}}h$ /J g^{-1}
4.7781	463.78	465.57	151.99
9.1400	462.79	465.48	153.43
4.5667	463.85	465.33	151.72
2.9994	463.56	465.08	150.58
5.4389	463.87	465.73	152.30

[a] $u(m)$ = ±0.00005 mg; $u(T)$= ±0.1 K; $u(p)$= ±5 kPa. For $\Delta_{\text{fus}}H_{\text{m}}^{\text{o}}$ the expanded uncertainty of 95% confidence level (U=2u) is indicated. The symbol u denotes standard uncertainty.

$$<T_{\text{fus}}>\pm u = 463.6 \pm 0.2\ \text{K}$$
$$<T_{\text{max}}>\pm u = 465.4 \pm 0.1\ \text{K}$$
$$<\Delta_{\text{fus}}h>\pm u = 152.0 \pm 0.5\ \text{J g}^{-1}$$
$$<\Delta_{\text{fus}}H_{\text{m}}^{\text{o}}>\pm U = 25.8 \pm 0.2\ \text{kJ mol}^{-1}$$

Table S9. DSC results obtained for clioquinol (CI) at a heating rate of 5 K min^{-1} (p^{o} = 0.1 MPa).[a]

	Phase Transition			Fusion		
m /mg	T_{trs} /K	$T_{\text{max, trs}}$ /K	$\Delta_{\text{trs}}h$ /J·g^{-1}	T_{fus} /K	T_{max} /K	$\Delta_{\text{fus}}h$ /J g^{-1}
1.3421	382.47	383.35	0.51	454.10	455.08	69.94
1.4907	380.85	382.58	1.02	450.99	453.79	73.05
1.0439	382.34	383.43	2.63	454.33	455.85	87.26
0.7540	379.24	381.12	2.42	455.33	456.53	84.45
0.6290	380.92	382.92	0.82	450.16	453.45	71.28

[a] $u(m)$ = ±0.00005 mg; $u(T)$= ±0.1 K; $u(p)$= ±5 kPa. For $\Delta_{\text{trs}}H_{\text{m}}^{\text{o}}$ and $\Delta_{\text{fus}}H_{\text{m}}^{\text{o}}$ the expanded uncertainty of 95% confidence level (U=2u) is indicated. The symbol u denotes standard uncertainty.

$$<T_{\text{trs}}>\pm u = 381.2 \pm 0.6\ \text{K}$$
$$<T_{\text{max, trs}}>\pm u = 382.7 \pm 0.4\ \text{K}$$
$$<\Delta_{\text{trs}}h>\pm u = 1.5 \pm 0.4\ \text{J g}^{-1}$$
$$<\Delta_{\text{trs}}H_{\text{m}}^{\text{o}}>\pm U = 0.5 \pm 0.2\ \text{kJ mol}^{-1}$$

$$<T_{\text{fus}}>\pm u = 453.0 \pm 1.0\ \text{K}$$
$$<T_{\text{max}}>\pm u = 454.9 \pm 0.6\ \text{K}$$
$$<\Delta_{\text{fus}}h>\pm u = 77.2 \pm 3.6\ \text{J g}^{-1}$$
$$<\Delta_{\text{fus}}H_{\text{m}}^{\text{o}}>\pm U = 23.6 \pm 2.2\ \text{kJ mol}^{-1}$$

Table S10. DSC results obtained for clioquinol (CI) at a cooling rate of 5 K min^{-1} from 410 K to 298 K (p^{o} = 0.1 MPa).[a]

	Phase Transition		
m /mg	T_{trs} /K	$T_{max, trs}$ /K	$-\Delta_{trs}h$ /J·g^{-1}
2.1515	368.72	364.76	1.68
2.3290	367.15	365.04	0.53

[a] $u(m)$ = ±0.00005 mg; $u(T)$= ±0.1 K; $u(p)$= ±5 kPa. For $\Delta_{trs}H^{o}_{m}$ the expanded uncertainty of 95% confidence level (U=2u) is indicated. The symbol u corresponds to the mean deviation.

$$<T_{trs}>\pm u = 367.9 \pm 1.6 \text{ K}$$
$$<T_{max, trs}>\pm u = 364.9 \pm 0.3 \text{ K}$$
$$<\Delta_{trs}h>\pm u = -1.1 \pm 1.2 \text{ J g}^{-1}$$
$$<\Delta_{trs}H^{o}_{m}>\pm U = -0.3 \pm 0.7 \text{ kJ mol}^{-1}$$

Table S11. DSC results obtained for triclosan (TR) at a heating rate of 5 K min^{-1} (p^{o} = 0.1 MPa).[a]

m /mg	T_{fus} /K	T_{max} /K	$\Delta_{fus}h$ /J g^{-1}
1.4126	328.00	330.88	90.89
2.2474	329.98	332.45	90.23
4.5739	329.85	332.67	90.31
3.2669	327.88	331.88	90.28
2.6844	327.69	332.05	89.72

[a] $u(m)$ = ±0.00005 mg; $u(T)$= ±0.1 K; $u(p)$= ±5 kPa. For $\Delta_{fus}H^{o}_{m}$ the expanded uncertainty of 95% confidence level (U=2u) is indicated. The symbol u denotes standard uncertainty.

$$<T_{fus}>\pm u = 328.7 \pm 0.5 \text{ K}$$
$$<T_{max}>\pm u = 332.0 \pm 0.3 \text{ K}$$
$$<\Delta_{fus}h>\pm u = 89.9 \pm 0.6 \text{ J g}^{-1}$$
$$<\Delta_{fus}H^{o}_{m}>\pm U = 26.0 \pm 0.3 \text{ kJ mol}^{-1}$$

5. Calvet-drop microcalorimetry

The results from the Calvet-drop microcalorimetry experiments are given in Tables S12 to S21. Here, *m* and *M* correspond to the mass and the molar mass of the sample, respectively; *A* and A_b are the area of the sublimation and blank experiments; T_i and T_f are the temperatures of the drop furnace and the calorimeter, respectively; $\Delta_\mathrm{sub/vap}h$ is the specific enthalpy of vaporization or sublimation of the compound; $\Delta_\mathrm{sub}H^\circ_\mathrm{m}$ is the standard molar enthalpy of sublimation; ε is the energy equivalent of the calorimeter; $\Delta^{\mathrm{cr,\ 298.15\ K}}_{\mathrm{cr/l},\ T_\mathrm{f}}H^\circ_\mathrm{m}$ and $\Delta^{\mathrm{g,\ 298.15\ K}}_{\mathrm{g},\ T_\mathrm{f}}H^\circ_\mathrm{m}$ are the enthalpy variation associated to the temperature change of the solid and gas at 298.15 K to the crystal/liquid and gas at T_f, respectively. Details regarding the uncertainty calculations can be found in section 1.

The gas phase enthalpy correction was evaluated from:

$$\Delta^{\mathrm{g,\ 298.15\ K}}_{\mathrm{g},\ T_\mathrm{f}}H^\circ_\mathrm{m} = \int_{T_\mathrm{f}}^{298.15} C^\circ_{p,\mathrm{m}}(\mathrm{g})\ dT \qquad \text{(S\textbackslash*}$$

MERGEFORMAT 3)

and

$$C^\circ_{p,\mathrm{m}}(\mathrm{g}) / \left(\mathrm{J\ K^{-1}\ mol^{-1}}\right) = a\left(T/\mathrm{K}\right)^2 + b\left(T/\mathrm{K}\right) + c \qquad \text{(S\textbackslash*}$$

MERGEFORMAT 4)

The coefficients of eq. S* MERGEFORMAT 4 are given in Table S22 and were obtained by fitting the heat capacity values obtained from the DFT calculations for the compounds in the gaseous phase using statistical thermodynamic calculations (see details in the main text).

Table S12. Calvet-drop microcalorimetry results obtained for the standard enthalpy of sublimation of sulfanilamide, SN (p^{o} = 1 bar).[a]

m /mg	A-A_{b} /mV s	T_{i} /K	T_{f} /K	$\Delta_{\mathrm{sub}}h$ /J g^{-1}
3.4596	160.115	297.02	419.11	740.177
5.0337	235.112	297.62	419.08	746.995
3.7046	171.384	298.02	419.09	739.876
4.8170	219.605	298.04	419.10	729.114
1.4300	66.170	298.00	419.13	740.040

[a] m is the mass of sample; $A - A_{\mathrm{b}}$ is the area of the calorimetric curve corrected with the blank contribution, $<A_{\mathrm{b}}>\pm u = -(3.875\pm0.261)$ mV s, corresponding to the system evacuation process (mean of 10 experiments); T_{i} and T_{f} are the temperatures of the drop furnace and the calorimetric cell, respectively; $u(m) = \pm0.00005$ mg; $u(T) = \pm0.01$ K; $u(p) = \pm0.05$ bar; ε is the energy equivalent of the calorimeter. For $\Delta_{\mathrm{sub}}H^{\mathrm{o}}_{\mathrm{m}}$ the expanded uncertainty of 95% confidence level ($U_{\mathrm{c}}=2u$) is indicated. The symbol u denotes standard uncertainty.

$$<T_{\mathrm{i}}>\pm u = 297.74\pm0.20 \text{ K}$$

$$<T_{\mathrm{f}}>\pm u = 419.10\pm0.01 \text{ K}$$

$$<\varepsilon>\pm u = 15.993\pm0.008 \text{ W V}^{-1}$$

$$<\Delta_{\mathrm{sub}}h>\pm u = 739.240\pm2.869 \text{ J g}^{-1}$$

$$\text{Overall uncertainty } U_{\mathrm{c}} = 2.893 \text{ J g}^{-1}$$

$$\Delta_{\mathrm{sub}}H^{\mathrm{o}}_{\mathrm{m}} \pm U_{\mathrm{c}} = 127.30\pm1.00 \text{ kJ mol}^{-1}$$

Table S13. Calvet-drop microcalorimetry results obtained for the standard enthalpy of sublimation of sulfapyridine, SP (p^{o} = 1 bar).[a]

m /mg	A-A_b /mV s	T_i /K	T_f /K	$\Delta_{sub}h$ /J g^{-1}
1.3853	51.176	297.96	423.98	593.882
1.9714	71.618	298.05	423.96	584.017
2.1763	79.461	298.02	423.95	586.966
1.2765	47.650	298.07	423.94	600.095
1.3080	48.538	298.09	423.85	596.557
1.4367	52.534	297.97	423.87	587.831

[a] m is the mass of sample; $A - A_b$ is the area of the calorimetric curve corrected with the blank contribution, $\langle A_b \rangle \pm u = -(3.293 \pm 0.196)$ mV s, corresponding to the system evacuation process (mean of 10 experiments); T_i and T_f are the temperatures of the drop furnace and the calorimetric cell, respectively; $u(m) = \pm 0.00005$ mg; $u(T) = \pm 0.01$ K; $u(p) = \pm 0.05$ bar; ε is the energy equivalent of the calorimeter. For $\Delta_{sub}H_m^{o}$ the expanded uncertainty of 95% confidence level ($U_c = 2u$) is indicated. The symbol u denotes standard uncertainty.

$$\langle T_i \rangle \pm u = 298.04 \pm 0.02 \text{ K}$$

$$\langle T_f \rangle \pm u = 423.94 \pm 0.02 \text{ K}$$

$$\langle \varepsilon \rangle \pm u = 16.076 \pm 0.008 \text{ W V}^{-1}$$

$$\langle \Delta_{sub}h \rangle \pm u = 591.558 \pm 2.550 \text{ J g}^{-1}$$

$$\text{Overall uncertainty } U_c = 2.567 \text{ J g}^{-1}$$

$$\Delta_{sub}H_m^{o} \pm U_c = 147.47 \pm 1.28 \text{ kJ mol}^{-1}$$

Table S14. Calvet-drop microcalorimetry results obtained for the standard enthalpy of sublimation of chlorzoxazone, CZ (p^{o} = 1 bar).[a]

m /mg	A-A_{b} /mV s	T_{i} /K	T_{f} /K	$\Delta_{\mathrm{sub}}h$ /J g^{-1}
4.2651	169.166	298.55	419.27	634.328
6.3985	252.934	298.51	419.29	632.207
8.1779	323.147	298.42	419.28	631.958
6.4553	254.785	298.50	419.28	631.230
7.0767	277.650	298.52	419.29	627.476

[a] m is the mass of sample; $A - A_{\mathrm{b}}$ is the area of the calorimetric curve corrected with the blank contribution, $\langle A_{\mathrm{b}}\rangle \pm u = -(3.875\pm0.261)$ mV s, corresponding to the system evacuation process (mean of 10 experiments); T_{i} and T_{f} are the temperatures of the drop furnace and the calorimetric cell, respectively; $u(m) = \pm0.00005$ mg; $u(T) = \pm0.01$ K; $u(p) = \pm0.05$ bar; ε is the energy equivalent of the calorimeter. For $\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{\mathrm{o}}$ the expanded uncertainty of 95% confidence level ($U_{\mathrm{c}} = 2u$) is indicated. The symbol u denotes standard uncertainty.

$$\langle T_{\mathrm{i}}\rangle \pm u = 298.50\pm0.02 \text{ K}$$

$$\langle T_{\mathrm{f}}\rangle \pm u = 419.28\pm0.00 \text{ K}$$

$$\langle \varepsilon\rangle \pm u = 15.993\pm0.008 \text{ W V}^{-1}$$

$$\langle \Delta_{\mathrm{sub}}h\rangle \pm u = 631.440\pm1.117 \text{ J g}^{-1}$$

$$\text{Overall uncertainty } U_{\mathrm{c}} = 1.161 \text{ J g}^{-1}$$

$$\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{\mathrm{o}} \pm U_{\mathrm{c}} = 107.07\pm0.39 \text{ kJ mol}^{-1}$$

Table S15. Calvet-drop microcalorimetry results obtained for the standard enthalpy of sublimation of clioquinol, CI (p^{o} = 1 bar).[a]

m /mg	A-A_{b} /mV s	T_{i} /K	T_{f} /K	$\Delta_{\mathrm{sub}}h$ /J g^{-1}
2.5437	59.548	298.42	369.72	363.817
3.0717	71.936	298.43	369.73	363.953
3.3231	78.001	298.38	369.74	364.784
4.0923	94.325	298.33	369.71	358.209
2.9614	68.068	298.33	369.70	357.210

[a] m is the mass of sample; $A - A_{\mathrm{b}}$ is the area of the calorimetric curve corrected with the blank contribution, $<A_{\mathrm{b}}>\pm u = -(4.293\pm0.089)$ mV s, corresponding to the system evacuation process (mean of 6 experiments); T_{i} and T_{f} are the temperatures of the drop furnace and the calorimetric cell, respectively; $u(m) = \pm0.00005$ mg; $u(T) = \pm0.01$ K; $u(p) = \pm0.05$ bar; ε is the energy equivalent of the calorimeter. For $\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{\mathrm{o}}$ the expanded uncertainty of 95% confidence level ($U_{\mathrm{c}} = 2u$) is indicated. The symbol u denotes standard uncertainty.

$$<T_{\mathrm{i}}>\pm u = 298.38\pm0.02 \text{ K}$$

$$<T_{\mathrm{f}}>\pm u = 369.72\pm0.01 \text{ K}$$

$$<\varepsilon>\pm u = 15.541\pm0.009 \text{ W V}^{-1}$$

$$<\Delta_{\mathrm{sub}}h>\pm u = 361.595\pm1.603 \text{ J g}^{-1}$$

$$\text{Overall uncertainty } U_{\mathrm{c}} = 1.617 \text{ J g}^{-1}$$

$$\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{\mathrm{o}} \pm U_{\mathrm{c}} = 110.47\pm0.99 \text{ kJ mol}^{-1}$$

Table S16. Calvet-drop microcalorimetry results obtained for the standard enthalpy of vaporization of triclosan, TR (p^{o} = 1 bar).[a]

m /mg	A-A_{b} /mV·s	T_{i} /K	T_{f} /K	$\Delta_{\mathrm{vap}}h$ /J g^{-1}
5.4441	108.416	298.37	351.43	308.036
3.3123	65.591	298.32	351.44	306.301
3.7123	73.994	298.44	351.43	308.310
5.0002	101.929	298.37	351.44	315.315
4.5585	89.961	298.41	351.44	305.258

[a] m is the mass of sample; $A - A_{\mathrm{b}}$ is the area of the calorimetric curve corrected with the blank contribution, $<A_{\mathrm{b}}>\pm u = -(3.390\pm0.128)$ mV s, corresponding to the system evacuation process (mean of 4 experiments); T_{i} and T_{f} are the temperatures of the drop furnace and the calorimetric cell, respectively; $u(m) = \pm0.00005$ mg; $u(T) = \pm0.01$ K; $u(p) = \pm0.05$ bar; ε is the energy equivalent of the calorimeter. For $\Delta_{\mathrm{vap}}H_{\mathrm{m}}^{\mathrm{o}}$ the expanded uncertainty of 95% confidence level ($U_{\mathrm{c}} = 2u$) is indicated. The symbol u denotes standard uncertainty.

$$<T_{\mathrm{i}}>\pm u = 298.38\pm0.02 \text{ K}$$

$$<T_{\mathrm{f}}>\pm u = 351.44\pm0.00 \text{ K}$$

$$<\varepsilon>\pm u = 15.468\pm0.005 \text{ W V}^{-1}$$

$$<\Delta_{\mathrm{vap}}h>\pm u = 308.644\pm1.760 \text{ J g}^{-1}$$

$$\text{Overall uncertainty } U_{\mathrm{c}} = 1.763 \text{ J g}^{-1}$$

$$\Delta_{\mathrm{vap}}H_{\mathrm{m}}^{\mathrm{o}}\pm U_{\mathrm{c}} = 89.36\pm1.02 \text{ kJ mol}^{-1}$$

Table S17. Calvet-drop microcalorimetry results obtained for the enthalpy change, $\Delta_{\mathrm{cr},\,T_\mathrm{f}}^{\mathrm{cr},\,T_\mathrm{i}} H_\mathrm{m}^\mathrm{o}$, between the temperatures of the drop furnace, T_i, and the calorimetric cell T_f, used in the sublimation experiments of sulfanilamide, SN (p^o = 1 bar).[a]

m /mg	m_cap /mg	A_aq /mV·s	T_i /K	T_f /K	$-\Delta_{\mathrm{cr},\,T_\mathrm{f}}^{\mathrm{cr},\,T_\mathrm{i}} H_\mathrm{m}^\mathrm{o}$ /kJ mol^{-1}
3.4596	44.4924	326.112	297.02	419.11	28.16
5.0337	52.9069	398.392	297.62	419.08	29.79
4.8170	46.0056	344.265	298.04	419.10	26.40
1.4300	45.4463	309.809	298.00	419.13	29.21
4.8412	49.2967	372.975	297.94	419.10	30.32
4.6304	44.4569	337.959	298.11	419.12	29.75
6.6416	42.7905	350.634	298.09	419.13	30.44

[a] m and m_cap are the mass of the sample and the glass capillary, respectively; A_aq is the area of the calorimetric curve; $c_{p,\,\mathrm{glass}}$ is the glass capillary heat capacity obtained from the average of 8 measurements. $u(m)$ = ±0.00005 mg; $u(T)$= ±0.01 K; $u(p)$= ±0.05 bar; ε is the energy equivalent of the calorimeter; The symbol u denotes standard uncertainty.

$$<T_\mathrm{i}>\pm u = 297.83\pm0.15\ \mathrm{K}$$

$$<T_\mathrm{f}>\pm u = 419.11\pm0.01\ \mathrm{K}$$

$$<\varepsilon>\pm u = 15.993\pm0.008\ \mathrm{W\ V^{-1}}$$

$$<c_{p,\,\mathrm{glass}}> = 0.856\pm0.001\ \mathrm{J\ K^{-1}\ g^{-1}}$$

$$<\Delta_{\mathrm{cr},\,T_\mathrm{f}}^{\mathrm{cr},\,T_\mathrm{i}} H_\mathrm{m}^\mathrm{o}>\pm u = -(29.15\pm0.54)\ \mathrm{kJ\ mol^{-1}}$$

Table S18. Calvet-drop microcalorimetry results obtained for the enthalpy change, $\Delta_{\mathrm{cr},\,T_\mathrm{f}}^{\mathrm{cr},\,T_\mathrm{i}} H_\mathrm{m}^\mathrm{o}$, between the temperatures of the drop furnace, T_i, and the calorimetric cell T_f, used in the sublimation experiments of sulfapyridine, SP (p^o = 1 bar).[a]

m /mg	m_cap /mg	A_aq /mV·s	T_i /K	T_f /K	$-\Delta_{\mathrm{cr},\,T_\mathrm{f}}^{\mathrm{cr},\,T_\mathrm{i}} H_\mathrm{m}^\mathrm{o}$ /kJ mol^{-1}
2.1763	46.0575	330.749	298.02	423.95	41.02
4.8421	43.3268	339.835	298.34	424.44	40.77
6.1839	47.8657	384.953	298.34	424.44	41.44
4.0481	44.7208	341.348	298.35	424.44	41.03
4.5358	46.3467	355.934	298.31	424.44	39.79
5.0725	29.6785	243.896	298.31	424.44	35.40
5.7021	39.1684	320.680	298.34	424.44	40.76
6.8886	51.1998	413.370	298.25	424.44	40.58
15.2341	29.6179	335.924	298.19	424.44	36.05

[a] m and m_cap are the mass of sample and the glass capillary, respectively; A_aq is the area of the calorimetric curve; $c_{p,\,\mathrm{glass}}$ is the glass capillary heat capacity obtained from the average of 4 measurements. $u(m) = \pm 0.00005$ mg; $u(T) = \pm 0.01$ K; $u(p) = \pm 0.05$ bar; ε is the energy equivalent of the calorimeter; The symbol u denotes standard uncertainty.

$$<T_\mathrm{i}>\pm u = 298.27\pm0.04\ \mathrm{K}$$

$$<T_\mathrm{f}>\pm u = 424.39\pm0.05\ \mathrm{K}$$

$$<\varepsilon>\pm u = 16.076\pm0.008\ \mathrm{W\ V^{-1}}$$

$$<c_{p,\,\mathrm{glass}}> = 0.855\pm0.002\ \mathrm{J\ K^{-1}\ g^{-1}}$$

$$<\Delta_{T_\mathrm{f}}^{T_\mathrm{i}} H_\mathrm{m}^\mathrm{o}>\pm u = -(39.65\pm0.76)\ \mathrm{kJ\ mol^{-1}}$$

Table S19. Calvet-drop microcalorimetry results obtained for the enthalpy change, $\Delta_{\mathrm{cr},\,T_\mathrm{f}}^{\mathrm{cr},\,T_\mathrm{i}} H_\mathrm{m}^\mathrm{o}$, between the temperatures of the drop furnace, T_i, and the calorimetric cell T_f, used in the sublimation experiments of chlorzoxazone, CZ (p^o = 1 bar).[a]

m /mg	m_cap /mg	A_aq /mV·s	T_i /K	T_f /K	$-\Delta_{\mathrm{cr},\,T_\mathrm{f}}^{\mathrm{cr},\,T_\mathrm{i}} H_\mathrm{m}^\mathrm{o}$ /kJ mol^{-1}
4.2651	66.4452	460.200	298.55	419.27	19.63
6.3985	57.7060	424.001	298.51	419.29	21.60
8.1779	57.2534	435.355	298.42	419.28	21.55
6.4553	52.9989	396.413	298.50	419.28	22.60
7.0767	49.9746	379.873	298.52	419.29	21.78

[a] m and m_cap are the mass of sample and the glass capillary, respectively; A_aq is the area of the calorimetric curve; $c_{p,\,\mathrm{glass}}$ is the glass capillary heat capacity obtained from the average of 5 measurements. $u(m)$ = ±0.00005 mg; $u(T)$= ±0.01 K; $u(p)$= ±0.05 bar; ε is the energy equivalent of the calorimeter; The symbol u denotes standard uncertainty.

$$\langle T_\mathrm{i} \rangle \pm u = 298.50 \pm 0.02\ \mathrm{K}$$

$$\langle T_\mathrm{f} \rangle \pm u = 419.28 \pm 0.00\ \mathrm{K}$$

$$\langle \varepsilon \rangle \pm u = 15.993 \pm 0.008\ \mathrm{W\ V^{-1}}$$

$$\langle c_{p,\,\mathrm{glass}} \rangle = 0.856 \pm 0.001\ \mathrm{J\ K^{-1}\ g^{-1}}$$

$$\langle \Delta_{\mathrm{cr},\,T_\mathrm{f}}^{\mathrm{cr},\,T_\mathrm{i}} H_\mathrm{m}^\mathrm{o} \rangle \pm u = -(21.43 \pm 0.49)\ \mathrm{kJ\ mol^{-1}}$$

Table S20. Calvet-drop microcalorimetry results obtained for the enthalpy change, $\Delta_{\mathrm{cr},\,T_\mathrm{f}}^{\mathrm{cr},\,T_\mathrm{i}} H_\mathrm{m}^\mathrm{o}$, between the temperatures of the drop furnace, T_i, and the calorimetric cell T_f, used in the sublimation experiments of clioquinol, CI (p^o = 1 bar).[a]

m /mg	m_cap /mg	A_aq /mV·s	T_i /K	T_f /K	$-\Delta_{\mathrm{cr},\,T_\mathrm{f}}^{\mathrm{cr},\,T_\mathrm{i}} H_\mathrm{m}^\mathrm{o}$ /kJ mol^{-1}
3.0717	45.8139	183.842	298.43	369.73	18.73
3.3231	45.3959	183.620	298.38	369.74	19.03
4.0923	37.0554	153.870	298.33	369.71	17.19
2.9614	40.1231	161.893	298.33	369.70	18.20

[a] m and m_cap are the mass of sample and the glass capillary, respectively; A_aq is the area of the calorimetric curve; $c_{p,\,\mathrm{glass}}$ is the glass capillary heat capacity obtained from the average of 5 measurements. $u(m) = \pm 0.00005$ mg; $u(T) = \pm 0.01$ K; $u(p) = \pm 0.05$ bar; ε is the energy equivalent of the calorimeter; The symbol u denotes standard uncertainty.

$$<T_\mathrm{i}>\pm u = 298.37\pm0.02\ \mathrm{K}$$

$$<T_\mathrm{f}>\pm u = 369.72\pm0.01\ \mathrm{K}$$

$$<\varepsilon>\pm u = 15.541\pm0.009\ \mathrm{W\ V^{-1}}$$

$$<c_{p,\,\mathrm{glass}}> = 0.817\pm0.002\ \mathrm{J\ K^{-1}\ g^{-1}}$$

$$<\Delta_{\mathrm{cr},\,T_\mathrm{f}}^{\mathrm{cr},\,T_\mathrm{i}} H_\mathrm{m}^\mathrm{o}>\pm u = -(18.29\pm0.40)\ \mathrm{kJ\ mol^{-1}}$$

Table S21. Calvet-drop microcalorimetry results obtained for the enthalpy change, $\Delta_{\mathrm{l},\,T_\mathrm{f}}^{\mathrm{cr},\,T_\mathrm{i}} H_\mathrm{m}^\mathrm{o}$, between the temperatures of the drop furnace, T_i, and the calorimetric cell T_f, used in the sublimation experiments of triclosan, TR (p^o = 1 bar).[a]

m /mg	m_cap /mg	A_aq /mV·s	T_i /K	T_f /K	$-\Delta_{\mathrm{l},\,T_\mathrm{f}}^{\mathrm{cr},\,T_\mathrm{i}} H_\mathrm{m}^\mathrm{o}$ /kJ mol^{-1}
3.3123	45.8118	157.458	298.32	351.44	42.30
3.7123	45.6661	162.837	298.44	351.43	45.08
5.0002	44.7166	173.047	298.37	351.44	44.79
4.5585	48.5899	178.053	298.41	351.44	43.67

[a] m and m_cap are the mass of sample and the glass capillary, respectively; A_aq is the area of the calorimetric curve; $c_{p,\,\mathrm{glass}}$ is the glass capillary heat capacity obtained from the average of 5 measurements. $u(m) = \pm 0.00005$ mg; $u(T) = \pm 0.01$ K; $u(p) = \pm 0.05$ bar; ε is the energy equivalent of the calorimeter; The symbol u denotes standard uncertainty.

$$<T_\mathrm{i}>\pm u = 298.39\pm 0.03 \text{ K}$$

$$<T_\mathrm{f}>\pm u = 351.44\pm 0.00 \text{ K}$$

$$<\varepsilon>\pm u = 15.468\pm 0.005 \text{ W V}^{-1}$$

$$<c_{p,\,\mathrm{glass}}> = 0.802\pm 0.002 \text{ J K}^{-1} \text{ g}^{-1}$$

$$<\Delta_{\mathrm{l},\,T_\mathrm{f}}^{\mathrm{cr},\,T_\mathrm{i}} H_\mathrm{m}^\mathrm{o}>\pm u = -(43.96\pm 0.63) \text{ kJ mol}^{-1}$$

Table S22. Coefficients of eq. S* MERGEFORMAT 4 obtained by fitting the standard molar heat capacity of the gaseous state of the compounds, $C^{\circ}_{p,\mathrm{m}}(\mathrm{g})$, computed in the temperature range 200 K to 400 K using statistical thermodynamic calculations. [a]

Compound	$-a$ /·10^4	b	c	R^2
Sulfanilamide	3.839±0.023	0.7112±0.0014	7.142±0.208	0.99999
Sulfapyridine	4.603±0.068	1.026±0.004	–4.665±0.602	0.99998
Chlorzoxazone	3.058±0.034	0.5953±0.0021	-4.719±0.301	0.99998
Clioquinol	3.034±0.039	0.6579±0.0023	10.40±0.34	0.99998
Triclosan	5.132±0.067	0.9529±0.0022	11.22±0.32	0.99999

[a] Uncertainties correspond to standard deviations (u).

Table S23. Correction to 298.15 K, of the enthalpy of sublimation data previously reported for SP, and CI by Nagrimanov *et al.*,[5] and Ribeiro da Silva *et al,*[6] respectively, from vapor pressure measurements.

Compound		SP	CI
Temperature range / K [a]		459.6-419.2	359.18–378.30
T_m /K [b]		439.4	368.7
Clausius–Clapeyron equation:	a	43.66±0.54	35.35±0.12
ln (p/Pa) = a + b/T	$-b$	20035.7±239.0	13386±45
$< C^{o}_{p,m}(\mathrm{cr}) >$ / J K^{-1} mol^{-1} [c]		314.4±6.0 (298-424)	256.3±8.8 (298-370)
$\Delta_{\mathrm{sub}}H^{\circ}_{\mathrm{m}}$ (T_m)±U / kJ mol^{-1} [d]		166.6±4.6	111.3±0.8
$-\Delta^{\mathrm{cr,\ 298.15\ K}}_{\mathrm{cr,\ }T_\mathrm{m}} H^{\circ}_{\mathrm{m}} \pm u$ / kJ mol^{-1} [e]		44.4±0.8	18.1±0.6
$-\Delta^{\mathrm{g,\ 298.15\ K}}_{\mathrm{g,\ }T_\mathrm{m}} H^{\circ}_{\mathrm{m}} \pm u$ / kJ mol^{-1} [f]		43.8±0.9	13.8±0.3
$\Delta_{\mathrm{sub}}H^{\circ}_{\mathrm{m}}$ (298.15 K) ±U / kJ·mol^{-1}		167.2±4.8	115.6±1.0

[a] temperature range used in the vapor pressure measurements; [b] mean temperature of the experimental values; [c] average heat capacity of the solids obtained from $< C^{o}_{p,m}(\mathrm{cr}) >= \Delta^{\mathrm{cr,\ }T_\mathrm{i}}_{\mathrm{cr,\ }T_\mathrm{f}} H^{\circ}_{\mathrm{m}} / (T_\mathrm{f} - T_\mathrm{i})$ using the data in Tables S18 and S20. The temperature range is given in parentheses; [d] expanded uncertainty using the student's t factor for the number of values in the fitting of Clausius–Clapeyron equation and for a 95% confidence; [e] obtained from $< C^{o}_{p,m}(\mathrm{cr}) >$; [f] obtained from eq S* MERGEFORMAT 3 and the values in Table S22.

6. Molecular Dynamics (MD)

The force field parametrization and the DLPGEN 3.0 [7] input files necessary to replicate the simulations performed in this work are available in the “Computational Files” archive, which is also included as SI. This folder also contains files with the atomic coordinates used in the atomic point charges (APCs) calculations by the ChelpG and RESP methodologies using Orca 5.0.4[8] and Multiwfn 3.8,[9] respectively. All atomic point charges were based on wave functions computed with Orca 5.0.4,[8] using the B3LYP-D3[10-12] model with def2-TZVP[13] and def2/J[14] basis set and auxiliary basis set, respectively, and the RIJCOSX approximation.[15] The different models refer to:

MODEL A: original OPLS-AA force field charges, q_{opls}.

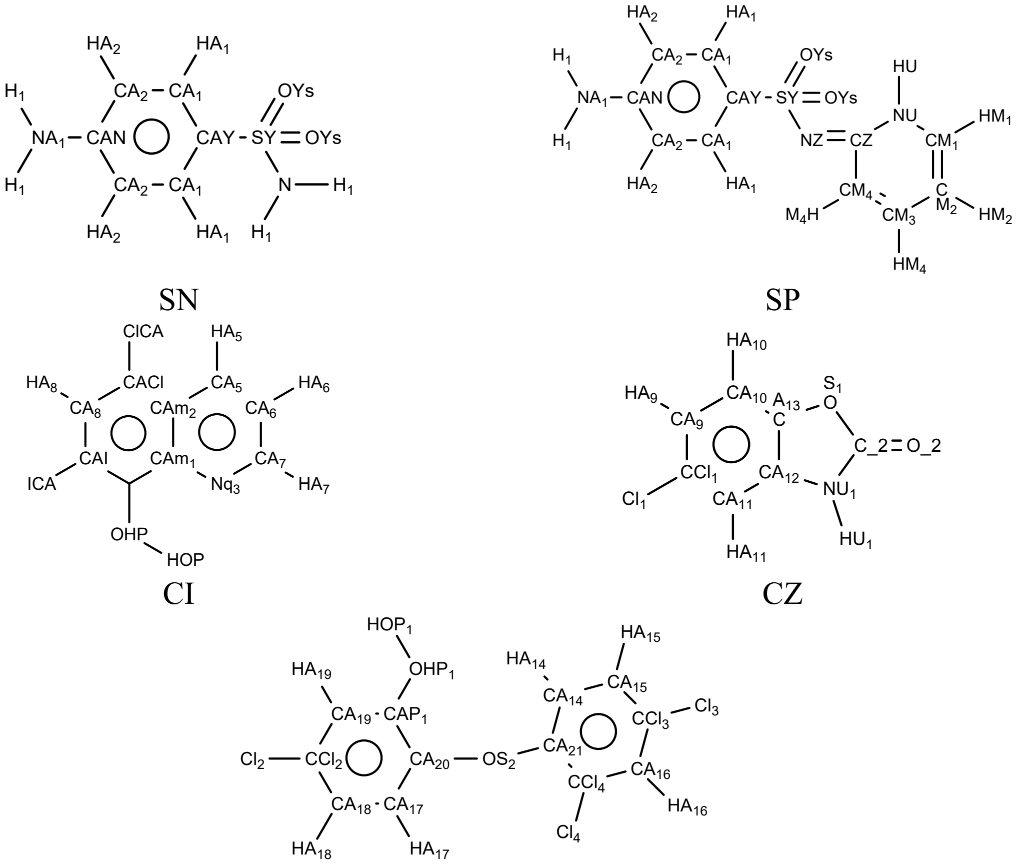
MODEL $\mathbf{B^C}$ and $\mathbf{B^R}$: APCs computed for an isolated molecule in the **gas phase** using the ChelpG, and RESP, methodologies, respectively.

MODEL $\mathbf{C^C}$ and $\mathbf{C^R}$: APCs computed for the central molecule of small clusters of molecules retrieved from the single crystal structures (e.g., molecules connected by hydrogen bonds or interacting by halogen bonds),[16-17] by the ChelpG and RESP methodologies, respectively.

MODEL $\mathbf{D^C}$ and $\mathbf{D^R}$: APCs computed as the average of the values obtained by the ChelpG and RESP methods obtained by models B and C.

In the case of the B models full geometry optimization of the molecules was performed before the APC’s calculations. In turn, in the case of the C models, geometry optimization was performed keeping all heavy atoms as in the crystal structure but optimizing the hydrogen atoms positions. All previous calculations were run with the composite model B97-3c[18] using ORCA. In the simulations with models B, C, and D, the different APCs were used by replacing the charge values of the OPLS-AA force field (file opls.lib) with those in Tables S24 to S28. The atoms labeling scheme used in the tables and the simulation files are given in Figure S14.

As mentioned in the main text, several dihedrals present in the investigated molecules have not been previously parametrized in the OPLS-AA force field, namely the rotation around the bonds SY–NZ and NZ–CZ of SP, and the bonds CA_{20}–OS_2 and OS_2–CA_{21} of TR (see Figure S14). The evaluation of the dihedral parameters for the Fourier series in eq 9 of the main text, followed the procedures previously described.[19] In brief, PES were computed at the MP2/aug-cc-pVDZ[20-23] level of theory using the program Orca 5.0.4,[8] for the following dihedral angles: SP dihedrals CAY–SY–NZ–CZ and SZ–NZ–CZ–NU; TR dihedrals CAP_1–CA_{20}–OS_2–CA_{21} and CA_{20}–OS_2–CA_{21}–CCl_4. The same procedure was then replicated using the MD force field considering that all the dihedrals that include the bonds identified above are equal to zero. The difference between the MD and ab initio data was then adjusted to the Fourier series in eq 9 of the main text, using Solver in MS Excel. The complete list of parameters used in the simulations is given in the file "opls.lib".



SN

SP

CI

CZ

TR

Figure S14. Atoms labeling scheme followed in this work to prepare the MD simulations.

Table S24. Atomic point charges obtained for the different models tested in this work, used in the MD simulations of the two polymorphs of SN with CSD reference codes SULMAD03 and SULMAD10.[24]

MODEL	A	B^C	B^R	SULMAD03				SULMAD10			
				C^C	C^R	D^C	D^R	C^C	C^R	D^C	D^R
CA_1	-0.115	-0.172	-0.153	-0.087	-0.069	-0.13	-0.111	-0.079	-0.045	-0.126	-0.099
CA_2	-0.115	-0.230	-0.209	-0.366	-0.336	-0.298	-0.273	-0.333	-0.353	-0.282	-0.281
CAN_1	-0.100	0.334	0.270	0.571	0.515	0.453	0.393	0.458	0.435	0.396	0.353
CAY	0.000	-0.053	-0.02	-0.156	-0.145	-0.105	-0.083	-0.161	-0.080	-0.107	-0.050
H_1	0.440	0.328	0.308	0.371	0.367	0.350	0.338	0.401	0.334	0.365	0.321
H_1	0.440	0.328	0.308	0.371	0.367	0.350	0.338	0.401	0.334	0.365	0.321
HA_1	0.115	0.163	0.149	0.143	0.128	0.153	0.139	0.142	0.126	0.153	0.138
HA_2	0.115	0.160	0.154	0.187	0.178	0.174	0.166	0.187	0.199	0.174	0.177
HN_1	0.300	0.320	0.294	0.378	0.355	0.349	0.325	0.350	0.334	0.335	0.314
N_1	-1.000	-0.736	-0.677	-0.825	-0.806	-0.781	-0.742	-0.867	-0.67	-0.802	-0.674
NA_1	-0.500	-0.700	-0.622	-0.873	-0.821	-0.787	-0.722	-0.837	-0.789	-0.769	-0.707
OYs	-0.680	-0.484	-0.453	-0.497	-0.46	-0.491	-0.457	-0.567	-0.501	-0.526	-0.477
SY	1.480	0.985	0.869	1.025	0.931	1.006	0.900	1.205	0.916	1.096	0.892

Table S25. Atomic point charges obtained for the different models tested in this work, used in the MD simulations of SP crystal form with CSD reference code BEWKUJ04.[24]

MODEL	A	B^C	B^R	C^C	C^R	D^C	D^R
SY	1.480	0.950	0.891	0.979	0.867	0.966	0.878
OYs	-0.680	-0.536	-0.513	-0.563	-0.525	-0.550	-0.520
NZ	-0.753	-0.736	-0.712	-0.667	-0.618	-0.702	-0.665
NA$_1$	-0.500	-0.750	-0.688	-1.045	-0.980	-0.898	-0.834
NU	-0.533	-0.309	-0.248	-0.251	-0.207	-0.280	-0.228
CAY	0.000	0.076	0.029	-0.001	0.038	0.038	0.034
CA$_1$	-0.115	-0.181	-0.117	-0.176	-0.201	-0.179	-0.159
CA$_2$	-0.115	-0.255	-0.251	-0.317	-0.234	-0.286	-0.243
CAN$_1$	-0.100	0.370	0.324	0.604	0.519	0.487	0.422
CZ	0.576	0.737	0.677	0.615	0.541	0.676	0.609
CM$_4$	-0.115	-0.416	-0.358	-0.377	-0.296	-0.397	-0.327
CM$_3$	-0.115	0.057	0.029	0.059	0.032	0.058	0.031
CM$_2$	-0.115	-0.287	-0.240	-0.237	-0.205	-0.262	-0.223
CM$_1$	0.080	-0.030	-0.062	-0.033	-0.045	-0.032	-0.054
HA$_1$	0.115	0.164	0.137	0.144	0.142	0.154	0.140
HA$_2$	0.115	0.161	0.157	0.154	0.116	0.158	0.137
HN$_1$	0.300	0.329	0.309	0.467	0.444	0.398	0.377
HM$_1$	0.100	0.193	0.174	0.203	0.167	0.198	0.171
HM$_4$	0.115	0.162	0.164	0.154	0.154	0.158	0.159
HM$_3$	0.115	0.162	0.145	0.157	0.143	0.160	0.144
HM$_2$	0.115	0.119	0.118	0.120	0.120	0.120	0.119
HU	0.410	0.338	0.313	0.302	0.286	0.320	0.300

Table S26. Atomic point charges obtained for the different models tested in this work, used in the MD simulations of SI crystal form with CSD reference code CIQUOL02.[24]

MODEL	A	B^C	B^R	C^C	C^R	D^C	D^R
ICA	-0.100	-0.004	-0.006	-0.064	-0.067	-0.034	-0.037
ClCA	-0.180	-0.084	-0.084	-0.070	-0.067	-0.077	-0.076
OHP	-0.585	-0.479	-0.456	-0.436	-0.422	-0.458	-0.439
HOP	0.435	0.372	0.350	0.366	0.344	0.369	0.347
Nq$_3$	-0.678	-0.582	-0.535	-0.617	-0.564	-0.600	-0.550
CAm$_2$	-0.016	-0.053	-0.045	-0.088	-0.054	-0.071	-0.050
CAI	0.100	-0.178	-0.178	0.001	-0.047	-0.089	-0.113
CAm$_1$	0.241	0.381	0.330	0.450	0.367	0.416	0.349
CA$_8$	-0.115	-0.032	0.004	-0.186	-0.098	-0.109	-0.047
HA$_8$	0.115	0.125	0.105	0.157	0.134	0.141	0.120
CAP	0.150	0.268	0.257	0.112	0.153	0.190	0.205
CACl	0.180	-0.081	-0.081	0.007	-0.035	-0.037	-0.058
CA$_5$	-0.115	0.063	0.062	0.067	0.059	0.065	0.061
HA$_5$	0.115	0.106	0.097	0.115	0.105	0.111	0.101
CA$_7$	0.425	0.310	0.309	0.359	0.348	0.335	0.329
HA$_7$	0.028	0.067	0.051	0.056	0.041	0.062	0.046
CA$_6$	-0.115	-0.371	-0.343	-0.408	-0.361	-0.390	-0.352
HA$_6$	0.115	0.172	0.163	0.179	0.164	0.176	0.164

Table S27. Atomic point charges obtained for the different models tested in this work, used in the MD simulations of CZ crystal form with CSD reference code NEWKOP.[24]

MODEL	A	B^C	B^R	C^C	C^R	D^C	D^R
Cl_1	-0.180	-0.097	-0.109	-0.098	-0.101	-0.097	-0.106
NU_1	-0.500	-0.601	-0.571	-0.654	-0.620	-0.628	-0.597
OS_1	-0.400	-0.337	-0.329	-0.327	-0.319	-0.332	-0.324
O_2	-0.430	-0.522	-0.539	-0.531	-0.548	-0.527	-0.544
CA_{13}	0.220	0.299	0.280	0.260	0.243	0.280	0.262
C_2	0.510	0.739	0.761	0.717	0.747	0.728	0.754
CA_{12}	0.220	0.264	0.219	0.318	0.269	0.291	0.244
CA_{11}	-0.115	-0.281	-0.265	-0.319	-0.287	-0.300	-0.276
CCl_1	0.180	0.031	0.048	0.073	0.057	0.052	0.053
CA_9	-0.115	-0.111	-0.096	-0.144	-0.102	-0.128	-0.099
CA_{10}	-0.115	-0.327	-0.317	-0.308	-0.307	-0.318	-0.312
HA_{11}	0.115	0.186	0.185	0.200	0.198	0.193	0.192
HA_9	0.115	0.149	0.138	0.151	0.131	0.150	0.135
HA_{10}	0.115	0.211	0.209	0.202	0.200	0.207	0.205
HU_1	0.380	0.397	0.386	0.460	0.439	0.429	0.413

Table S28. Atomic point charges obtained for the different models tested in this work, used in the MD simulations of TR crystal form with CSD reference code QUBQIO01.[24]

MODEL	A	B^C	B^R	C^C	C^R	D^C	D^R
Cl_2	-0.180	-0.096	-0.102	-0.087	-0.091	-0.093	-0.096
Cl_4	-0.180	-0.062	-0.073	-0.074	-0.077	-0.069	-0.074
Cl_3	-0.180	-0.099	-0.106	-0.126	-0.124	-0.113	-0.115
OS_2	-0.400	-0.391	-0.356	-0.308	-0.237	-0.350	-0.297
OHP_1	-0.585	-0.512	-0.500	-0.623	-0.568	-0.568	-0.534
HOP_1	0.435	0.417	0.411	0.460	0.431	0.439	0.421
CA_{20}	0.200	0.397	0.351	0.266	0.201	0.332	0.276
CAP_1	0.150	0.212	0.216	0.335	0.300	0.274	0.258
CA_{19}	-0.115	-0.288	-0.286	-0.332	-0.264	-0.310	-0.275
HA_{19}	0.115	0.166	0.160	0.181	0.150	0.174	0.155
CC_{l2}	0.180	0.053	0.075	0.032	0.015	0.043	0.045
CA_{18}	-0.115	-0.112	-0.120	-0.095	-0.066	-0.104	-0.093
HA_{18}	0.115	0.146	0.140	0.139	0.126	0.143	0.133
CA_{17}	-0.115	-0.339	-0.304	-0.254	-0.235	-0.297	-0.270
HA_{17}	0.115	0.195	0.188	0.174	0.164	0.185	0.176
CA_{21}	0.200	0.513	0.405	0.335	0.239	0.424	0.322
CCl_4	0.180	-0.148	-0.072	-0.036	-0.019	-0.092	-0.046
CA_{16}	-0.115	0.019	-0.027	-0.021	0.012	-0.001	-0.008
HA_{16}	0.115	0.117	0.115	0.132	0.116	0.125	0.116
CCl_3	0.180	-0.073	-0.020	-0.007	-0.022	-0.040	-0.021
CA_{15}	-0.115	0.012	-0.040	-0.028	-0.053	-0.008	-0.047
HA_{15}	0.115	0.127	0.131	0.136	0.134	0.132	0.133
CA_{14}	-0.115	-0.432	-0.341	-0.360	-0.270	-0.396	-0.306
HA_{14}	0.115	0.178	0.155	0.161	0.138	0.170	0.147

Table S29. Comparison between the enthalpy of sublimation ($\Delta_{\mathrm{sub}}H^{\mathrm{o}}_{\mathrm{m}}$), crystal unit cell parameters (a, b, c, α, β, and γ), and crystal density (ρ), obtained experimentally (Exp.; bold) in this work or retrieved from the literature, and the theoretical predictions from the MD simulations of SP, and the polymorphs of SN.[a]

Model	$\Delta_{\mathrm{sub}}H^{\mathrm{o}}_{\mathrm{m}}$ / kJ mol^{-1}	a /Å	b /Å	c /Å	α /°	β /°	γ /°	ρ /g cm^{3}
			SN-γ					
Exp.[b]	**129.5±1.3**	**7.950**	**12.945**	**7.790**	**90.00**	**106.50**	**90.00**	**1.488**
A	150±2.9	7.578	14.266	7.362	90.00	102.07	90.00	1.470
$\mathrm{B^{C}}$	123.0±3.0	7.800	12.987	7.956	90.00	106.68	90.00	1.482
$\mathrm{B^{R}}$	120.1±2.3	7.809	12.966	7.997	90.00	106.73	90.00	1.475
$\mathrm{C^{C}}$	136.2±2.6	7.814	13.104	7.738	90.00	106.02	90.00	1.502
$\mathrm{C^{R}}$	130.6±3.1	7.851	12.944	7.869	90.00	106.90	90.00	1.495
$\mathrm{D^{C}}$	128.9±3.1	7.808	13.047	7.844	90.00	106.33	90.00	1.492
$\mathrm{D^{R}}$	123.6±2.3	7.831	12.958	7.952	90.00	106.82	90.00	1.481
			SN-β					
Exp.[c]	**130.8±1.2**	**8.994**	**9.023**	**10.052**	**90.00**	**111.52**	**90.00**	**1.507**
A	141.4±2.9	8.670	9.483	9.831	90.00	99.13	90.00	1.433
$\mathrm{B^{C}}$	117.7±3.0	9.102	9.099	10.285	90.00	114.81	90.00	1.479
$\mathrm{B^{R}}$	114.6±2.3	9.024	9.050	10.358	90.00	113.80	90.00	1.478
$\mathrm{C^{C}}$	127.7±2.6	9.123	9.130	10.201	90.00	115.23	90.00	1.488
$\mathrm{C^{R}}$	120.8±3.3	8.898	9.081	10.340	90.00	112.42	90.00	1.481
$\mathrm{D^{C}}$	123.1±2.5	9.124	9.114	10.241	90.00	115.17	90.00	1.484
$\mathrm{D^{R}}$	117.4±2.7	8.711	9.052	10.415	90.00	109.85	90.00	1.481
			SP					
Exp.[d]	**148.7±1.7**	**12.715**	**11.669**	**15.373**	**90.00**	**93.70**	**90.00**	**1.455**
A	171.5±3.7	12.911	11.804	15.246	90.00	92.74	90.00	1.427
$\mathrm{B^{C}}$	173.3±4.0	13.010	11.871	15.121	90.00	94.94	90.00	1.423
$\mathrm{B^{R}}$	168.4±3.8	13.030	11.914	15.106	90.00	95.41	90.00	1.419
$\mathrm{C^{C}}$	205.1±4.0	13.049	11.663	15.096	90.00	95.32	90.00	1.448
$\mathrm{C^{R}}$	196.3±3.0	13.018	11.707	15.117	90.00	95.05	90.00	1.443
$\mathrm{D^{C}}$	189.1±2.6	13.034	11.758	15.108	90.00	95.16	90.00	1.436
$\mathrm{D^{R}}$	182.5±3.5	13.027	11.799	15.111	90.00	95.23	90.00	1.432

[a] The experimental $\Delta_{\mathrm{sub}}H^{\mathrm{o}}_{\mathrm{m}}$ values correspond to those obtained in this work and included in Table 1 of the main text; [b] Crystallographic data from reference 25; [c] Crystallographic data from reference 26; [d] Crystallographic data from reference 27.

Table S30. Comparison between the enthalpy of sublimation ($\Delta_{\text{sub}}H_{\text{m}}^{\text{o}}$), crystal unit cell parameters (*a, b, c, α, β,* and *γ*), and crystal density (*ρ*), obtained experimentally (Exp.; bold) in this work or retrieved from the literature and the theoretical predictions from the MD simulations for the CI.[a]

Model	$\Delta_{\text{sub}}H_{\text{m}}^{\text{o}}$ / kJ mol^{-1}	*a* /Å	*b* /Å	*c* /Å	α /°	β /°	γ /°	ρ /g cm^3
Exp.[b]	**114.7±1.1**	**14.554**	**4.127**	**16.605**	**90.00**	**111.63**	**90.00**	**2.189**
				Standard Force Field				
A	111.0±4.9	15.102	4.240	16.147	90.00	113.82	90.00	2.145
B^C	109.8±3.5	14.958	4.032	16.843	90.00	113.69	90.00	2.181
B^R	108.5±4.3	15.001	4.030	16.850	90.01	113.73	90.00	2.176
C^C	110.0±4.2	15.009	4.040	16.800	90.00	113.91	90.00	2.179
C^R	108.6±3.9	15.048	4.042	16.797	90.00	113.91	90.00	2.173
D^C	111.1±4.3	14.986	4.036	16.821	90.01	113.81	90.01	2.180
D^R	108.9±4.7	15.026	4.036	16.823	90.00	113.83	90.00	2.174
				Model with X-site in Cl and I				
A	115.2±7.1	14.911	4.150	16.238	90.01	112.82	90.00	2.191
B^C	114.6±5.9	14.785	4.035	16.683	90.00	112.59	90.00	2.209
B^R	111.4±4.7	14.825	4.032	16.689	90.01	112.61	90.00	2.203
C^C	113.8±6.1	14.788	4.026	16.739	90.00	112.69	90.00	2.207
C^R	112.1±6.0	14.831	4.026	16.739	90.00	112.74	90.00	2.201
D^R	110.5±7.3	14.828	4.029	16.715	90.00	112.68	90.00	2.202
D^C	112.1±6.8	14.785	4.030	16.710	90.00	112.63	90.01	2.208

[a] The experimental $\Delta_{\text{sub}}H_{\text{m}}^{\text{o}}$ values correspond to those obtained in this work and included in Table 1 of the main text; [b] Crystallographic data from reference 28.

Table S31. Comparison between the enthalpy of sublimation ($\Delta_{\mathrm{sub}}H^{\mathrm{o}}_{\mathrm{m}}$), crystal unit cell parameters (*a, b, c,* α, β, and γ), and crystal density (ρ), obtained experimentally (Exp.; bold) in this work or retrieved from the literature and the theoretical prediction from the MD simulations for the CZ.[a]

Model	$\Delta_{\mathrm{sub}}H^{\mathrm{o}}_{\mathrm{m}}$ / kJ mol^{-1}	a /Å	b /Å	c /Å	α /º	β /º	γ /º	ρ /g cm^3
Exp.	**108.0±0.7**	**3.817**	**9.021**	**10.048**	**93.38**	**95.50**	**98.32**	**1.657**
				Standard Force Field				
A	109.8±3.9	3.955	8.768	10.305	94.10	97.55	98.96	1.616
B^{C}	116.6±3.8	3.971	8.610	10.211	93.24	96.70	98.07	1.645
B^{R}	112.1±5.4	3.983	8.593	10.198	93.67	95.98	97.37	1.641
C^{C}	122.3±5.0	3.964	8.610	10.234	93.00	97.14	98.41	1.647
C^{R}	120.4±4.2	3.971	8.593	10.239	93.12	96.86	98.14	1.644
D^{R}	116.6±3.8	3.971	8.610	10.211	93.24	96.70	98.07	1.645
D^{C}	116.9±4.4	3.976	8.593	10.221	93.40	96.43	97.73	1.643
				Model with X-site in Cl				
A	118.6±0.2	3.797	8.913	10.835	97.01	109.29	100.16	1.685
B^{C}	117.3±0.2	3.819	8.817	10.343	95.50	101.74	99.79	1.692
B^{R}	117.7±0.2	3.803	8.817	10.398	95.86	102.29	99.54	1.693
C^{C}	127.2±0.2	3.832	8.809	10.345	94.83	102.30	100.61	1.693
C^{R}	125.9±0.2	3.822	8.808	10.399	95.14	102.84	100.51	1.693
D^{R}	117.3±0.2	3.819	8.817	10.343	95.50	101.74	99.79	1.692
D^{C}	121.9±0.2	3.814	8.809	10.388	95.43	102.42	100.01	1.694

[a] The experimental $\Delta_{\mathrm{sub}}H^{\mathrm{o}}_{\mathrm{m}}$ values correspond to those obtained in this work and included in Table 1 of the main text; [b] Crystallographic data from reference 29.

Table S32. Comparison between the enthalpy of sublimation ($\Delta_{\text{sub}}H_{\text{m}}^{\text{o}}$), crystal unit cell parameters (a, b, c, α, β, and γ), and crystal density (ρ), obtained experimentally (Exp.; bold) in this work or retrieved from the literature and the theoretical prediction from the MD simulations for the TR.[a]

Model	$\Delta_{\text{sub}}H_{\text{m}}^{\text{o}}$ / kJ mol^{-1}	a /Å	b /Å	c /Å	α /$^{\text{o}}$	β /$^{\text{o}}$	γ /$^{\text{o}}$	ρ /g cm^{3}
Exp.	**119.1±1.2**	**12.644**	**12.644**	**6.721**	**90.00**	**90.00**	**120.00**	**1.550**
Standard Force Field								
A	106.6±1.8	12.947	12.947	6.683	90.00	90.00	120.00	1.487
B^{C}	104.2±2.5	12.937	12.939	6.672	89.99	90.01	120.00	1.491
B^{R}	104.3±2.6	12.947	12.947	6.676	90.00	90.00	120.00	1.488
C^{C}	110.9±2.4	12.927	12.952	6.625	89.95	90.07	119.93	1.500
C^{R}	110.9±2.1	12.964	12.966	6.639	89.99	90.01	120.00	1.493
D^{R}	106.9±2.2	12.937	12.938	6.650	90.00	90.00	120.00	1.496
D^{C}	107.1±2.5	12.954	12.954	6.658	90.00	90.00	120.00	1.491
Model with X-site in Cl								
A	111.4±8.6	12.916	12.952	6.671	89.86	90.08	120.13	1.494
B^{C}	106.9±7.8	12.901	12.897	6.694	90.01	89.97	120.01	1.496
B^{R}	110.4±8.7	12.910	12.907	6.700	90.01	89.97	120.01	1.492
C^{C}	108.2±6.1	12.902	12.899	6.670	90.01	89.98	120.00	1.500
C^{R}	109.6±8.8	12.931	12.928	6.678	90.01	89.99	120.00	1.492
D^{C}	112.2±4.0	12.906	12.905	6.648	90.01	90.00	120.00	1.504
D^{R}	112.5±4.9	12.958	12.956	6.645	90.00	89.99	120.00	1.493

[a] The experimental $\Delta_{\text{sub}}H_{\text{m}}^{\text{o}}$ values correspond to those obtained in this work and included in Table 1 of the main text; [b] Crystallographic data from reference 30.

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