Electronic Supporting Information

Co-crystallisation through halogen bonding with racemic or enantiopure sulfinamides

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## Table of Contents

Analytical Data and Figures for (±)–2  
[IR, PXRD, ORTEP, Intermolecular interactions]  
03

Analytical Data and Figures for (S)–2  
[IR, PXRD, ORTEP, Intermolecular interactions]  
05

Analytical Data and Figures for 1.(±)–2  
[IR, PXRD, ORTEP, Intermolecular interactions]  
07

Analytical Data and Figures for 1.(S)–2  
[IR, PXRD, ORTEP, Intermolecular interactions]  
11

Analytical Data and Figures for (R)–2  
[IR, PXRD]  
15

Analytical Data and Figures for 1.(R)–2  
[IR, PXRD]  
16

Intermolecular Interactions  
17
Analytical Data and Figures for (±)-2

IR spectra for (±)-2.

PXRD pattern of (±)-2 obtained from solution crystallization (red) overlaid with theoretical pattern (black).
ORTEP plot of (±)-2 (ellipsoids shown at 30% probability).

Hydrogen bonding in (±)-2. (The p-tolyl group is removed for clarity.)
Analytical Data and Figures for (S)-2

IR spectra for (S)-2

-4000.0 3400 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600 450.0

PXRD pattern of (S)-2 obtained from solution crystallization (black).
ORTEP plot of (S)-2 (ellipsoids shown at 30% probability).

Hydrogen bonding in (S)-2. (The p-tolyl group is removed for clarity.)
Analytical Data and Figures for 1.(±)-2

IR spectra for 1.(±)-2

PXRD pattern of neat grind in ratio of 2:1. 1: (±)-2 (black), overlaid with theoretical patterns of 1.(±)-2 cocrystal, (red), 1 (blue) and (±)-2 (green).
PXRD pattern of neat grind in ratio of 1:1. 1: (±)-2 (black), overlaid with theoretical patterns of 1:(±)-2 cocrystal, (red), 1 (blue) and (±)-2 (green).

PXRD pattern of neat grind in ratio of 1:2. 1: (±)-2 (black), overlaid with theoretical patterns of 1:(±)-2 cocrystal, (red), 1 (blue) and (±)-2 (green).
PXRD pattern of neat grind in ratio of 1:4. \(1: (\pm)-2\) (black), overlaid with theoretical patterns of \(1,(\pm)-2\) cocrystal, (red), \(1\) (blue) and \((\pm)-2\) (green).

PXRD pattern of \(1,(\pm)-2\) obtained from solution crystallization (red) overlaid with theoretical pattern (black).
ORTEP plot of $\text{1.}(\pm)-2$ (ellipsoids shown at 30% probability).

Hydrogen bonding in $\text{1.}(\pm)-2$
Analytical Data and Figures for 1.(S)-2

IR spectra for 1.(S)-2

PXRD pattern of neat grind in ratio of 2:1. 1: (S)-2 (black), overlaid with theoretical patterns of 1.(S)-2 cocrystal, (red), 1 (blue) and (S)-2 (green).
PXRD pattern of neat grind in ratio of 1:1. 1: (S)-2 (black), overlaid with theoretical patterns of 1-(S)-2 cocrystal, (red), 1 (blue) and (S)-2 (green).

PXRD pattern of neat grind in ratio of 1:2. 1: (S)-2 (black), overlaid with theoretical patterns of 1-(S)-2 cocrystal, (red), 1 (blue) and (S)-2 (green).
PXRD pattern of 1.(S)-2 obtained from solution crystallization (red) overlaid with theoretical pattern (black).

* The PXRD patterns contain minor impurities of 1,4-diiodotetrafluorobenzene

ORTEP plot of 1.(S)-2 (ellipsoids shown at 50% probability).
Hydrogen bonding in 1.(S)-2
Analytical Data and Figures for \((R)\)-2

IR spectra for \((R)\)-2

PXRD pattern of \((R)\)-2 obtained from solution crystallization (red) overlaid with theoretical pattern (black).
Analytical Data and Figures for 1.(R)-2

IR spectra for 1.(R)-2

PXRD pattern of 1.(R)-2 obtained from solution crystallization (red) overlaid with theoretical pattern (black).

* The PXRD patterns contain minor impurities from both starting co-formers.
# Intermolecular Interactions

**Table 01.** Details of the Hydrogen Bonding Interactions Observed in the Co-crystals

<table>
<thead>
<tr>
<th>Cocrystal</th>
<th>Stoichiometry</th>
<th>Nature of interaction</th>
<th>Distance $^a$ (Å)</th>
<th>Angle at I (°)</th>
<th>Angle at O (°)</th>
<th>Number of donors to O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.(±)-2</td>
<td>1:4</td>
<td>I⋯O</td>
<td>2.958(2)</td>
<td>176.63(11)</td>
<td>121.88(12)</td>
<td>1</td>
</tr>
<tr>
<td>1.(S)-2</td>
<td>1:1</td>
<td>I⋯O</td>
<td>2.767(5)</td>
<td>173.4(2)</td>
<td>123.6(3)</td>
<td>1</td>
</tr>
</tbody>
</table>

**Table 02.** Details of the Moderate Hydrogen Bonding Interactions Observed in the Starting Materials and Co-crystals

<table>
<thead>
<tr>
<th>Cocrystal</th>
<th>Nature of interaction</th>
<th>Distance D-H (Å)</th>
<th>Distance H⋯A (Å)</th>
<th>Distance D⋯A (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(±)-2</td>
<td>N9–H9B⋯O8</td>
<td>0.88(3)</td>
<td>2.16(4)</td>
<td>2.981(4)</td>
<td>156.(4)</td>
</tr>
<tr>
<td></td>
<td>N9–H9A⋯O8</td>
<td>0.82(3)</td>
<td>2.20(3)</td>
<td>2.966(4)</td>
<td>155.(4)</td>
</tr>
<tr>
<td>(S)-2</td>
<td>N9–H9A⋯O8</td>
<td>0.838(17)</td>
<td>2.198(17)</td>
<td>3.021(3)</td>
<td>168.(3)</td>
</tr>
<tr>
<td></td>
<td>N9–H9B⋯O8</td>
<td>0.94(3)</td>
<td>2.05(3)</td>
<td>2.947(3)</td>
<td>160.(2)</td>
</tr>
<tr>
<td>1.(±)-2</td>
<td>N25–H25B⋯O14</td>
<td>0.89(4)</td>
<td>2.15(4)</td>
<td>3.024(5)</td>
<td>167.(3)</td>
</tr>
<tr>
<td></td>
<td>N25–H25A⋯O14</td>
<td>0.85(4)</td>
<td>2.45(4)</td>
<td>3.210(4)</td>
<td>150.(4)</td>
</tr>
<tr>
<td></td>
<td>N15–H15A⋯O24</td>
<td>0.872(18)</td>
<td>2.14(2)</td>
<td>2.994(4)</td>
<td>168.(3)</td>
</tr>
<tr>
<td></td>
<td>N15–H15B⋯S23</td>
<td>0.886(19)</td>
<td>2.93(3)</td>
<td>3.580(3)</td>
<td>132.(3)</td>
</tr>
<tr>
<td></td>
<td>N15–H15B⋯O24</td>
<td>0.886(19)</td>
<td>2.12(3)</td>
<td>2.921(4)</td>
<td>150.(4)</td>
</tr>
<tr>
<td>1.(S)-2</td>
<td>N21–H21A⋯O20</td>
<td>0.81</td>
<td>2.27</td>
<td>2.905(8)</td>
<td>135.6</td>
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</tbody>
</table>