Supporting Information

Experimental and computational insights into the nature of weak intermolecular interactions in trifluoromethyl substituted isomeric crystalline N-methyl-N-phenylbenzamides.

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Section 1. List of synthesized compounds along with their synthesized yields (after column), melting points (from DSC, onset value), and spectroscopic characterization (FTIR, \textsuperscript{1}H NMR):

1. \textit{N}-methyl-N-phenyl-2-(trifluoromethyl)benzamide (NM01): Colourless thick oil; yield = 78%; M.P. = not determined; FTIR (in cm\textsuperscript{-1}: KBr): 3066, 2930, 1660; \textsuperscript{1}H NMR (400MHz, CDCl\textsubscript{3}): \(\delta\) 7.56 (d, \(J = 6.67\) Hz, 1H), 7.30 (m, 2H), 7.20 (t, \(J = 7.06\) Hz, 2H), 7.11 (m, 4H), 3.53 (s, 3H).

(a) \textit{N}-methyl-N-phenyl-3-(trifluoromethyl)benzamide (NM02): White solid; yield = 84%; M.P. = 65°C; FTIR (in cm\textsuperscript{-1}: NaCl round cell plate): 3066, 2930, 1651; \textsuperscript{1}H NMR (400MHz, CDCl\textsubscript{3}): \(\delta\) 7.58 (s, 1H), 7.49 (t, \(J = 7.43\) Hz, 2H), 7.28 (m, 3H), 7.19 (tt, \(J = 7.43\) Hz, 1.44 Hz, 1H), 7.05 (d, \(J = 7.43\) Hz, 2H), 3.53 (s, 3H)

2. \textit{N}-methyl-N-phenyl-4-(trifluoromethyl)benzamide (NM03): White solid; yield = 91%; M.P. = 86°C; FTIR (in cm\textsuperscript{-1}: NaCl round cell plate): 3064, 2932, 1658; \textsuperscript{1}H NMR (400MHz, CDCl\textsubscript{3}): \(\delta\) 7.43 (dt, \(J = 10.87\) Hz, 4.25Hz, 4H), 7.27 (tt, \(J = 7.26\) Hz, 1.70 Hz, 2H), 7.19 (tt, \(J = 7.35\)Hz, 1.43 Hz, 1H), 7.05 (d, \(J = 7.35\) Hz, 2H), 3.53 (s, 3H).
3. N-methyl-N-(2-(trifluoromethyl)phenyl)benzamide (NM10): White solid; yield = 88%; M.P. 74°C =; FTIR (in cm\(^{-1}\): NaCl round cell plate): 3066, 2925, 1658; \(^1\)H NMR (400MHz, CDCl\(_3\)): δ 7.65 (d, J = 7.44 Hz, 2H), 7.45 (m, 3H), 7.36 (t, J = 7.44 Hz, 1H), 7.21 (d, J = 6.65 Hz, 1H), 7.16 (d, J = 7.00 Hz,3H), 3.45 (s, 3H).

4. N-methyl-N-(3-(trifluoromethyl)phenyl)benzamide (NM20): Colourless thick oil; yield = 81%; M.P. = not determined; FTIR (in cm\(^{-1}\): NaCl round cell plate): 3063, 2930, 1659; \(^1\)H NMR (400MHz, CDCl\(_3\)): δ 7.41 (d, J = 7.76 Hz, 1H), 7.35 (m, 2H), 7.29 (m, 2H), 7.22 (d, J = 7.42, 3H), 3.54 (s, 3H).

5. N-methyl-N-(4-(trifluoromethyl)phenyl)benzamide (NM30): White low melting solid; yield = 86 %; M.P. = 39°C; FTIR (in cm\(^{-1}\): NaCl round cell plate): 3062, 2931, 1659; \(^1\)H NMR (400MHz, CDCl\(_3\)): 7.51 (d, J = 8.29 Hz, 2H), 7.31 (m, 3H), 7.23 (m, 2H), 7.17 (d, J = 8.29 Hz, 2H), 3.54 (s, 3H).

6. N-methyl-2-(trifluoromethyl)-N-(2-(trifluoromethyl)phenyl)benzamide (NM11): White solid; yield = 93 %; M.P. = 88°C; FTIR (in cm\(^{-1}\): NaCl round cell plate): 3074, 2923, 1667; \(^1\)H NMR (400MHz, CDCl\(_3\)): δ7.81 (d, J = 7.95Hz, 1H), 7.78 (d, J = 7.95Hz, 1H), 7.70 (qn, J = 9.00Hz, 2H), 7.60 (d, J = 7.76 Hz,1H), 7.55 (q, J = 7.45, 2H), 7.45 (d, J = 7.73Hz, 1H), 3.11 (s, 3H).

7. N-methyl-3-(trifluoromethyl)-N-(2-(trifluoromethyl)phenyl)benzamide (NM12): White solid; yield = 91 %; M.P. = 58°C; FTIR (in cm\(^{-1}\): NaCl round cell plate): 3076, 2944, 1661; \(^1\)H NMR (400MHz, CDCl\(_3\)): δ 7.66 (d, J = 7.70 Hz, 1H), 7.54 (s, 1H), 7.49 (t, J = 6.80 Hz, 3H), 7.41 (t, J = 7.43 Hz, 1H), 7.30 (t, J = 7.42 Hz, 1H), 7.22 (d, J = 7.77 Hz, 1H), 3.47 (s, 3H).

8. N-methyl-4-(trifluoromethyl)-N-(2-(trifluoromethyl)phenyl)benzamide (NM13): Colourless thick oil; yield = 81%; M.P. = not determined; FTIR (in cm\(^{-1}\): NaCl round cell plate): 3069, 2930, 1652; \(^1\)H NMR (400MHz, CDCl\(_3\)): δ 7.48 (m, 3H), 7.40 (t, J = 7.73 Hz, 3H), 7.36 (d, J = 7.72 Hz, 1H), 7.21 (d, J = 7.72 Hz, 1H), 3.55 (s, 3H).

9. N-methyl-2-(trifluoromethyl)-N-(3-(trifluoromethyl)phenyl)benzamide (NM21): Colourless thick oil; yield = 88%; M.P. = not determined; FTIR (in cm\(^{-1}\): NaCl round cell plate): 3072, 2926, 1664; \(^1\)H NMR (400MHz, CDCl\(_3\)): δ 7.68 (s, 1H), 7.57 (m, 2H), 7.34 (m, 4H), 7.15 (s, 1H), 3.56 (s, 3H).
10. *N*-methyl-3-(trifluoromethyl)-*N*-(3-(trifluoromethyl)phenyl)benzamide (NM22): White solid; yield = 89 %; M.P. = 60°C; FTIR (in cm⁻¹: NaCl round cell plate): 3070, 2930, 1660; 1H NMR (400MHz, CDCl₃): δ 7.55 (d, J = 8.42 Hz, 2H), 7.48 (t, J = 9.05 Hz, 2H), 7.38 (m, 3H), 7.23 (d, J = 7.96Hz, 1H), 3.56 (s, 3H).

11. *N*-methyl-4-(trifluoromethyl)-*N*-(3-(trifluoromethyl)phenyl)benzamide (NM23): White solid; yield = 93 %; M.P. = 67°C; FTIR (in cm⁻¹: NaCl round cell plate): 3069, 2932, 1660; 1H NMR (400MHz, CDCl₃): δ 7.48 (m, 3H), 7.40 (t, J = 7.01 Hz, 3H), 7.36 (d, J = 7.43 Hz, 1H), 7.21 (d, J = 7.85 Hz, 1H), 3.55 (s, 3H).

12. *N*-methyl-2-(trifluoromethyl)-*N*-(4-(trifluoromethyl)phenyl)benzamide (NM31): White solid; yield = 87 %; M.P. = 72°C; FTIR (in cm⁻¹: NaCl round cell plate): 3071, 2931, 1667; 1H NMR (400MHz, CDCl₃): δ 7.61 (d, J = 7.84Hz, 2H), 7.48 (d, J = 6.90Hz, 2H), 7.36 (t, J = 6.93Hz, 2H), 7.20 (d, J = 6.90Hz, 2H), 3.56 (s, 3H).

13. *N*-methyl-3-(trifluoromethyl)-*N*-(4-(trifluoromethyl)phenyl)benzamide (NM32): Colourless thick oil; yield = 90%; M.P. = not determined; FTIR (in cm⁻¹: NaCl round cell plate): 3075, 2930, 1660; 1H NMR (400MHz, CDCl₃): δ 7.59 (s, 1H), 7.55 (t, J = 9.11Hz, 3H), 7.48 (d, J = 7.56Hz, 1H), 7.36 (t, J = 7.83Hz, 1H), 7.18 (d, J = 7.90Hz, 2H), 3.56 (s, 3H).

14. *N*-methyl-4-(trifluoromethyl)-*N*-(4-(trifluoromethyl)phenyl)benzamide (NM33): White solid; yield = 93 %; M.P. = 66°C; FTIR (in cm⁻¹: NaCl round cell plate): 3066, 2931, 1659; 1H NMR (400MHz, CDCl₃): δ 7.54 (t, J = 7.65 Hz, 3H), 7.50 (s, 1H), 7.44 (d, J = 8.31 Hz, 2H), 7.18 (d, J = 8.02 Hz, 2H), 3.55 (s, 3H).

Table S1: Details of Crystallization Experiments:

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Compound Code</th>
<th>Solvent and Crystallization conditions (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>NM02</td>
<td>Hexane (5°C), Chloroform (5°C),</td>
</tr>
<tr>
<td>2.</td>
<td>NM03</td>
<td>Hexane (5°C)</td>
</tr>
<tr>
<td>3.</td>
<td>NM10</td>
<td>Hexane (5°C), Ether (-20°C), Dichloromethane (5°C), Chloroform (5°C), Benzene (5°C)</td>
</tr>
<tr>
<td>4.</td>
<td>NM30(^b)</td>
<td>--------</td>
</tr>
</tbody>
</table>
5. NM11 Hexane (5°C), Ether (-20°C), Methanol (RT), Dichloromethane + cyclohexane (1:1, 5°C)
6. NM12 Hexane (5°C), Ether (-20°C)
7. NM22 Dichloromethane (5°C), Hexane (5°C)
8. NM23 Hexane (5°C)
9. NM31 Hexane (5°C), Dichloromethane (5°C)
10. NM33 Hexane (5°C), Dichloromethane + cyclohexane (1:1, 5°C)

\(^a\) All crystals, crystallized from different solvents or conditions for a particular compound, were found to be of the same phase. \(^b\) No solid aggregate could be obtained after crystallization from any solvent. Single crystal of NM30 was observed directly in the sample vial.

**Figure S1: IR-Spectra of the compounds:** All IR spectra were recorded on NaCl round cell plate on Perkin Elmer instrument.

(a) NM01:

(b) NM02:
(c) NM03:
(d) NM10:
(g) NM11:
(h) NM12:

(i) NM13:
(I) NM 23:
(o) NM33:
Figure S2: $^1$HNMR of all compounds: All NMR spectra were recorded on a 400MHz spectrometer (from Bruker) in CDCl$_3$ as solvent.

(a) NM01 (12 H): $\delta$ 7.56 (d, $J = 6.67$ Hz, 1H), 7.30 (m, 2H), 7.20 (t, $J = 7.06$ Hz, 2H), 7.11 (m, 4H), 3.53 (s, 3H).

(b) NM02 (12 H): $\delta$ 7.58 (s, 1H), 7.49 (t, $J = 7.43$ Hz, 2H), 7.28 (m, 3H), 7.19 (tt, $J = 7.43$ Hz, 1.44 Hz, 1H), 7.05 (d, $J = 7.43$ Hz, 2H), 3.53 (s, 3H)
(c) **NM03** (12 H): δ 7.43 (td, $J = 10.87$ Hz, 4.25 Hz, 4H), 7.27 (tt, $J = 7.26$ Hz, 1.70 Hz, 2H), 7.19 (tt, $J = 7.35$ Hz, 1.43 Hz, 1H), 7.05 (d, $J = 7.35$ Hz, 2H), 3.53 (s, 3H)

(d) **NM10** (12 H): δ 7.65 (d, $J = 7.44$ Hz, 2H), 7.45 (m, 3H), 7.36 (t, $J = 7.44$ Hz, 1H), 7.21 (d, $J = 6.65$ Hz, 1H), 7.16 (d, $J = 7.00$ Hz, 2H), 3.45 (s, 3H)
(e) **NM20** (12 H): $\delta$ 7.41 (d, $J = 7.76$ Hz, 1H), 7.35 (m, 2H), 7.29 (m, 3H), 7.22 (d, $J = 7.42$, 3H), 3.54 (s, 3H).

(f) **NM30** (12 H): 7.51 (d, $J = 8.29$ Hz, 2H), 7.31 (m, 3H), 7.23 (m, 2H), 7.17 (d, $J = 8.29$ Hz, 2H), 3.54 (s, 3H).
(g) **NM11** (11 H): δ 7.81 (d, J = 7.95 Hz, 1H), 7.78 (d, J = 7.95 Hz, 1H), 7.70 (qn, J = 9.00 Hz, 2H), 7.60 (d, J = 7.73 Hz, 1H), 7.55 (q, J = 7.45, 2H), 7.45 (d, J = 7.73 Hz, 1H), 3.11 (s, 3H).

![NM11 NMR spectrum](image)

(h) **NM12** (11 H): δ 7.66 (d, J = 7.70 Hz, 1H), 7.54 (s, 1H), 7.49 (t, J = 6.80 Hz, 3H), 7.41 (t, J = 7.43 Hz, 1H), 7.30 (t, J = 7.42 Hz, 1H), 7.22 (d, J = 7.77 Hz, 1H), 3.47 (s, 3H).

![NM12 NMR spectrum](image)
(i) **NM13** (11 H): $\delta$ 7.48 (m, 3H), 7.40 (t, $J = 7.73$ Hz, 3H), 7.36 (d, $J = 7.72$ Hz, 1H), 7.21 (d, $J = 7.72$ Hz, 1H), 3.55 (s, 3H).

![NM13 Spectrum](image)

(j) **NM21** (11H): $\delta$ 7.68 (s, 1H), 7.57 (m, 2H), 7.34 (m, 4H), 7.15 (s, 1H), 3.56 (s, 3H)

![NM21 Spectrum](image)
(k) **NM22** (11H): δ 7.55 (d, J = 8.42 Hz, 2H), 7.48 (t, J = 9.05 Hz, 2H), 7.38 (m, 3H), 7.23 (d, J = 7.96 Hz, 1H), 3.56 (s, 3H).

(l) **NM23** (11H): δ 7.48 (m, 3H), 7.40 (t, J = 7.01 Hz, 3H), 7.36 (d, J = 7.43 Hz, 1H), 7.21 (d, J = 7.85 Hz, 1H), 3.55 (s, 3H).
(m) NM31 (1H): $\delta$ 7.61 (d, $J = 7.84$Hz, 2H), 7.48 (d, $J = 6.90$Hz, 2H), 7.36 (t, $J = 6.93$Hz, 2H), 7.20 (d, $J = 6.90$Hz, 2H), 3.56 (s, 3H).

(n) NM32 (1H): $\delta$ 7.59 (s, 1H), 7.55 (t, $J = 9.11$Hz, 3H), 7.48 (d, $J = 7.56$Hz, 1H), 7.36 (t, $J = 7.83$Hz, 1H), 7.18 (d, $J = 7.90$Hz, 2H), 3.56 (s, 3H).
(o) NM33 (11H): δ 7.54 (t, \( J = 7.65 \) Hz, 3H), 7.50 (s, 1H), 7.44 (d, \( J = 8.31 \) Hz, 2H), 7.18 (d, \( J = 8.02 \) Hz, 2H), 3.55 (s, 3H).

Figure S3: DSC curves of solids (@ 5°C/min) recorded on Perkin Elmer DSC 6000.

(a) NM02

(b) NM03:
(c) NM10:

(d) NM30:

(e) NM11:
(f) NM12:

(Onset = 58.05 °C)

(g) NM22:

(Onset = 59.95 °C)

(h) NM23:
(i) NM31:

Onset $= 72.15^\circ C$

Peak $= 74.35^\circ C$

(j) NM33:

Onset $= 66.18^\circ C$

Peak $= 65.18^\circ C$
Figure S4: Experimental powder pattern for all solid compounds and its comparison with the simulated powder pattern.

(a) NM02:
(b) NM03

(c) NM10:

(d) NM30:
(e) NM11:

(f) NM12:
(g) NM22:

(h) NM23:
(i) NM31:

(j) NM33:
Figure S5: ORTEP of all compounds drawn with 50% ellipsoidal probability with atom-numbering scheme. Only the major component was shown in case of disorder for clarity. The dotted lines indicate presence of intra or intermolecular interactions.

(a) NM02:

(b) NM03:
Section 2: XPac analysis: Comparison of Crystal Structures
For XPAC analysis, the circled atoms, were considered for the ‘corresponding ordered sets of points’ (COSPs) [Fig S6]. The filter setting was set to ‘High’: a/p/d: 12/18/1.50 for all comparisons. The results of the analysis are presented in Table S2 and S3. The observed Supramolecular constructs (SC) are shown in the Figures S7 – S11.

Figure S6: Molecule structure representing COSPs (in red circle), considered for XPac analysis.

Table S2: Result of XPac analysis. ‘An’, ‘Bn’ and ‘Cn’ (n = integer) represents presence of 0D SC, 1D SC and 2D SC respectively. Numbers in bracket represent corresponding dissimilarity index, ‘X’. The blank boxes correspond to no similarity observed.
Figure S7: Presence of 2D supramolecular constructs (SC) in NM02_1 / NM03_2

Figure S8: Presence of 1D supramolecular constructs (SC)

(a) B1

(b) B2
Figure S9: Presence of 0D supramolecular constructs (SC)
(a) A1:

(b) A2:
Comparison of crystal structure reported in CSD with the present series by XPac
Table S2: Result of XPac analysis with crystal structure reported in CSD

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<td>0D (14.9)</td>
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</tbody>
</table>

Figure S10: Presence of 1D supramolecular constructs (SC)

(a)

(b)
Figure S11: Presence of 0D supramolecular constructs (SC)

(a)

(b)
Figure S12: XPac result for comparison of NM11 with molecules reported in CSD having *trans*-geometry (Ref code: YEGJYEY, DIBGIF and DIBGAX)
(a) NM11 with DIBGAX_1 (Dissimilarity index, $X = 13.3$)

(b) NM11 with DIBGAX_4 (Dissimilarity index, $X = 13.3$)