# Relative importance of C=O···X versus X···X halogen bonding as structural determinants in 4-halotriaroylbenzenes

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## Supplementary Information (ESI)

(12 pages)

### Table of contents

**(i) Preparation of 4-halotriaroylbenzenes**

All triaroylbenzenes were prepared according to literature procedures.[1] Compounds **1**-**2**[1] and **4**[2] have been previously reported. Triaroylbenzene **3**: Mp = 210 ºC. $^{1}$H-NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 6H), 7.89 (d, *J* = 8.4 Hz, 6H), 8.33 (s, 3H). $^{13}$C-NMR (75 MHz, $CDCl_3$) δ 101.7, 131.5, 134.1, 135.7, 138.2, 138.3, 194.1. IR (neat) ν ($cm^{-1}$) 1659. Anal. Calcd. for $C_{27}H_{15}I_3O_3$: C, 42.22; H, 1.97. Found: C, 42.46; H, 2.02.

**References**

1. I. Elghamry, *Synthesis*, 2003, **15**, 2301.

2. H. M. Colquhoun, F. Arico and D. J. Williams, *Chem. Commun*., 2001, 2574.

**(ii) ORTEP plot of [1+2] solid solution**

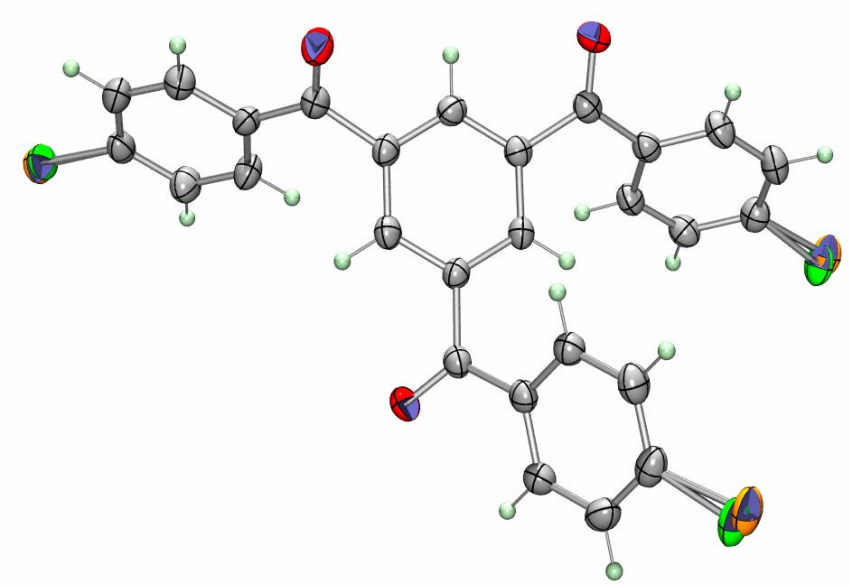


**Figure 1.** ORTEP plot of solid solution (**1**+**2**) drawn at 50% probability level for non-H atoms. The occupancies of Br (orange) and Cl (green) atoms are 55% and 45%, respectively.

**(iii) Differential Scanning Calorimetry (DSC)**

DSC was performed using a TA instruments 2010 DSC Ramp module. The sample was placed in crimped but vented aluminum pan and heated from 30 – 250 °C at a rate of 1 °C $min^{-1}$ under dry nitrogen.

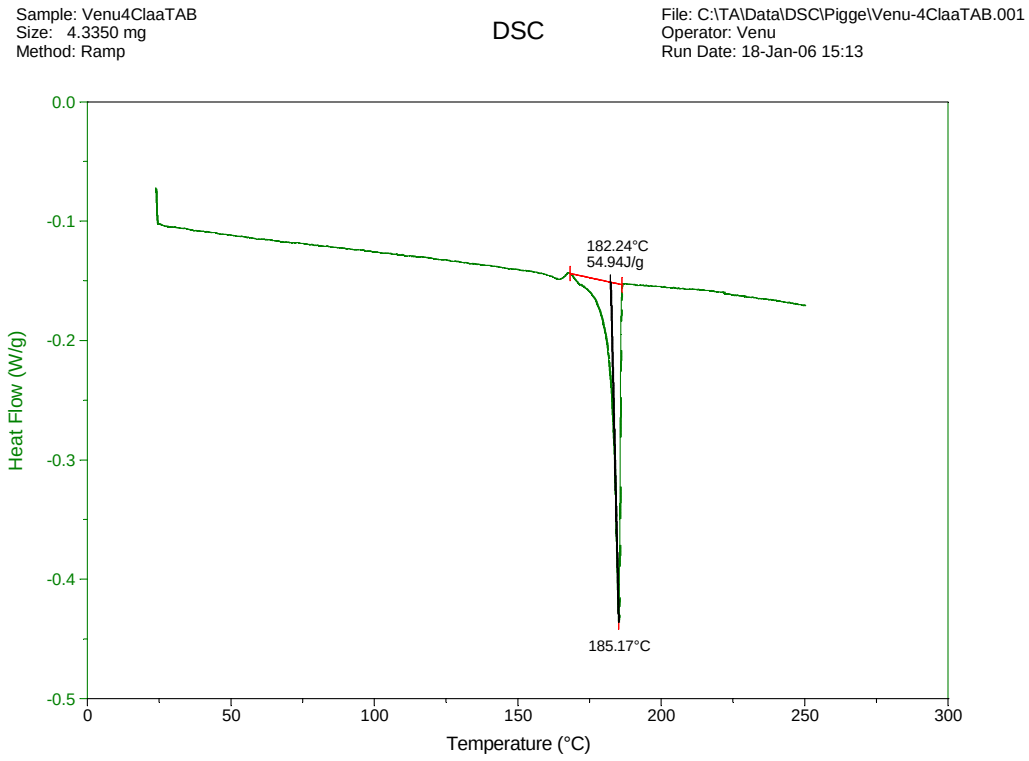



**Figure 2.** DSC trace of amorphous (4-chloro)TAB **1** obtained after the purification by column chromatography. Thermogram shows the presence of form A exclusively.

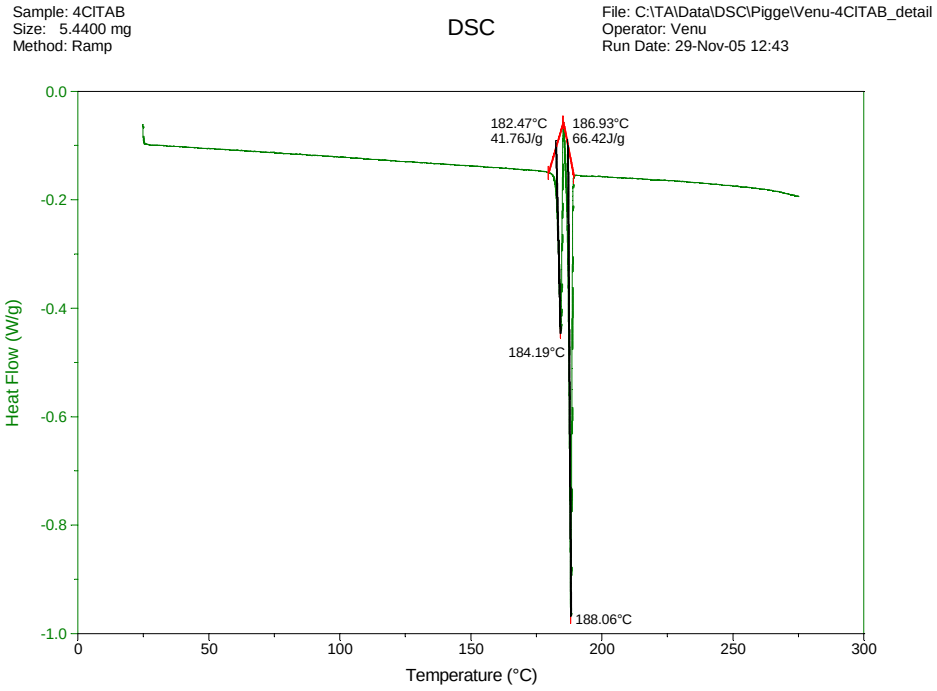



**Figure 3.** DSC trace of **1** (dimorphic mixture).

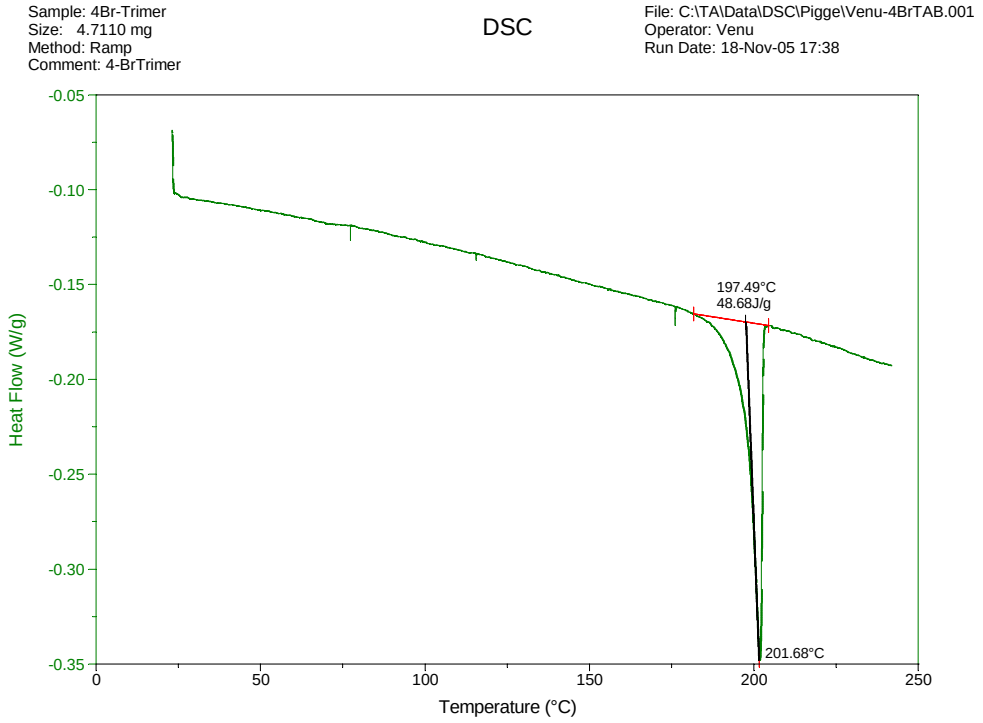



**Figure 4.** DSC trace of (4-bromo)TAB **2**.

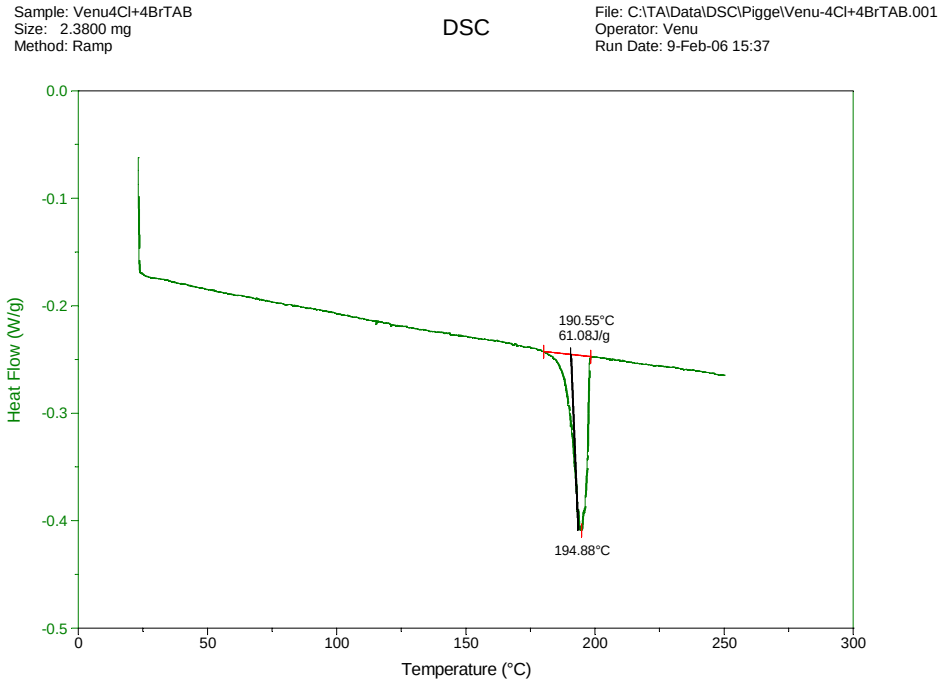



**Figure 5.** DSC thermogram of **1**+**2** solid solution.

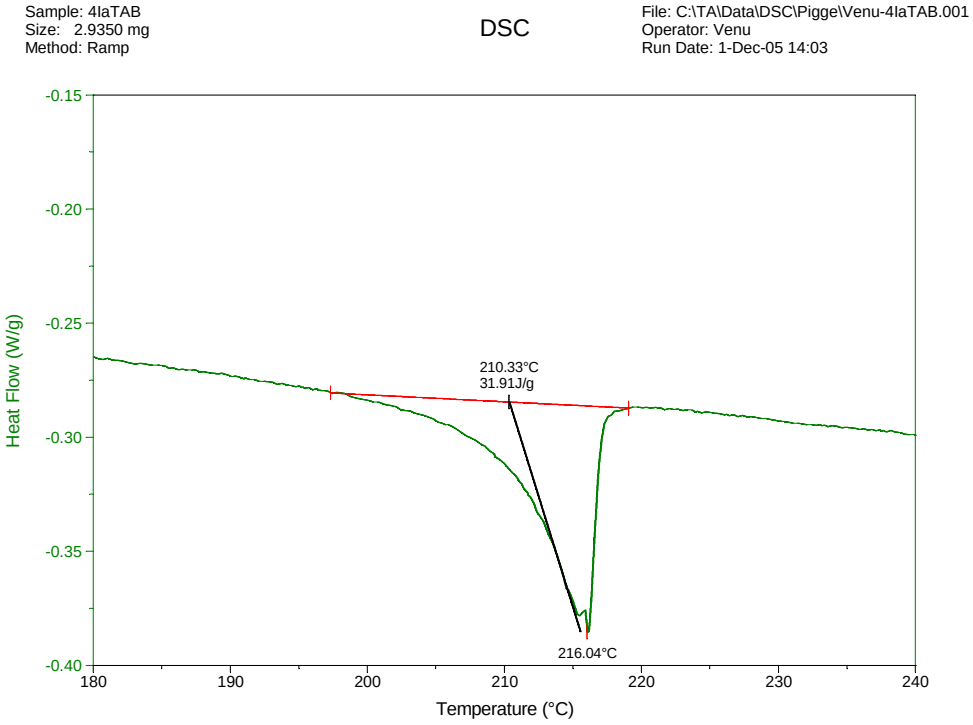



**Figure 6.** DSC thermogram of (4-iodo)TAB **3**.

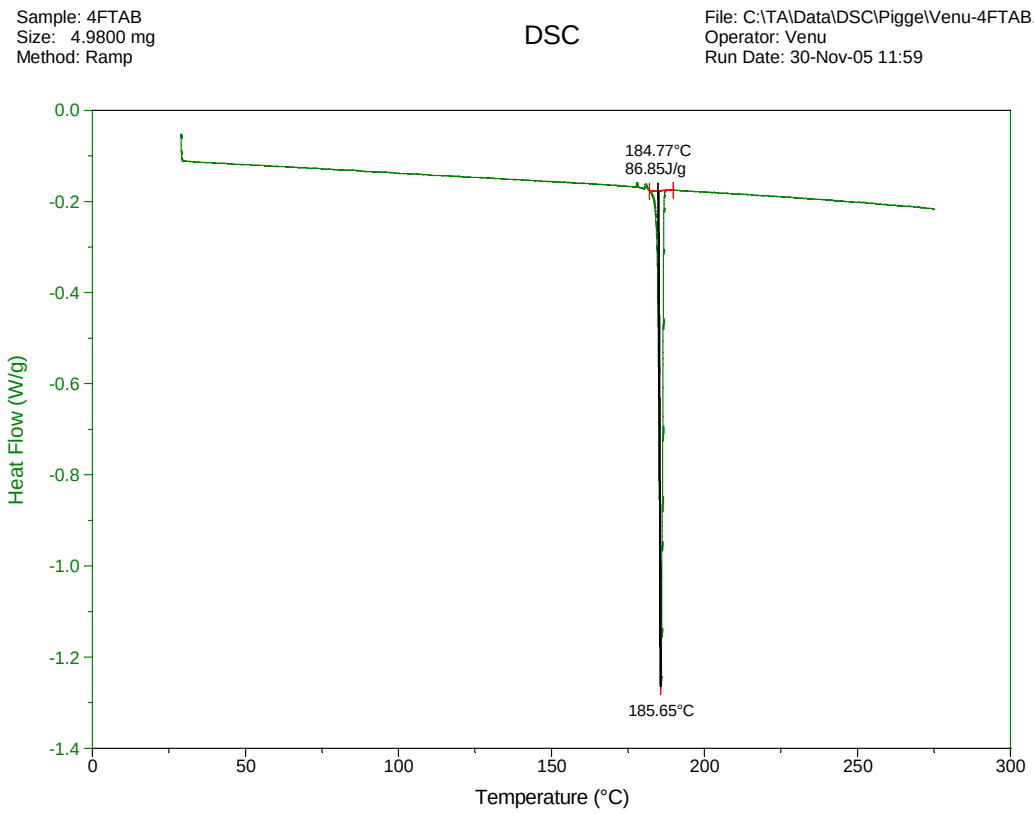



**Figure 7.** DSC trace of (4-fluoro)TAB **4**.

### (iv) X-Ray powder diffraction (PXRD)

X-ray powder diffraction data were recorded on a Siemens D5000 diffractometer using Cu Kα X-radiation at 50 kV and 30 mA. Diffraction patterns were collected over a range of 5 - 45° $2\theta$ at a scan rate of 1° $2\theta$ $min^{-1}$. The software Powder Cell 2.3 was used for Rietveld refinement (N. Kraus and G. Nolze, *POWDER CELL*, version 2.3; Federal Institute for Materials Research and Testing: Berlin, Germany, 2000).

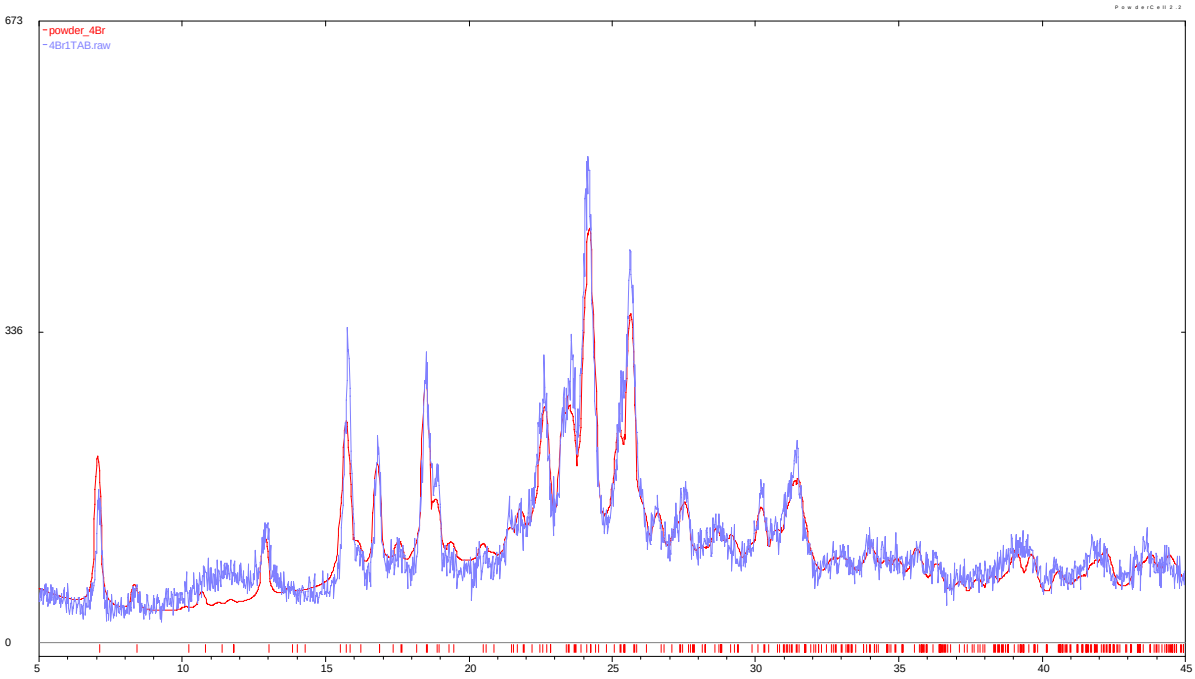



**Figure 4.** Comparision of Rietveld simulated (red) and experimental (violet) powder patterns for (4-bromo)TAB **2**.

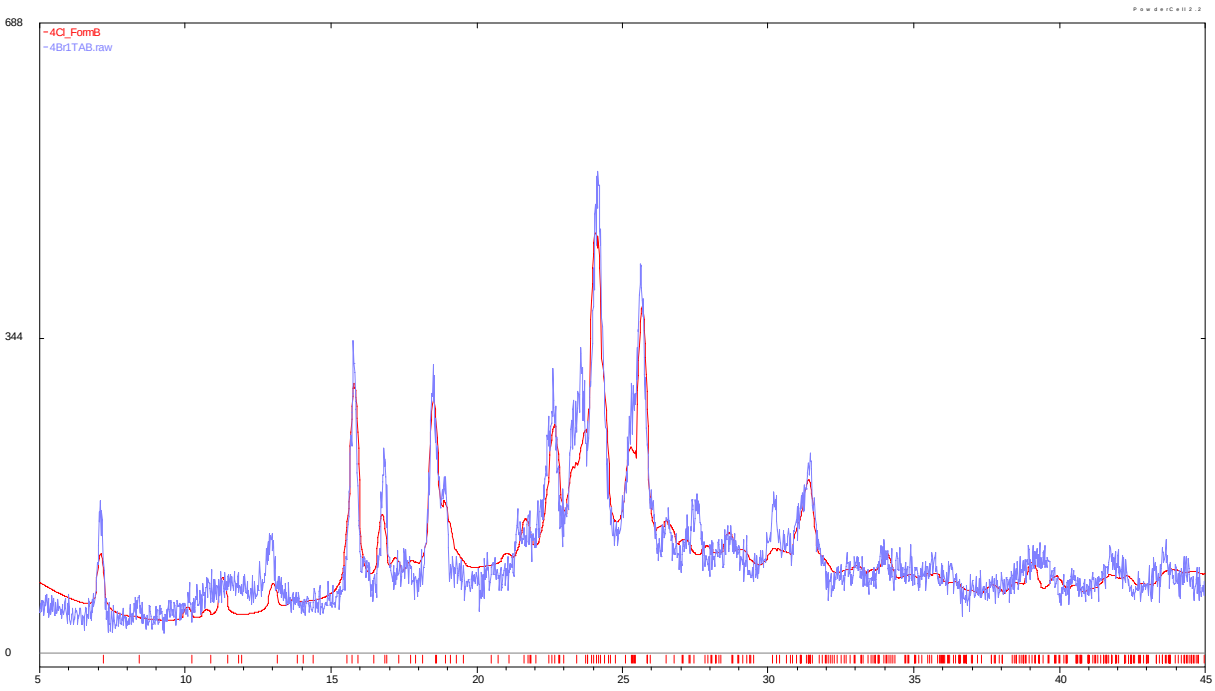



**Figure 5.** Comparision of Rietveld simulated (red) and experimental (violet) powder patterns for (4-chloro)TAB **1** (form B).

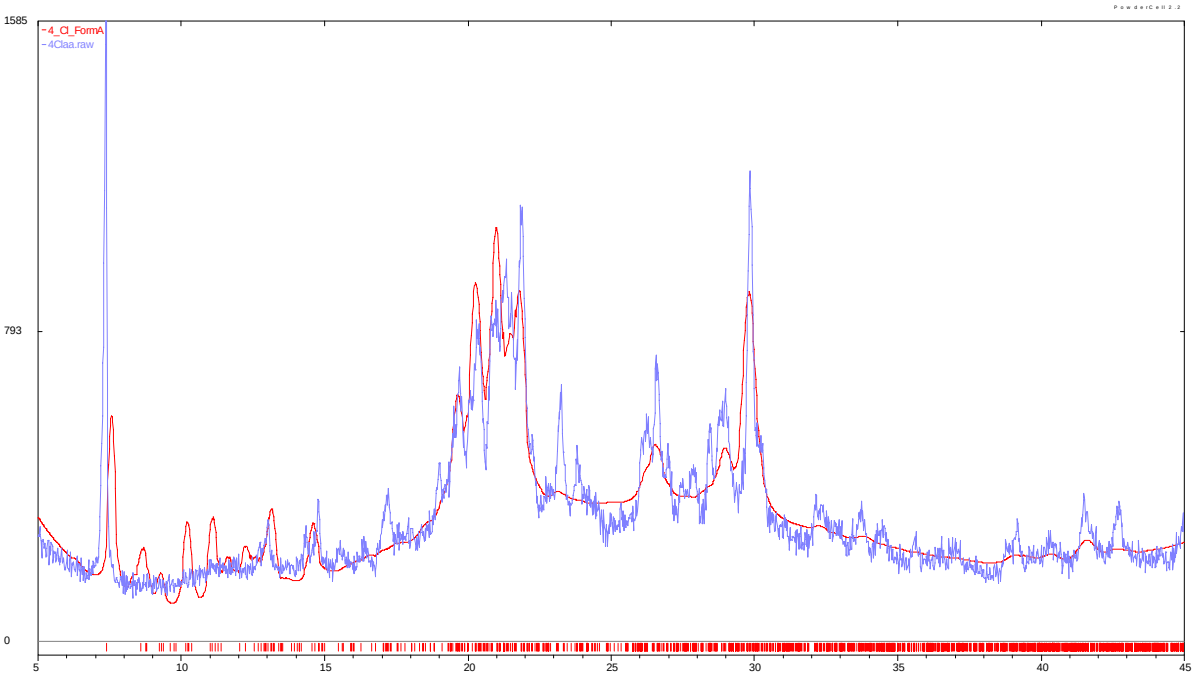



**Figure 6.** Comparision of Rietveld simulated (red) and experimental (violet) powder patterns for (4-chloro)TAB **1** (form A). Experimental data collected on amorphous material obtained from column chromatography.

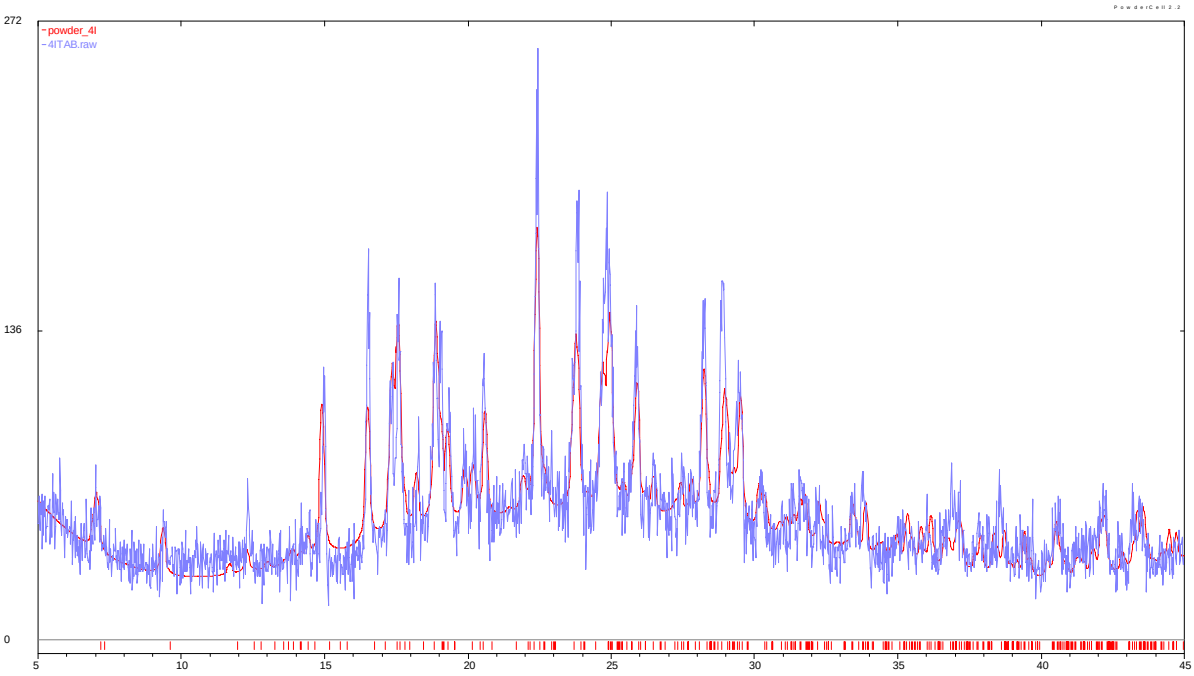



**Figure 7.** Comparision of Rietveld simulated (red) and experimental (violet) powder patterns for (4-iodo)TAB **3**.

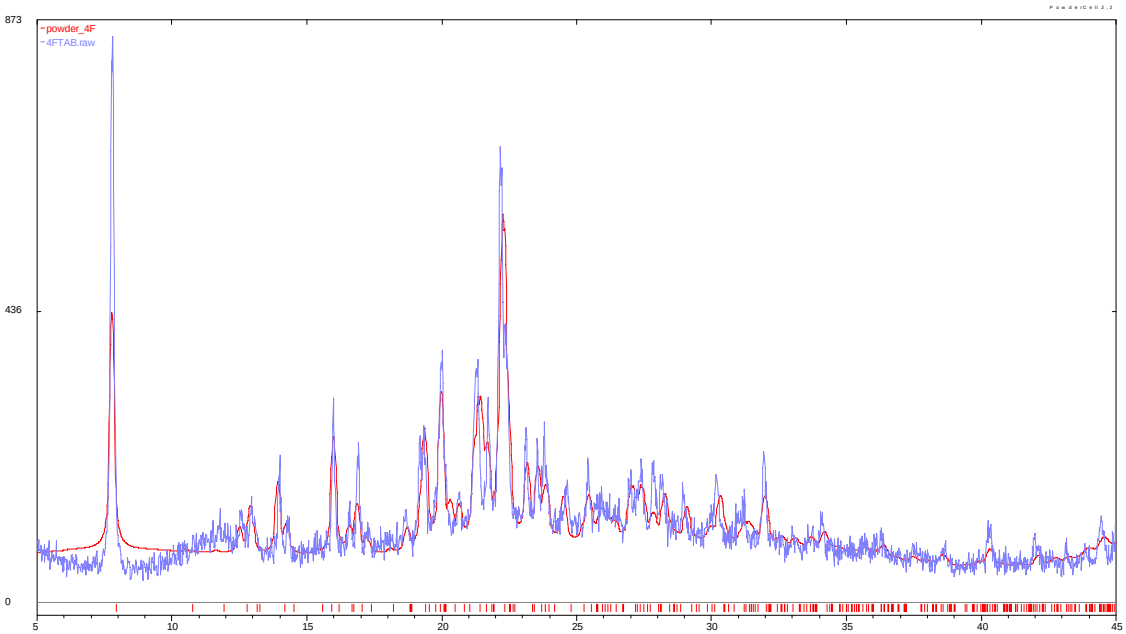



**Figure 8.** Comparision of Rietveld simulated (red) and experimental (violet) powder patterns for (4-fluoro)TAB **4**.

### (v) Determination of unit cell similarity index

**Table 1.** Lattice parameters after orthogonalisation are the following

| compound | *a* [Å] | *b* [Å] | *c* [Å] |
|---|---|---|---|
| **1** | 8.48114 | 11.0109 | 12.4306 |
| **2** | 8.56813 | 10.9684 | 12.6573 |
| (**1**+**2**) | 8.49821 | 10.9473 | 12.5738 |

Unit cell similarity Index (Π) = 0.0085 for **2** in relation to **1**.
Unit cell similarity Index (Π) = 0.0054 for **2** in relation to the solid solution (**1+2)**.

A value of zero indicates an exact unit cell match. For a thorough discussion, see: L. Fábián and A. Kálmán, *Acta Crystallogr.*, 1999, **B55**, 1099.

**(vi) CSD search of C–H···F interactions**

A search of the CSD (Version 5.27 / Conquest 1.8, January 2006) for error-free C–F organic, non-polymeric structures with R < 0.075 was performed. "No co-ordinates present" structures were excluded from the search. Of the 4039 structures with C–F in the subset, 888 hits with the (6 membered aromatic)C–H···F-C(6 membered aromatic) interactions [distance (*d*) and angle (*θ*) range: 2.0–2.8 Å, 120–180°] were found. Data is displayed in the form of a scatter plot (Fig. 9) to show the significance of the C–H···F interactions observed in **4** (2.32 Å, 162°; 2.34, 178 Å).

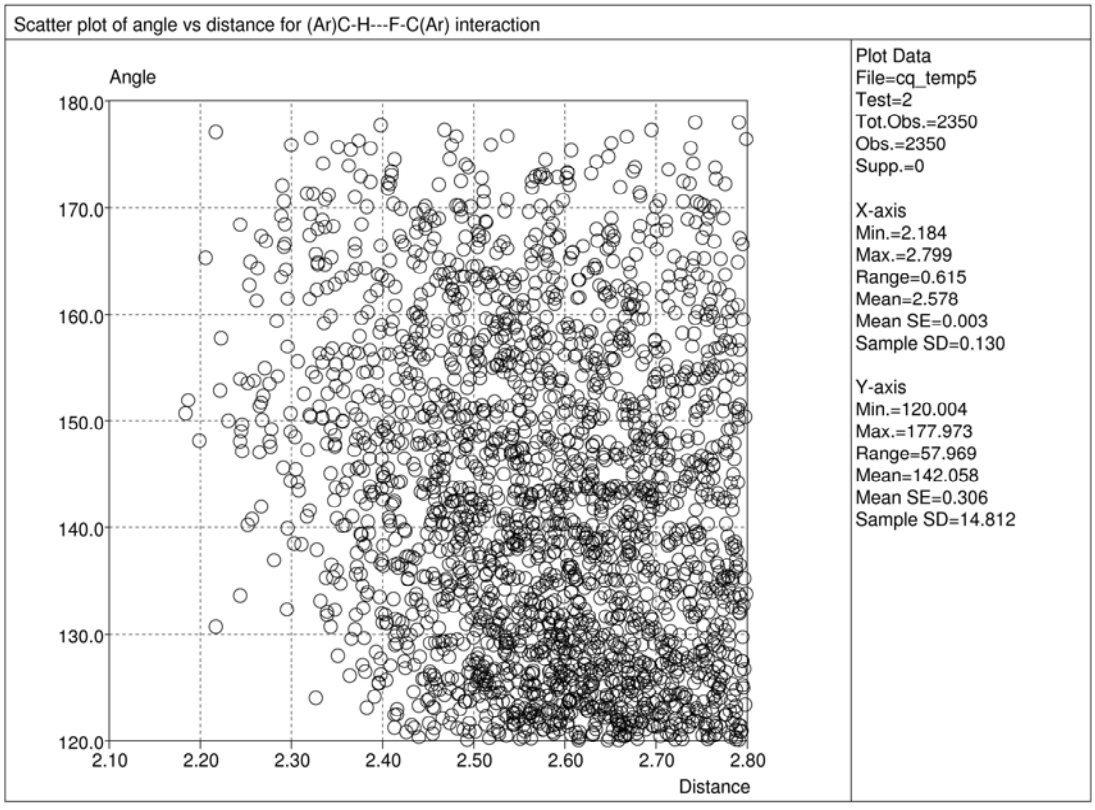


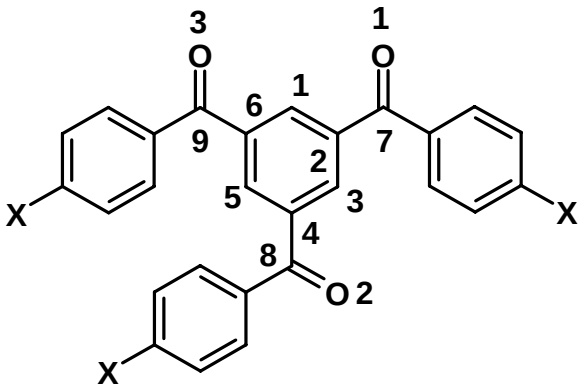

**Figure 9.** Scatter plot of (Ar)C–H···F-C(Ar) interactions.

**(vii) Table 2. Relevant intermolecular interactions for the compounds in this study**

| Compound | H-bond | *d* (Å)[a] | *D* (Å) | *θ* (deg) |
|---|---|---|---|---|
| **2** | C–H···Br | 2.75 | 3.794(5) | 162.6 |
| | C–H···O | 2.59 | 3.401(5) | 131.5 |
| | C–H···O | 2.58 | 3.445(5) | 136.3 |
| | C–Br···O=C | 3.105 | | 166.9, 138.5 |
| | C–Br···O=C | 3.190 | | 166.5, 134.7 |
| | Br···Br | 3.496 | | 146.4 |
| | C–H···π | 2.85 | 3.918 | 167.7 |
| **1**+**2** | C–Br···O=C, | 3.054, | | 165.3, 138.2 |
| | C–Cl···O=C | 3.227 | | 167.9, 139.3 |
| | C–Br···O=C, | 3.139, | | 166.3, 135.4 |
| | C–Cl···O=C | 3.267 | | 162.5, 132.0 |
| | C–Br···Br–C, | 3.296, | | 148.4, |
| | C–Cl···Br–C, | 3.547, | | 139.0, 146.5 |
| | C–Br···Cl–C | 3.547 | | 146.5, 139.0 |
| | C–H···Br | 2.73 | 3.778(4) | 163.0 |
| | C–H···Cl | 2.75 | 3.787 | 160.8 |
| | C–H···O | 2.57 | 3.415(3) | 134.6 |
| | C–H···O | 2.58 | 3.402(3) | 132.4 |
| **3** | I···I (type II) | 4.075 | | 153.1, 108.8 |
| | C–I···O=C | 3.072 | | 179.0, 138.4 |
| | C–H···O | 2.32 | 3.217(5) | 139.3 |
| | C–H···O | 2.56 | 3.417(4) | 135.2 |
| | C–H···I | 3.11 | 4.174 | 166.8 |
| | C–H···π(C=C) | 2.78 | 3.774 | 152.5 |
| **4** | C–H···F | 2.32 | 3.369(2) | 162.0 |
| | C–H···F | 2.34 | 3.4232(18) | 177.9 |
| | C–H···O | 2.33 | 3.2826(18) | 145.4 |
| | C–H···O | 2.27 | 3.3322(18) | 164.8 |
| | C–H···O | 2.48 | 3.4397(18) | 147.5 |
| | C–H···O | 2.42 | 3.4440(19) | 156.5 |
| | C–H···π(C=C) | 2.82 | 3.818 | 153.4 |

[a] C–H distance is neutron normalized to 1.083.

**(viii) Torsion angles observed in the (4-halo)TABs**




**X = Cl, Br, I, F**

| Compound | $\tau_1$(C1-C2-C7-O1)/° | $\tau_2$(C3-C4-C8-O2)/° | $\tau_3$(C5-C6-C9-O3)/° |
|---|---|---|---|
| **1** (Form A) | 119.3(2) | 26.3(3) | 37.6(2) |
| **2** | 127.2(6) | 37.7(6) | 33.4(4) |
| **1+2** | 127.2(3) | 37.2(3) | 32.8(2) |
| **3** | 161.9(5) | 27.9(5) | 30.3(3) |
| **4** | 24.41(18) | 144.04(18) | 24.90(14) |