

**Supplementary Information**Table S1a - Hirshfeld analysis for the covalent bonds in *trans*-cinnamic acid, **1a**.

Bond	DMSDA (x 10 <sup>-4</sup> )
C(1)-C(2)	0
C(1)-C(6)	-3
C(2)-C(3)	1
C(3)-C(4)	1
C(4)-C(5)	-4
C(5)-C(6)	-1
C(6)-C(7)	-1
C(7)-C(8)	-2
C(8)-C(9)	-2
C(9)-O(1)	3
C(9)-O(2)	6

Table S1b - Hirshfeld analysis for the covalent bonds in coumarin-3-carboxylic acid, **2a**.

Bond	DMSDA (x 10 <sup>-4</sup> )
C(1)-C(2)	4
C(1)-C(6)	0
C(2)-C(3)	1
C(3)-C(4)	0
C(4)-C(5)	-1
C(5)-C(6)	-3
C(6)-C(7)	1
C(7)-C(8)	-2
C(8)-C(9)	0
C(8)-C(10)	2
C(1)-O(1)	2
C(9)-O(1)	2
C(9)-O(2)	0
C(10)-O(3)	-1
C(10)-O(4)	2

Table S2a - Radial parameters and net atomic charge for **1a** obtained from monopole populations after multipole refinement.

Atom	Kappa	Kappa'	Net Charge
C(1)	0.998	0.985	-0.092
C(2)	0.998	0.985	-0.039
C(3)	0.998	0.985	-0.076
C(4)	0.998	0.985	-0.092
C(5)	0.998	0.985	-0.155
C(6)	0.998	0.985	-0.050
C(7)	0.990	0.982	-0.117
C(8)	0.990	0.982	-0.155
C(9)	1.009	0.987	+0.178
O(1)	0.980	1.006	-0.326
O(2)	0.968	0.951	-0.454
H(1A)	1.200	1.200	+0.384
H(1)	1.200	1.200	+0.144
H(2)	1.200	1.200	+0.068
H(3)	1.200	1.200	+0.149
H(4)	1.200	1.200	+0.099
H(5)	1.200	1.200	+0.153
H(7)	1.200	1.200	+0.205
H(8)	1.200	1.200	+0.178

Table S2b - Radial parameters and net atomic charge for **2a** obtained from monopole populations after multipole refinement.

Atom	Kappa	Kappa'	Net Charge
C(1)	1.020	0.982	+0.020
C(2)	1.017	0.989	-0.054
C(3)	1.017	0.989	-0.070
C(4)	1.017	0.989	-0.027
C(5)	1.017	0.989	-0.081
C(6)	1.017	0.989	-0.003
C(7)	1.017	0.989	-0.027
C(8)	1.017	0.989	-0.004
C(9)	1.020	0.982	+0.102
C(10)	1.023	0.975	+0.126
O(1)	0.998	1.030	-0.224
O(2)	0.993	0.984	-0.235
O(3)	0.994	0.986	-0.313
O(4)	0.993	0.984	-0.236
H(3A)	1.208	1.200	+0.335
H(2)	1.208	1.200	+0.131
H(3)	1.208	1.200	+0.125
H(4)	1.208	1.200	+0.119
H(5)	1.208	1.200	+0.152
H(7)	1.208	1.200	+0.164

Table S3a - Integrated Bader atomic charges for **1a** after multipole refinement. Total population for **1a** is 77.989 electrons, giving a net charge of 0.011 electrons.

Atom	Q	L
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C(1)	-0.057	+2.0x10 <sup>-3</sup>
C(2)	-0.020	+7.9x10 <sup>-4</sup>
C(3)	-0.079	+3.3x10 <sup>-3</sup>
C(4)	-0.049	+3.8x10 <sup>-3</sup>
C(5)	-0.144	+3.0x10 <sup>-3</sup>
C(6)	-0.073	-1.3x10 <sup>-3</sup>
C(7)	-0.091	-3.0x10 <sup>-3</sup>
C(8)	-0.112	+6.5x10 <sup>-5</sup>
C(9)	+1.455	+2.1x10 <sup>-3</sup>
O(1)	-1.143	+1.8x10 <sup>-3</sup>
O(2)	-1.209	+8.5x10 <sup>-5</sup>
H(1A)	+0.634	+4.2x10 <sup>-5</sup>
H(1)	+0.137	-2.2x10 <sup>-4</sup>
H(2)	+0.045	-2.3x10 <sup>-5</sup>
H(3)	+0.141	+1.0x10 <sup>-5</sup>
H(4)	+0.077	-1.7x10 <sup>-5</sup>
H(5)	+0.132	-1.1x10 <sup>-5</sup>
H(7)	+0.200	+1.2x10 <sup>-4</sup>
H(8)	+0.175	+1.5x10 <sup>-4</sup>

Table S3b - Integrated Bader atomic charges for **2a** after multipole refinement. Total population for **2a** is 98.027 electrons, giving a net charge of -0.027 electrons.

Atom	Q	L
C(1)	+0.350	-2.2x10 <sup>-2</sup>
C(2)	-0.031	-5.0x10 <sup>-3</sup>
C(3)	-0.079	-1.1x10 <sup>-3</sup>
C(4)	-0.049	-2.1x10 <sup>-3</sup>
C(5)	-0.080	-5.2x10 <sup>-3</sup>
C(6)	-0.008	-8.4x10 <sup>-3</sup>
C(7)	-0.029	-1.3x10 <sup>-3</sup>
C(8)	-0.009	+2.1x10 <sup>-3</sup>
C(9)	+1.284	+1.3x10 <sup>-2</sup>
C(10)	+1.386	+5.0x10 <sup>-3</sup>
O(1)	-1.029	+5.5x10 <sup>-4</sup>
O(2)	-0.968	+6.7x10 <sup>-4</sup>
O(3)	-1.061	-2.7x10 <sup>-3</sup>
O(4)	-1.039	+2.3x10 <sup>-4</sup>
H(3A)	+0.615	+1.2x10 <sup>-3</sup>
H(2)	+0.135	-1.5x10 <sup>-5</sup>
H(3)	+0.129	+2.8x10 <sup>-5</sup>
H(4)	+0.132	-5.9x10 <sup>-5</sup>
H(5)	+0.154	-2.6x10 <sup>-5</sup>
H(7)	+0.176	-5.8x10 <sup>-5</sup>

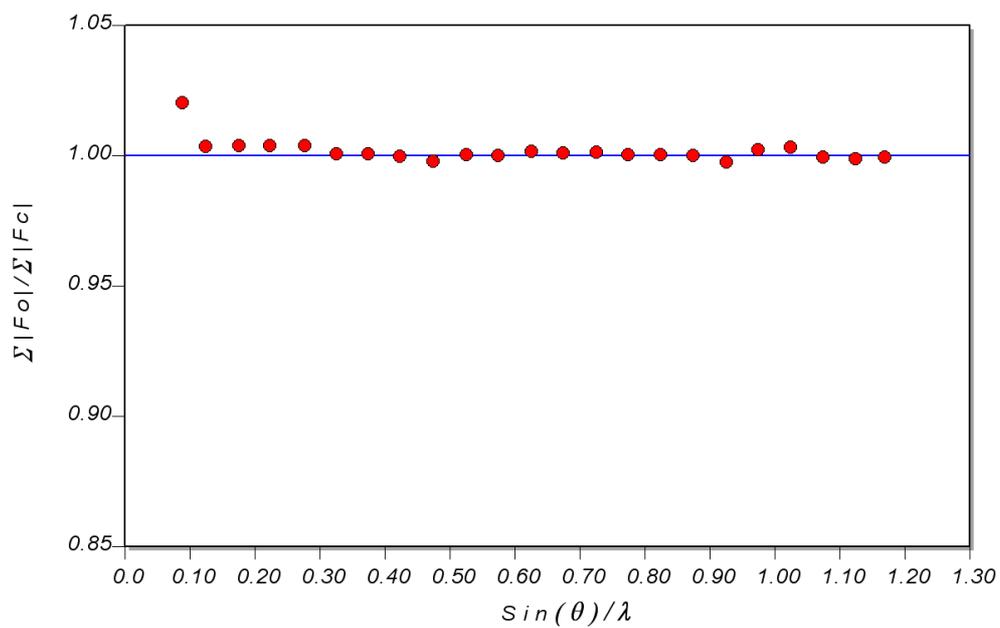
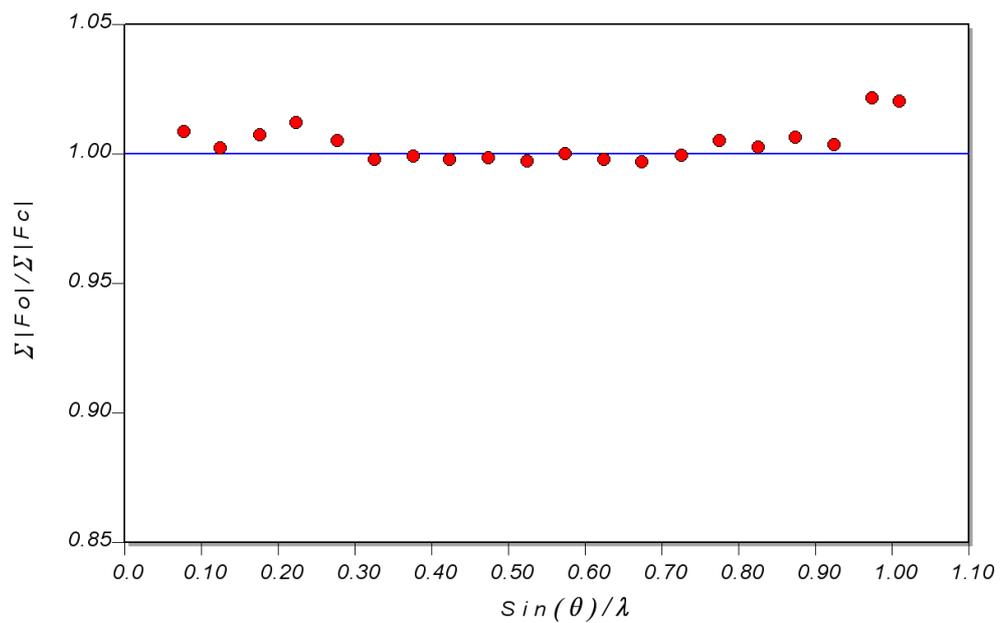


Figure S1 - Plot of  $\Sigma|F_o|/\Sigma|F_c|$  versus resolution for the merged data after multipole refinement in *trans*-cinnamic acid (top) coumarin-3-carboxylic acid.

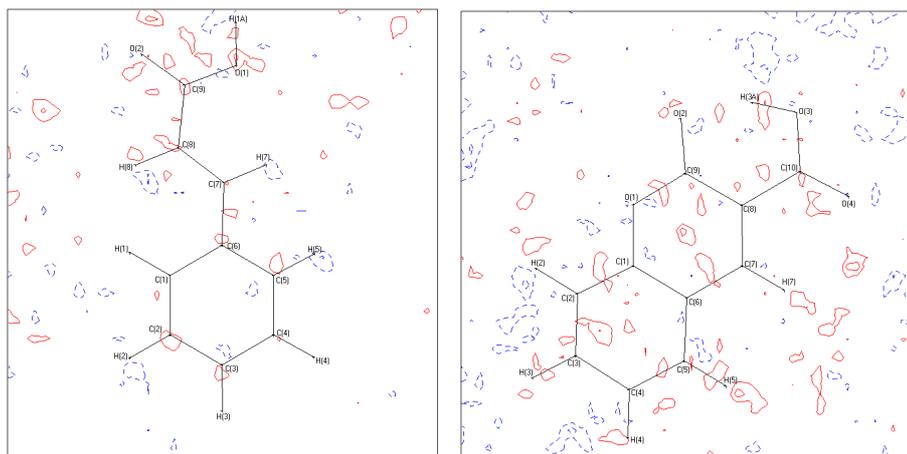


Figure S2 - Residual density maps after multipole refinement, all data used (left) **1a**, (right) **2a**. Contours are depicted at the  $0.05 \text{ e } \text{Å}^3$  level, with positive contours as solid red lines and negative contours as blue dashed lines.

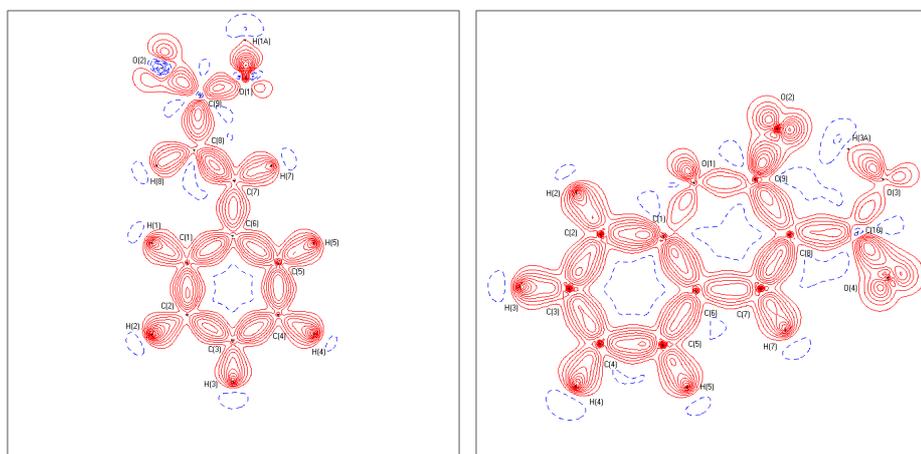


Figure S3 - Deformation density maps after multipole refinement (left) *trans*-cinnamic acid, (right) coumarin-3-carboxylic acid. Contours are depicted at the  $0.1 \text{ e } \text{Å}^3$  level, with positive contours as solid red lines and negative contours as blue dashed lines.

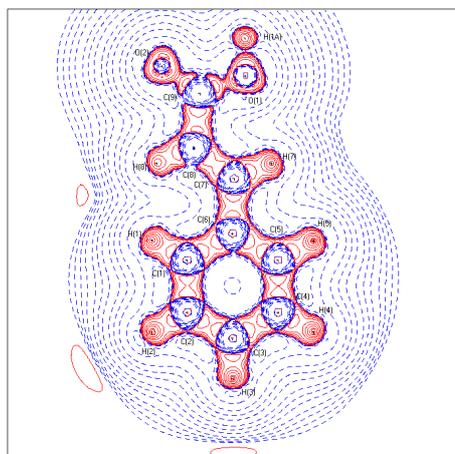


Figure S4 - Laplacian of the electron density for *trans*-cinnamic acid, positive contours are solid red lines, while negative contours are dashed blue lines.

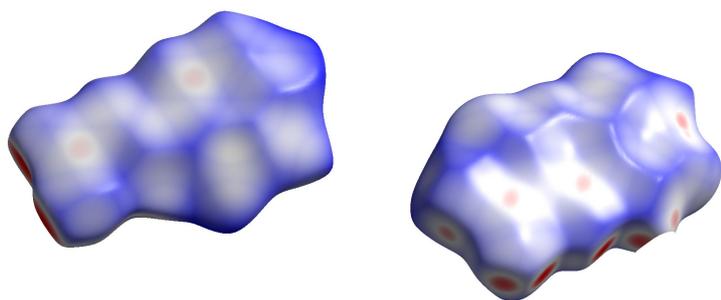


Figure S5 - Hirshfeld surfaces for (left) **1a**, (right) **2a** (red represents contacts shorter than the sum of the van der Waals contacts, white equal to the sum of the radii and blue greater than the sum of the radii).