Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary material for the paper

"XRD- and infrared-probed anisotropic thermal expansion properties of an organic semiconducting single crystal"

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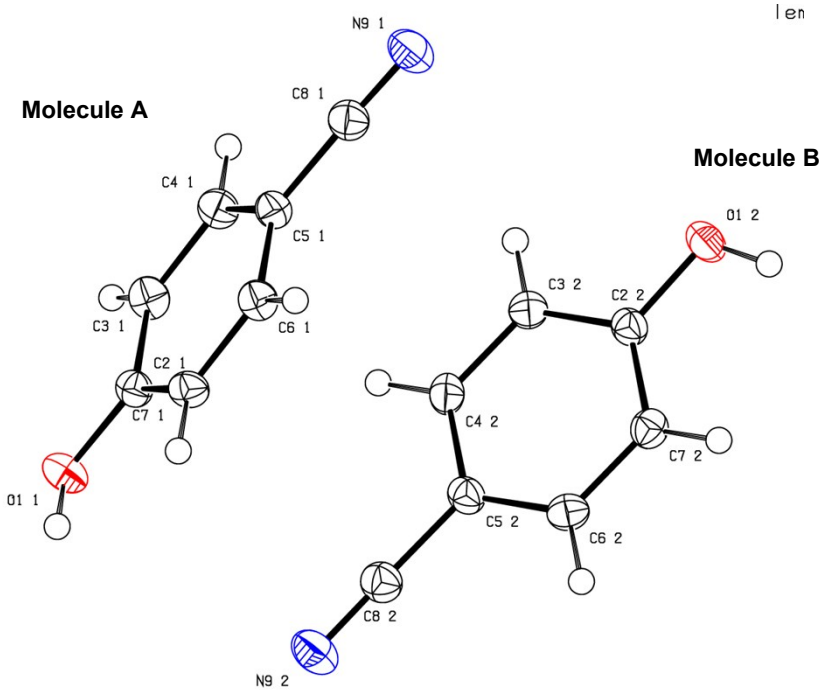

Figure S1 - Numbering of the carbon atoms of 4HCB in the crystal unit cell, as deposited in the CCDC database. The "Molecule A" and "Molecule B" labeling in this figure and in the manuscript text refers to the CCDC designation "Molecule 1" and "Molecule 2", respectively.

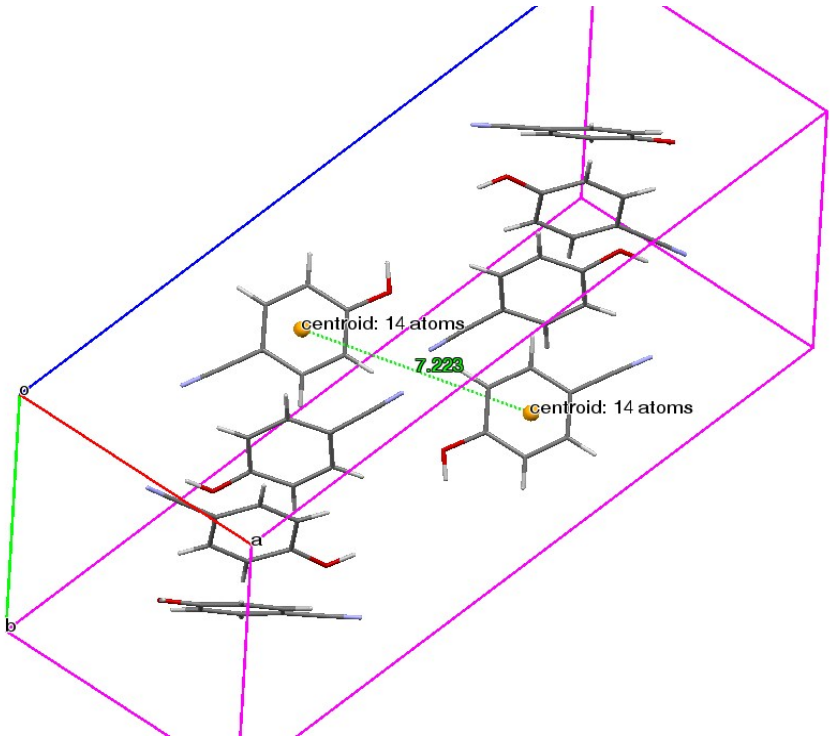

Figure S2 - Sketch of the development of pi-pi stacking along the axis c of the 4HCB unit cell. The π-π stacking is evidently broken in the middle of the unit cell, where a clear gap of more than 7 angstroms is found between the two nearest benzenic rings (some molecules in the figure have been deleted for more clarity).

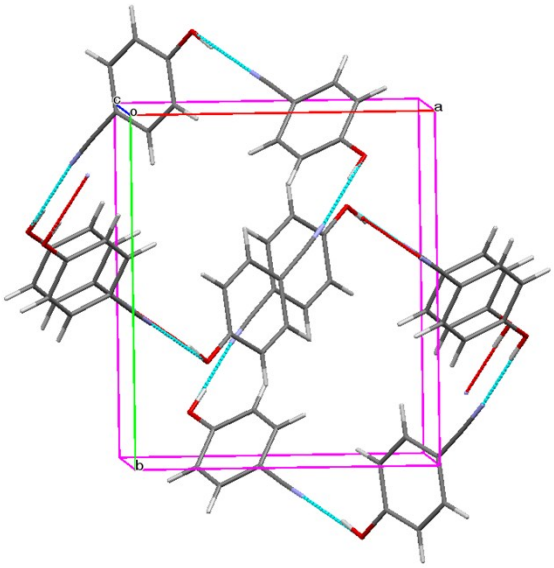

Figure S3 - Simplified unit cell (some molecules have been deleted for clarity) of 4HCB viewed along the axis c (i.e., with the axis a, red line, horizontally arranged and the axis b, green line, vertically arranged). It is possible to observe in cyan that the OH...NC hydrogen bond has some geometrical components along both the *a* and *b* axes.

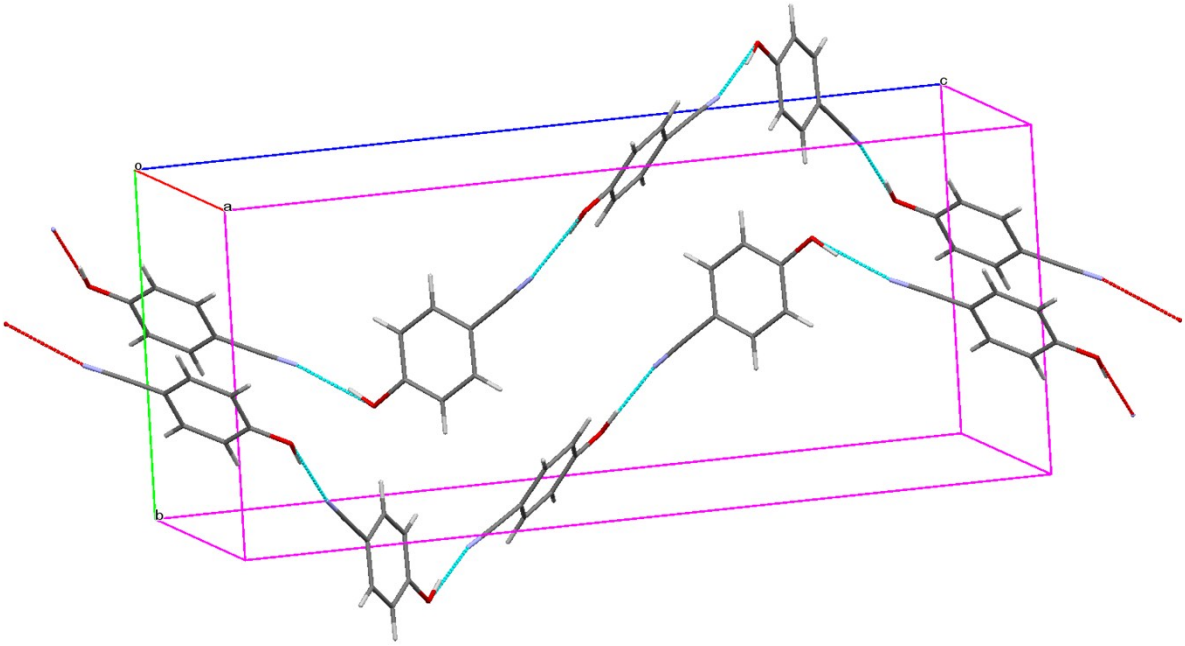

Figure S4 - Simplified unit cell (the same molecules of Fig. S3 have been deleted for clarity) of 4HCB viewed in three dimensions (axis *a*: red line; axis *b*: green line; axis *c*: blue line). The cyan OH...NC hydrogen bond interactions are clearly seen directing the 4HCB molecules arrangement as mostly developing along the axis *c* of the unit cell, despite having non-negligible geometrical components along both the *a* and *b* axes.

Additional rationale for the identification of the most relevant interactions along the three axes of the unit cell of the 4HCB crystal

As is visible in Fig. S3, looking at the hydrogen bonds perpendicularly to the *c* axis (i.e., considering their *a* and *b* components) it is evident that some vectorial component of the H-bond (in terms of bond length) is present along both the *b* and *a* axes (green and red axes, respectively). However, looking at the same simplified unit cell along the axis *c* (Fig. S4) it appears clear that the hydrogen bonds dictate the formation of the observed head-to-tail 4HCB spirals having their axes along the axis *c*, and that the stiffening effect induced by the hydrogen bond (in terms of force) is hence developed mainly along this axis. In other words, despite the fact that meaningful *geometrical* components of the H-bond along the axes *a* and *b* can be calculated with a vectorial analysis, in terms of *effective interaction* only its straight nucleous-to-nucleous component must be considered to be relevant.

Table S1 - lengths (in Å) of selected intra/intermolecular bonds/contacts at different temperatures.

Selected bond/contact*	**Length (A)**				
	@ 300 K	**@ 260 K**	**@ 200 K**	**@ 160 K**	**@ 120 K**
Ortho C^7C^2 bond 1 molecule A	1.388	1.387	1.394	1.397	1.398
Ortho C^2C^3 bond 2 Molecule A	1.391	1.394	1.395	1.396	1.397
Ortho C^4C^5 bond 3 molecule A	1.390	1.390	1.394	1.397	1.399
Ortho C^5C^6 bond 4 Molecule A	1.391	1.394	1.394	1.397	1.397
Ortho C^7C^2 bond 1 molecule B	1.387	1.389	1.392	1.393	1.394
Ortho C^2C^3 bond 2 Molecule B	1.382	1.383	1.389	1.393	1.395
Ortho C^4C^5 bond 3 molecule b	1.386	1.390	1.392	1.396	1.398
Ortho C^5C^6 bond 4 Molecule b	1.384	1.388	1.392	1.392	1.395
Meta C^6C^7bond 1' molecule A	1.372	1.377	1.379	1.380	1.381
Meta C^3C^4bond 2' Molecule A	1.369	1.372	1.376	1.377	1.380
Meta C^6C^7 bond 1' molecule B	1.373	1.375	1.375	1.378	1.380
Meta C^3C^4 bond 2' Molecule B	1.379	1.378	1.380	1.381	1.382
C^2O^1 molecule A	1.350	1.349	1.349	1.350	1.351
C^2O^1 molecule B	1.356	1.355	1.355	1.354	1.355
$N^9_A\cdots O^1_B$	2.815	2.814	2.812	2.811	2.810
$N^9_B\cdots O^1_A$	2.832	2.828	2.822	2.819	2.816

* the used numbering refers to the CCDC deposited CIFs, see Figure S1

Table S2 - angles (in °) of the two different N···H-O contacts (i.e., N_B···H-O_A and N_A···H-O_B) at different temperatures, as calculated via the Mercury software.[29]

Selected angle	**Length (A)**				
	@ 300 K	**@ 260 K**	**@ 200 K**	**@ 160 K**	**@ 120 K**
N_B···H-O_A	170±2	170±2	169±2	172±2	171±1
N_A···H-O_B	166±2	168±2	168±2	171±2	173±2

Table S3 - Fitting equations for the XRD- and LP-MIR-derived values of, respectively, dimensions and sizes of the 4HCB unit cell and projection of the N...H distance along the *a* and *b* axes of the unit cell (i.e., x_a and y_b sides of the cuboid, see Fig. 6a).

Fitted item (fitting equation: y = ax + b	**Derived from**		**a (·10^{-5} 1/K)**	**b (·10^{-2} 1/K)**	**R2**
	XRD	**LP-MIR**			
x axis of the 4HCB unit cell	X		5.799	-1.760	0.999
y axis of the 4HCB unit cell	X		8.405	-2.559	0.998
z axis of the 4HCB unit cell	X		3.579	-1.078	0.999
Volume of the unit cell	X		23.68	-7.082	0.979
x_a side of the cuboid		X	10.63	-3.172	0.936
y_b side of the cuboid		X	5.562	-1.676	0.930

Table S4 - Overview of the LP-MIR-derived asymmetrical -OH stretching energies, absolute values of the corresponding N···H bond length projections along the cuboid axes x_a and y_b (see Fig. 6a) obtained using the Rozenberg formula[45], and calculated cuboid volumes (on the basis of the cuboid being equivalent to a perfect cube having the side equal to the averabe of the x_a and y_b sides; see Fig. 6 and related text in the main paper) at the considered temperatures. The reference peak for the asymmetric stretching of the -OH bond in the diluted solution used for the calculations is υ_{OHa} = 3580 cm^{-1}.

Temperature (K)	**x_a**		**x_b**		**Cuboid Volume (Å^3)**
	$\upsilon_{OH\text{-}as}$ (cm^{-1})	**N···H bond length projection along *a* (Å)[a]**	**$\upsilon_{OH\text{-}as}$ (cm^{-1})**	**N···H bond length projection along *b* (Å)[a]**	
120	3258	1.853±0.003	3258	1.853±0.003	6.3625
140	3261.8	1.856±0.003	3259.9	1.854±0.003	6.3831
160	3261.8	1.856±0.003	3261.8	1.856±0.003	6.3934
180	3268.2	1.863±0.003	3262.8	1.857±0.003	6.4349
200	3265.7	1.860±0.003	3278.2	1.872±0.003	6.4973
220	3270.5	1.865±0.003	3279.2	1.873±0.003	6.5287
240	3270.5	1.865±0.003	3282	1.876±0.003	6.5444
260	3271.5	1.866±0.003	3283	1.877±0.003	6.5550
280	3278.2	1.872±0.003	3286.9	1.881±0.003	6.6076
300	3277.3	1.872±0.003	3290.8	1.886±0.003	6.6341

Table S5/1 - Crystallographic data and refinement details for **4HCB** data collections at different temperatures.

Temperature (K)	**120(2)**	**140(2)**	**160(2)**	**180(2)**	**200(2)**
CCDC Code	954029	954030	953962	953963	954031
Empirical formula	C_7 H_5 N O	C_7 H_5 N O	C_7 H_5 N O	C_7 H_5 N O	C_7 H_5 N O
Formula weight (Da)	119.12	119.12	119.12	119.12	119.12
Wavelength□□Å□	0.8266	0.8266	0.8266	0.8266	0.8266
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*P b c n*	*P b c n*	*P b c n*	*P b c n*	*P b c n*
Unit cell dimensions □□Å□ □□□= □□= □ = 90°]	a = 9.107(2) b = 10.5750(12) c = 25.296(2)	a = 9.116(2) b = 10.5900(11) c = 25.311(3)	a = 9.1260(16) b = 10.6060(11) c = 25.328(3)	a = 9.136(2) b = 10.6220(11) c = 25.346(3)	a = 9.147(2) b = 10.6400(11) c = 25.365(2)
Volume (Å^3)	2436.2(6)	2443.5(7)	2451.5(6)	2459.6(7)	2468.6(7)
Z	16	16	16	16	16
ρ (Kg/dm^3)	1.299	1.295	1.291	1.287	1.282
μ (mm^{-1})	0.125	0.125	0.124	0.123	0.123
F(000)	992	992	992	992	992
Theta range for data collection	1.873 to 31.104°.	1.871 to 31.093°.	1.870 to 31.099°.	1.869 to 31.102°.	1.867 to 31.086°.
Reflections collected	12739	12853	12929	12381	12913
Independent reflections [Fo>4σ(Fo)]	2416 (2388)	2433 (2400)	2439 (2398)	2422 (2397)	2442 (2401)
R(int) (HR) %	2.0 (2.4)	3.3 (4.0)	3.3 (4.3)	3.6 (4.1)	3.4 (4.9)
Completeness (HR) %	98.1 (97.8)	98.3 (97.7)	98.1 (97.9)	97.2 (96.9)	97.9 (97.4)
Multiplicity (HR)	5.1 (4.9)	5.1 (4.9)	5.1 (4.9)	4.9 (4.7)	5.1 (4.9)
I/□(I) (HR)	54.51 (51.30)	32.49 (30.94)	31.46 (30.08)	31.80 (30.64)	27.11 (25.90)
Data / restraints / parameters	2416 / 0 / 172	2433 / 0 / 172	2439 / 0 / 172	2422 / 0 / 172	2442 / 0 / 172
Goodness-of-fit on F^2	1.061	1.083	1.060	1.071	1.065
Final R indices [I>2σ(I)]	R_1 = 0.0348 wR_2 = 0.0892	R_1 = 0.0385 wR_2 = 0.1010	R_1 = 0.0383 wR_2 = 0.1024	R_1 = 0.0394 wR_2 = 0.1034	R_1 = 0.0416 wR_2 = 0.1081
R indices (all data)	R_1 = 0.0350 wR2 = 0.0894	R_1 = 0.0387 wR_2 = 0.1011	R_1 = 0.0386 wR_2 = 0.1028	R_1 = 0.0397 wR_2 = 0.1037	R_1 = 0.0419 wR_2 = 0.1085

[a] $R_1 = \Sigma \, ||Fo|-|Fc|| \, / \, \Sigma \, |Fo|$, $wR_2 = \{\Sigma \, [w(Fo^2 - Fc^2)^2] \, / \, \Sigma \, [w(Fo^2)^2]\}^{1/2}$.

Table S5/2 - Crystallographic data and refinement details for 4HCB data collections at different temperatures (continues from Table S5/1)

Temperature (K)	**220(2)**	**240(2)**	**260(2)**	**280(2)**	**300(2)**
CCDC Code	954032	954045	953965	953964	953966
Empirical formula	C_7 H_5 N O	C_7 H_5 N O	C_7 H_5 N O	C_7 H_5 N O	C_7 H_5 N O
Formula weight (Da)	119.12	119.12	119.12	119.12	119.12
Wavelength□□Å□	0.8266	0.8266	0.8266	0.8266	0.8266
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*P b c n*	*P b c n*	*P b c n*	*P b c n*	*P b c n*
Unit cell dimensions □□Å□ □□□= □□= □ = 90°]	a = 9.158(2) b = 10.6580(10) c = 25.3830(16)	a = 9.168(2) b = 10.6770(10) c = 25.4020(14)	a = 9.179(2) b = 10.6970(11) c = 25.4200(16)	a = 9.191(4) b = 10.716(3) c = 25.440(7)	a = 9.2030(19) b = 10.7370(11) c = 25.458(2)
Volume (Å^3)	2477.5(7)	2486.5(7)	2495.9(7)	2505.6(14)	2515.6(6)
Z	16	16	16	16	16
ρ (Kg/dm^3)	1.277	1.273	1.268	1.263	1.258
μ (mm^{-1})	0.122	0.122	0.121	0.121	0.120
F(000)	992	992	992	992	992
Theta range for data collection	1.866 to 31.095°.	1.865 to 31.102°.	1.863 to 31.098°.	1.862 to 30.266°.	3.391 to 31.104°.
Reflections collected	13354	13423	13384	6776	13515
Independent reflections [Fo>4σ(Fo)]	2458 (2382)	2463 (2375)	2463 (2386)	2187 (2009)	2484 (2387)
R(int) (HR) %	3.3 (4.8)	4.3 (4.7)	3.9 (4.6)	6.4 (6.0)	4.5 (4.5)
Completeness (HR) %	97.9 (97.8)	98.0 (97.7)	97.6 (97.8)	91.6 (95.4)	97.5 (97.6)
Multiplicity (HR)	5.2 (5.0)	5.2 (5.0)	5.2 (5.0)	2.8 (2.8)	5.2 (5.0)
I/□(I) (HR)	24.76 (23.25)	25.06 (23.45)	26.55 (24.87)	11.76 (11.23)	25.26 (23.45)
Data / restraints / parameters	2458 / 0 / 172	2463 / 0 / 172	2463 / 0 / 172	2187 / 0 / 172	2484 / 0 / 172
Goodness-of-fit on F^2	1.099	1.096	1.071	1.079	1.025
Final R indices [I>2σ(I)]	R_1 = 0.0426 wR_2 = 0.1118	R_1 = 0.0406 wR_2 = 0.1062	R_1 = 0.0422 wR_2 = 0.1099	R_1 = 0.0481 wR_2 = 0.1249	R_1 = 0.0436 wR_2 = 0.1192
R indices (all data)	R_1 = 0.0431 wR_2 = 0.1124	R_1 = 0.0413 wR_2 = 0.1069	R_1 = 0.0428 wR_2 = 0.1106	R_1 = 0.0507 wR_2 = 0.1305	R_1 = 0.0445 wR_2 = 0.1207

[a] $R_1 = \Sigma \, ||Fo|-|Fc|| \, / \, \Sigma \, |Fo|$, $wR_2 = \{\Sigma \, [w(Fo^2 - Fc^2)^2] \, / \, \Sigma \, [w(Fo^2)^2]\}^{1/2}$.