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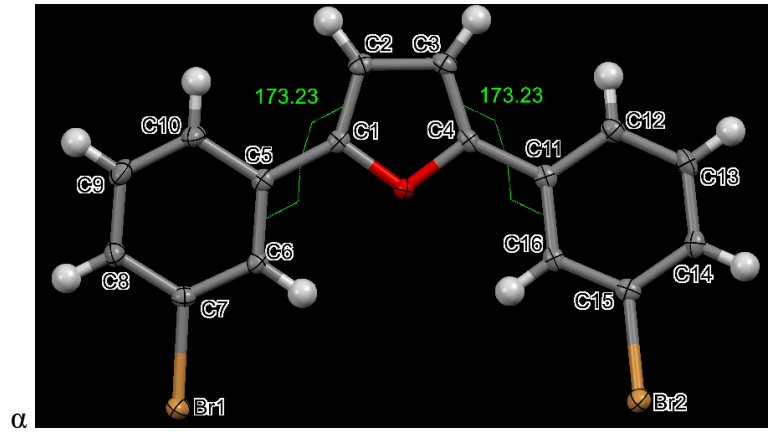
Supporting information for article:

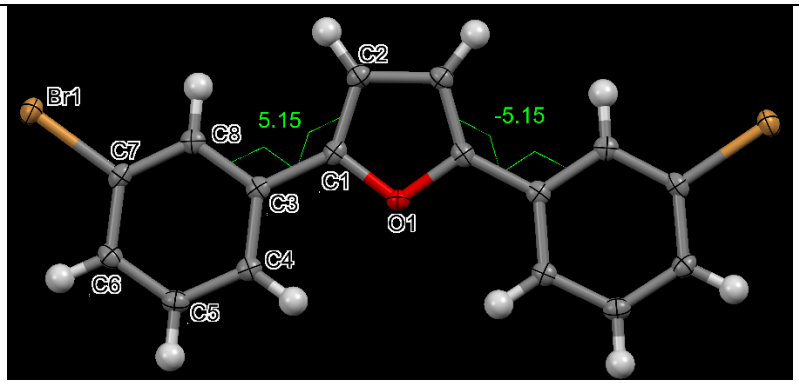
Bending the bonds: unveiling halogen interactions in the elastic polymorph of 2,5-bis(3-bromophenyl)furan

Konrad Dyk, Vasyl Kinzhybalo, Yuriy Horak, Serhii Butenko, Miłosz Siczek and Daniel M. Kamiński

Table S1 Summarized experimental results for the single crystal X-ray diffraction experiments

Polymorph	α	β	γ
Empirical formula	$C_{16}H_{10}Br_2O$	$C_{16}H_{10}Br_2O$	$C_{16}H_{10}Br_2O$
Conformer	**I**	**III**	**III**
Formula weight	378.06	378.06	378.06
Temperature [K]	100	100	100
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*Pna*2_1	*Pnma*	$P2_12_12_1$
a [Å]	8.226(3)	6.217(3)	3.977(2)
b [Å]	13.408(4)	30.110(8)	10.775(5)
c [Å]	12.222(4)	7.180(3)	31.239(8)
Volume [Å^3]	1348.0(8)	1344.1(9)	1338.7(10)
Z	4	4	4
ρ_{calc} [g/cm^3]	**1.86**	**1.87**	**1.88**
Morphological shape	cuboids	hexagonal plate	elongated plate
μ [mm^{-1}]	6.00	6.02	7.57
F(000)	736	736	736
Crystal size [mm]	0.44 × 0.19 × 0.09	0.42 × 0.22 × 0.06	0.7 × 0.06 × 0.02
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)
2Θ range for data collection [°]	5.81 to 59.02	5.41 to 59.02	5.66 to 151.37
Index ranges	$-11 \le h \le 11$, $-18 \le k \le 17$, $-15 \le l \le 16$	$-8 \le h \le 8$, $-40 \le k \le 41$, $-9 \le l \le 9$	$-4 \le h \le 4$, $-12 \le k \le 13$, $-39 \le l \le 38$
Reflections collected	27898	53049	11796
Independent reflections	3505 [R_{int} = 0.0374, R_{sigma} = 0.0275]	1831 [R_{int} = 0.0643, R_{sigma} = 0.0206]	2726 [R_{int} = 0.0336, R_{sigma} = 0.0253]
Data/restraints/parameters	3505/1/172	1831/0/88	2726/0/173
Goodness-of-fit on F^2	1.05	1.19	1.10
Final R indexes [I>=2σ (I)]	R_1 = 0.0218, wR_2 = 0.039	R_1 = 0.0355, wR_2 = 0.0880	R_1 = 0.0305, wR_2 = 0.0811
Final R indexes [all data]	R_1 = 0.0284, wR_2 = 0.0410	R_1 = 0.0477, wR_2 = 0.0941	R_1 = 0.0315, wR_2 = 0.0815
Largest diff. peak/hole [e Å^{-3}]	0.54/-0.34	0.73/-0.37	0.59/-0.90





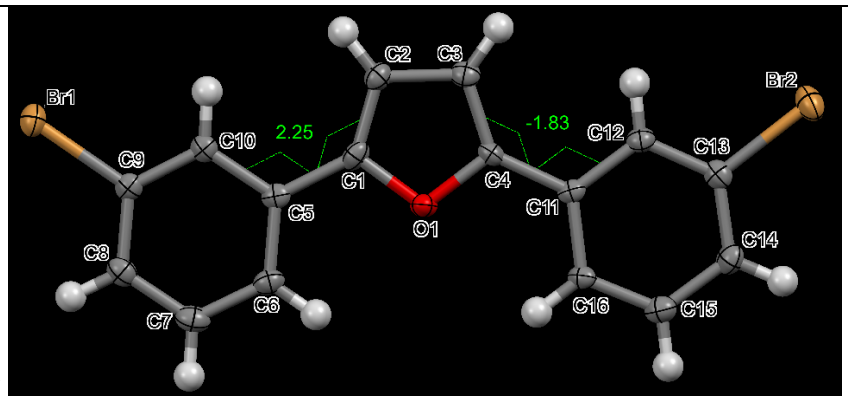


Figure S1 The molecular view of **MBPF** together with the numbering for the asymmetric part of polymorphs α, β and γ. The anisotropic displacement parameters are at the 50% level of probability. The green dashed line indicate the torsion angle with corresponding to it value also in green.

The bond lengths and angles are very similar for all **MBPF** polymorphs, see **S. Fig. 1**, **S. Table 2**, and **S. Table 3**. The most significant difference between the polymorphic forms α, β and γ is the conformation of the **MBPF** molecule. In the case of polymorph α the bromine atoms are on the same side as the oxygen atom of the furan ring. In the case of polymorphs, β and γ bromine atoms are on the opposite side of the furan's oxygen atom. The torsion angles

C3/C4/C11/C12 and C2/C1/C5/C10 for α are equal to 173.23°, whereas the identical torsion angles in the form β are equal to 5.15° and in the γ are 2.25° and -1.83°, see **S. Figure 1**.

The rotation around ϕ_1 and ϕ_2 (see **Figure 1**) is possible due to the absence of steric hindrance in the **MBPF** molecule; thus, both bromophenyl ring substituents can rotate freely about the furan ring in the gaseous phase. The factors that limit number of possible conformations of **MBPF** in the crystals are the interactions with the neighboring molecules.

Table S2 The bond lengths in the studied **MBPF** polymorphs at 100 K. The bond lengths are typical for phenyl rings and furan rings, which indicates their aromatic character. The C-Br distances are ~1.9 Å and are typical for the $C_{aromatic}$-Br bond lengths.

	α		**β**		**γ**	
	Bond	**Distance [Å]**	**Bond**	**Distance [Å]**	**Bond**	**Distance [Å]**
Furan ring	O1-C1	1.379(4)	O1-C1	1.372(3)	O1-C1	1.374(6)
	C1-C2	1.357(4)	C1-C2	1.368(5)	C1-C2	1.340(7)
	C2-C3	1.419(5)	C2-C2*	1.413(9)	C2-C3	1.422(7)
	C4-C3	1.365(5)			C4-C3	1.365(7)
	O1-C4	1.374(4)			O1-C4	1.387(6)
	C5-C1	1.453(5)	C3-C1	1.457(4)	C1-C5	1.462(7)
Phenyl ring	C5-C6	1.402(4)	C3-C4	1.403(4)	C6-C5	1.406(7)
	C7-C6	1.385(4)	C4-C5	1.387(4)	C6-C7	1.385(8)
	C7-C8	1.380(5)	C6-C5	1.384(4)	C8-C7	1.388(7)
	C8-C9	1.391(5)	C7-C6	1.390(5)	C8-C9	1.387(7)
	C9-C10	1.378(5)	C8-C7	1.386(4)	C10-C9	1.386(7)
	C5-C10	1.403(4)	C3-C8	1.402(4)	C10-C5	1.403(7)
	Br1-C7	1.915(3)	Br1-C7	1.901(3)	Br1-C9	1.907(5)
	C11-C4	1.456(5)			C4-C11	1.448(7)
Phenyl Ring	C11-C12	1.399(5)			C12-C11	1.405(7)
	C12-C13	1.373(5)			C12-C13	1.380(7)
	C14-C13	1.394(5)			C14-C13	1.386(7)
	C14-C15	1.388(5)			C14-C15	1.393(7)
	C16-C15	1.381(5)			C16-C15	1.389(7)
	C11-C16	1.405(5)			C16-C11	1.408(7)
	Br2-C15	1.904(3)			Br2-C13	1.894(5)

The bond lengths in the furan and phenyl rings are typical of these systems and are shown in the **S. Table 2**. The $C_{aromatic}$-Br bond distance is similar in all measured structures, being ~1.9 Å. This is in agreement with the other similar structures (Christensen & Stromme, 1969, Birnbaum & Ferguson, 1969, Matthews, 1965). The valence angles of **MBPF** in all studied crystals are typical of such systems (Sniady *et al.*, 2007, Meng & Wu, 2005, Zong *et al.*, 2016, Jones & Gray, 2002). **S. Table 3** shows all valence angles. Molecular geometries are very similar: the overlay is presented in **S. Fig. 2**.

A) B)

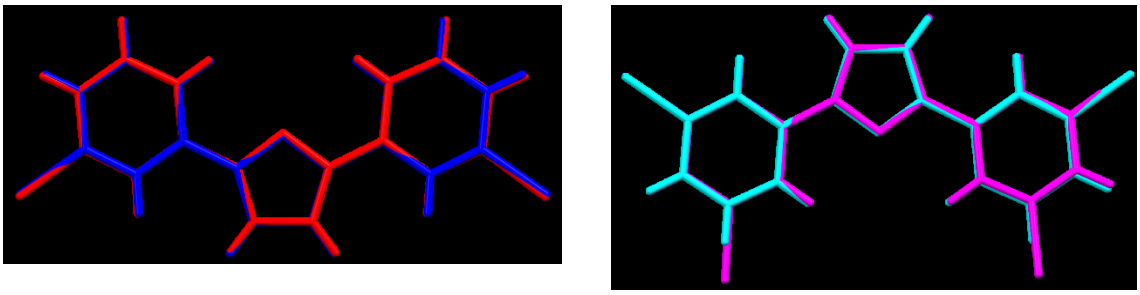


Figure S2 The structures overlay after mirroring the molecules. **A)** The molecules overlay from the β – blue and γ – red. These two structures adopt conformation **III** and are very similar. **B)** The molecule overlay of structures α (magenta) and β (cyan) differs due to the torsion angles between them. It can be seen that the structure β has one ring out and one in the plane of the furan ring. The structure β has a Z'=0.5 so both parts of the molecule are identical.

Table S3 Valence angles in studied **MBPF** polymorphs

	α		β		γ	
	Angle		Angle		Angle	
Furan ring	O1-C1-C2	109.4(3)	O1-C1-C2	109.7(3)	O1-C1-C2	110.41(42)
	C1-C2-C3	107.3(3)	C1-C2-C2*	107.2(3)	C1-C2-C3	107.50(44)
	C4-C3-C2	106.7(3)	C1-O1-C1*	107.8(4)	C4-C3-C2	106.30(43)
	C4-O1-C1	107.1(2)			C1-O1-C4	106.25(34)
	O1-C4-C3	109.5(3)			O1-C4-C3	109.54(40)
	O1-C1-C5	116.6(3)	O1-C1-C3	117.3(3)	O1-C1-C5	116.53(39)
	C5-C1-C2	133.9(3)	C3-C1-C2	133.0(3)	C5-C1-C2	133.03(45)
	C1-C5-C10	120.0(3)	C8-C3-C1	119.2(3)	C1-C5-C10	119.58(41)
	C1-C5-C6	121.1(3)	C1-C3-C4	121.5(3)	C1-C5-C6	121.73(43)
Phenyl ring	C6-C5-C10	118.9(3)	C8-C3-C4	119.4(3)	C6-C5-C10	118.70(43)
	C7-C6-C5	118.8(3)	C3-C4-C5	120.3(3)	C5-C6-C7	120.60(46)
	C8-C7-C6	122.9(3)	C4-C5-C6	120.8(3)	C6-C7-C8	120.82(49)
	C7-C8-C9	117.7(3)	C7-C6-C5	118.3(3)	C9-C8-C7	118.38(46)
	C8-C9-C10	121.2(3)	C8-C7-C6	122.4(3)	C8-C9-C10	122.17(44)
	C5-C10-C9	120.5(3)	C3-C8-C7	118.6(3)	C5-C10-C9	119.30(41)
	Br1-C7-C6	117.8(2)	Br1-C7-C8	118.2(2)	Br1-C9-C8	119.45(36)
	Br1-C7-C8	119.2(2)	Br1-C7-C6	119.3(2)	Br1-C9-C10	118.36(34)
	O1-C4-C11	117.3(3)			O1-C4-C11	117.51(38)
	C4-C11-C16	121.3(3)			C16-C11-C4	121.90(42)
	C4-C11-C12	119.8(3)			C12-C11-C4	118.30(41)
	C11-C4-C3	133.0(3)			C11-C4-C3	132.96(44)
Phenyl ring	C11-C12-C13	120.9(3)			C11-C12-C13	119.25(42)
	C12-C13-C14	120.8(3)			C12-C13-C14	122.09(47)
	C15-C14-C13	118.1(3)			C13-C14-C15	118.21(48)
	C16-C15-C14	122.2(3)			C16-C15-C14	121.75(48)
	C11-C16-C15	119.1(3)			C11-C16-C15	118.91(45)
	C16-C11-C12	118.8(3)			C16-C11-C12	119.80(43)
	Br2-C15-C16	119.1(2)			Br2-C13-C12	118.05(36)
	Br2-C15-C14	118.6(2)			Br2-C13-C14	119.86(38)

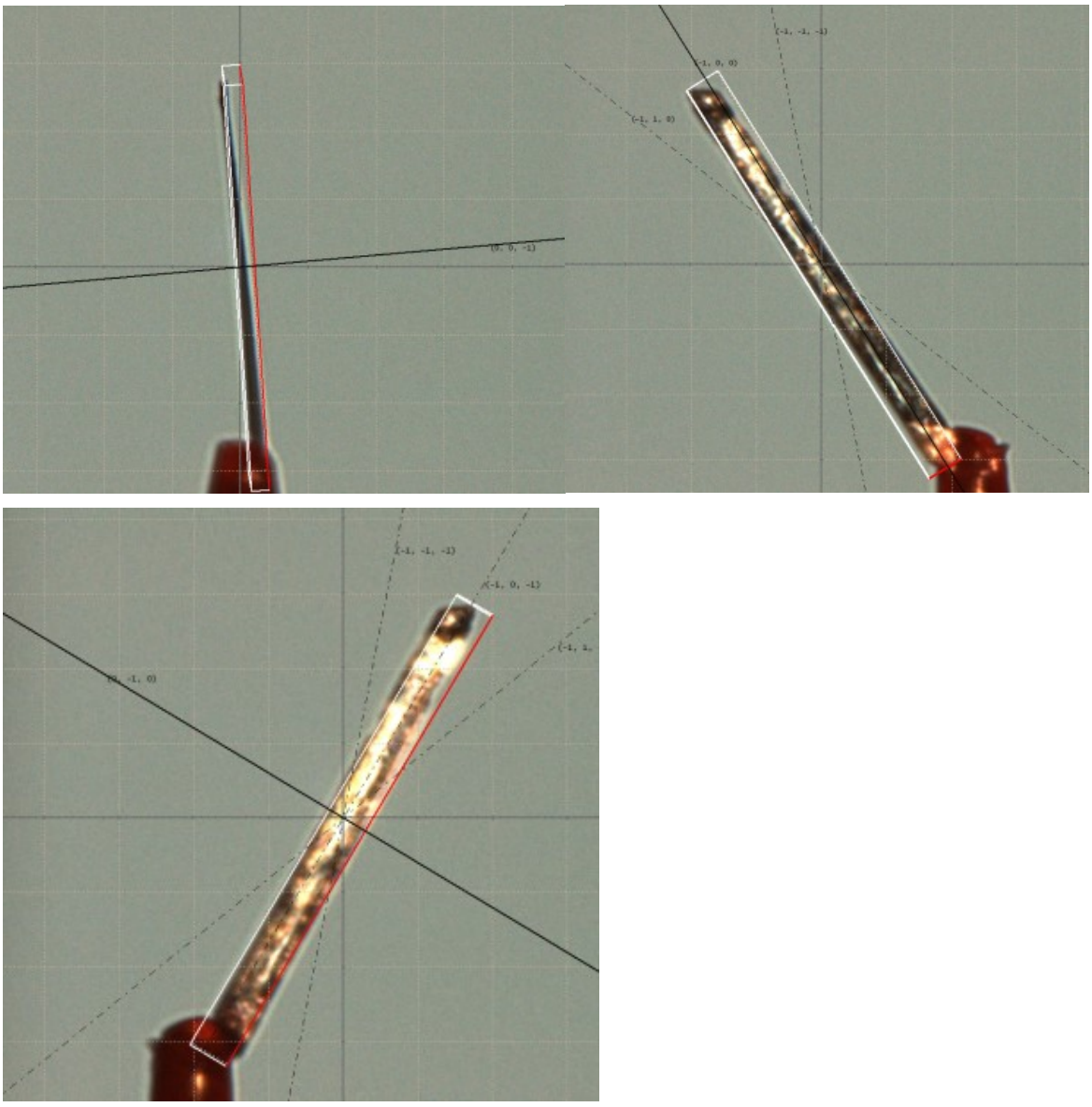


Figure S3 Crystal of γ form with crystallographic directions.

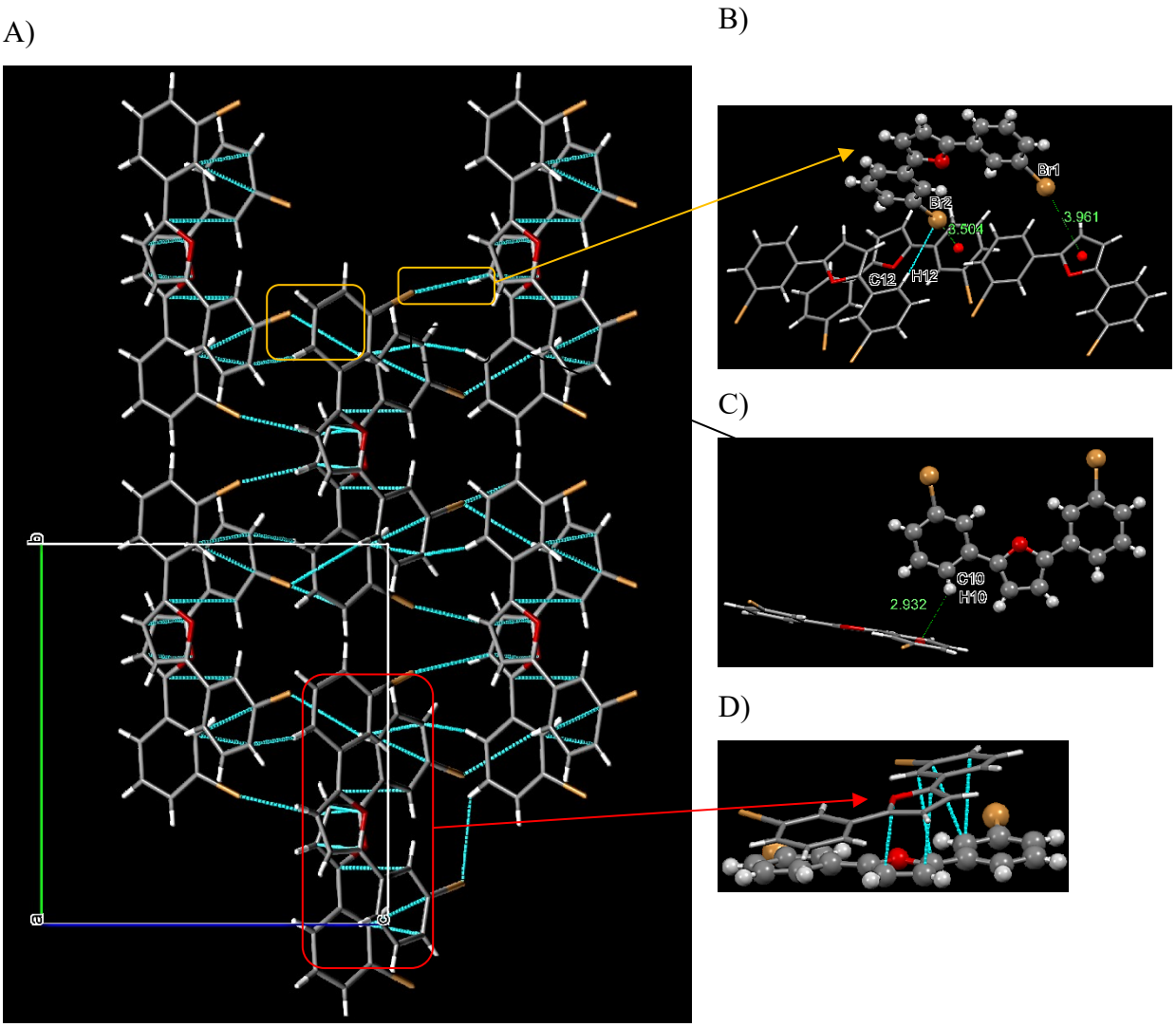


Figure S4 Intermolecular interactions in the crystal net of α polymorph; **A)** general interactions; **B)** interactions that include Br atoms; **C)** C-H…π interactions; **D)** π···π stacking.

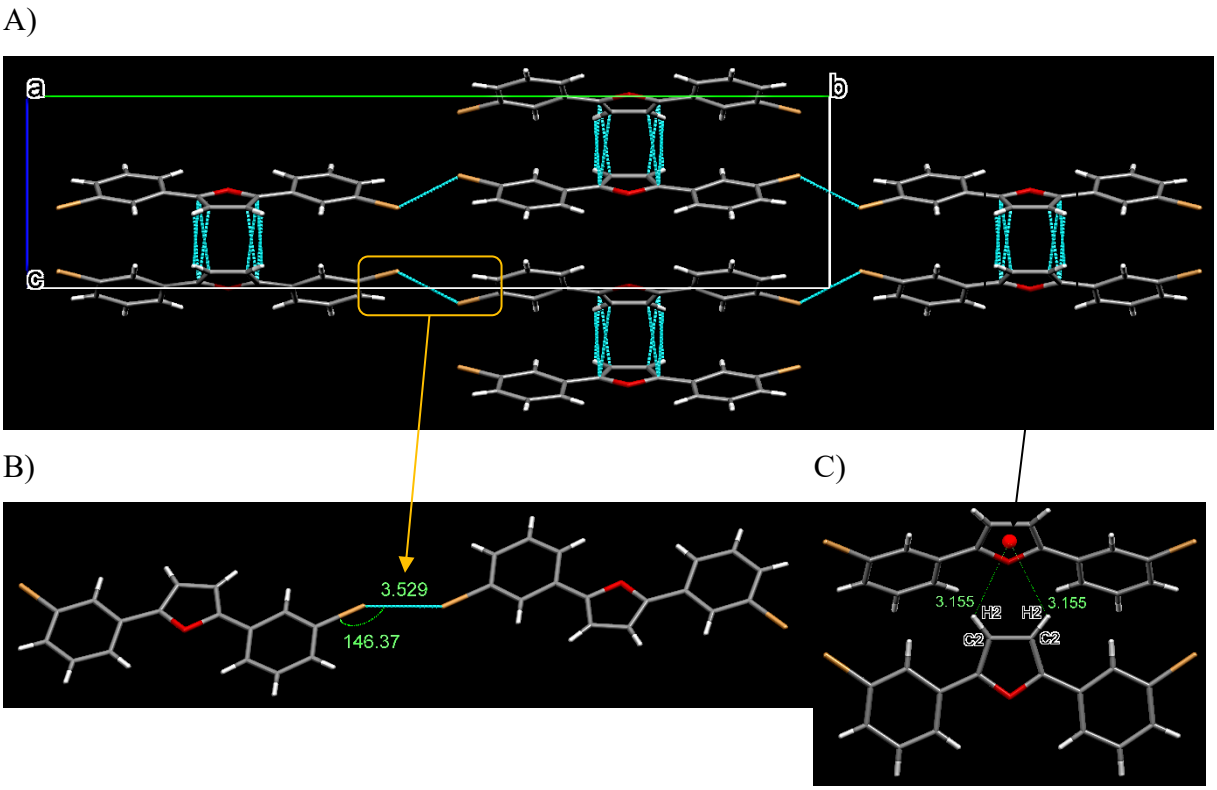


Figure S5 Intermolecular interactions in the crystal net of β polymorph; **A)** interactions between the molecules in the polymorph β; **B)** Br···Br interactions in the crystal form β; **C)** C-H···π interactions in the crystal form β.

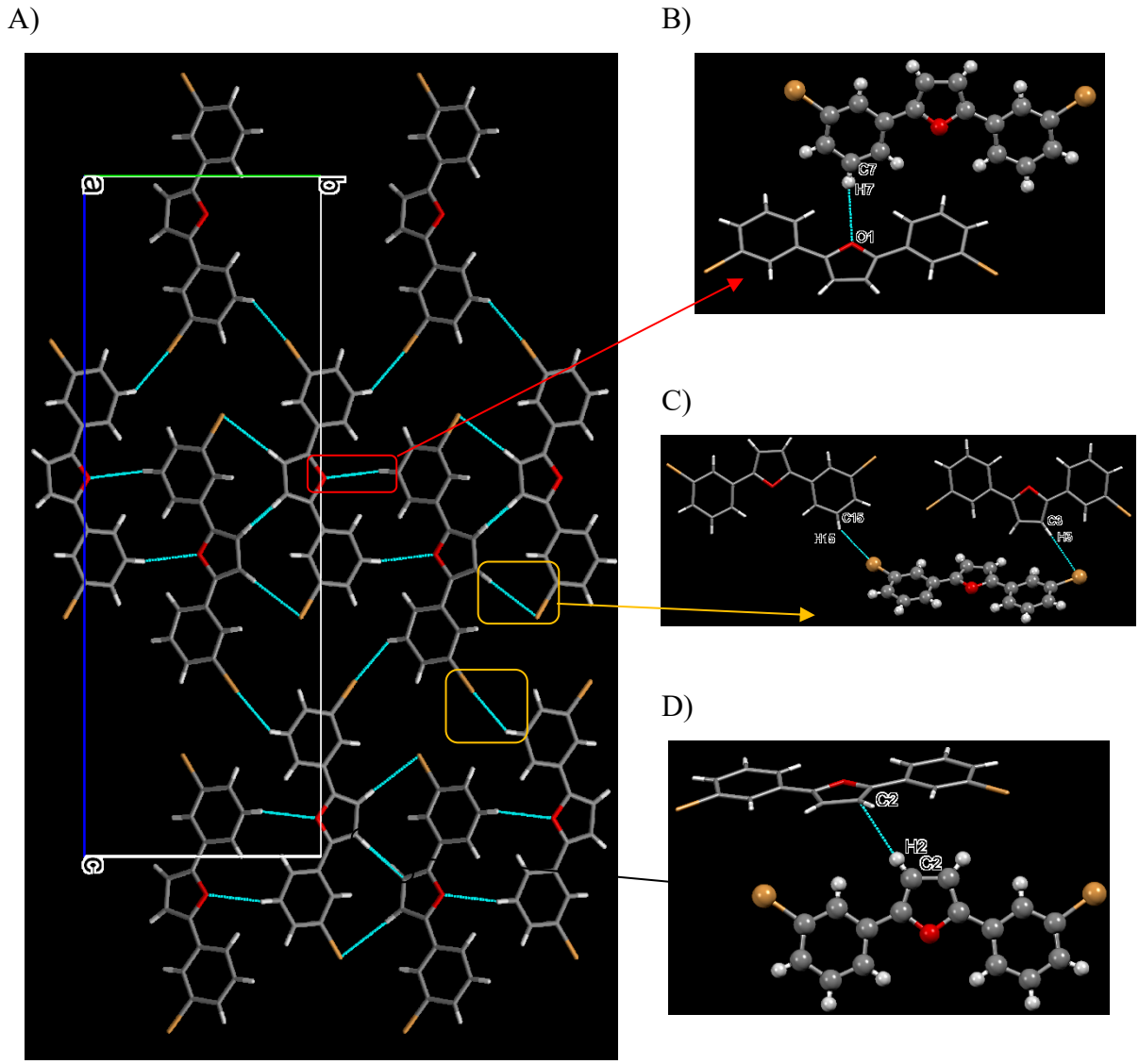
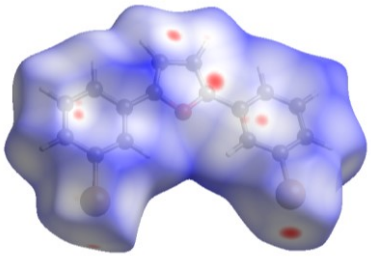
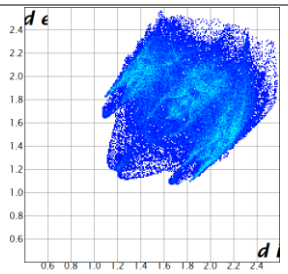
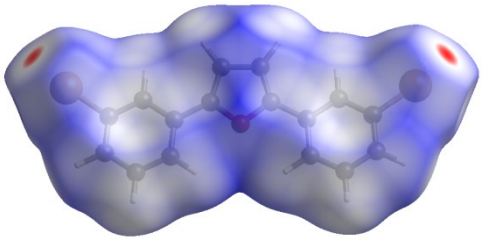
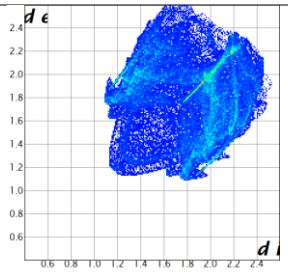
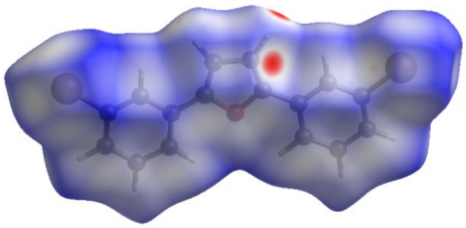
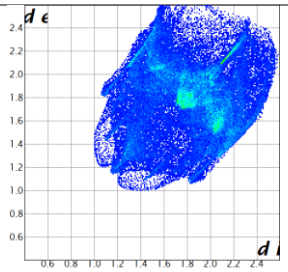


Figure S6 Intermolecular interactions in the crystal net of γ polymorph; **A)** interactions between the molecules in the polymorph γ; **B)** C-H···O interactions in the crystal γ; **C)** interactions between Br atoms and neighboring molecules; **D)** C2-H2···π interaction.

Table S4 Hirshfeld surfaces of studies polymorphs with fingerprint plots

Form	Hirshfeld surface	Fingerprint plot
α		
β		
γ		

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