

Supplementary Information to the typescript “A series of compounds forming polar crystals and showing single-crystal-to-single-crystal transitions between polar phases” by R. Centore, M. Jazbinsek, A. Tuzi, A. Roviello, A. Capobianco, A. Peluso.

Table S1. Crystal and refinement data for phases I and III of **2** collected at 173 K.

	2 (phase I)	2 (phase III)
formula sum	C ₁₀ H ₁₂ N ₂ O ₂	C ₁₀ H ₁₂ N ₂ O ₂
formula weight	192.2	192.2
crystal system	orthorhombic	orthorhombic
space group	<i>Pna2</i> ₁	<i>Pna2</i> ₁
<i>a</i> (Å)	9.008(1)	9.835(3)
<i>b</i> (Å)	7.064(1)	9.153(3)
<i>c</i> (Å)	15.833(2)	11.370(5)
<i>V</i> (Å ³)	1007.5(2)	1023.5(6)
<i>T</i> (K)	173	173
<i>Z</i>	4	4
ρ_{calcd} (g/cm ³)	1.267	1.247
R1 [<i>I</i> > 2σ(<i>I</i>)]	0.0313	0.0461
wR2 [<i>I</i> > 2σ(<i>I</i>)]	0.0890	0.1206

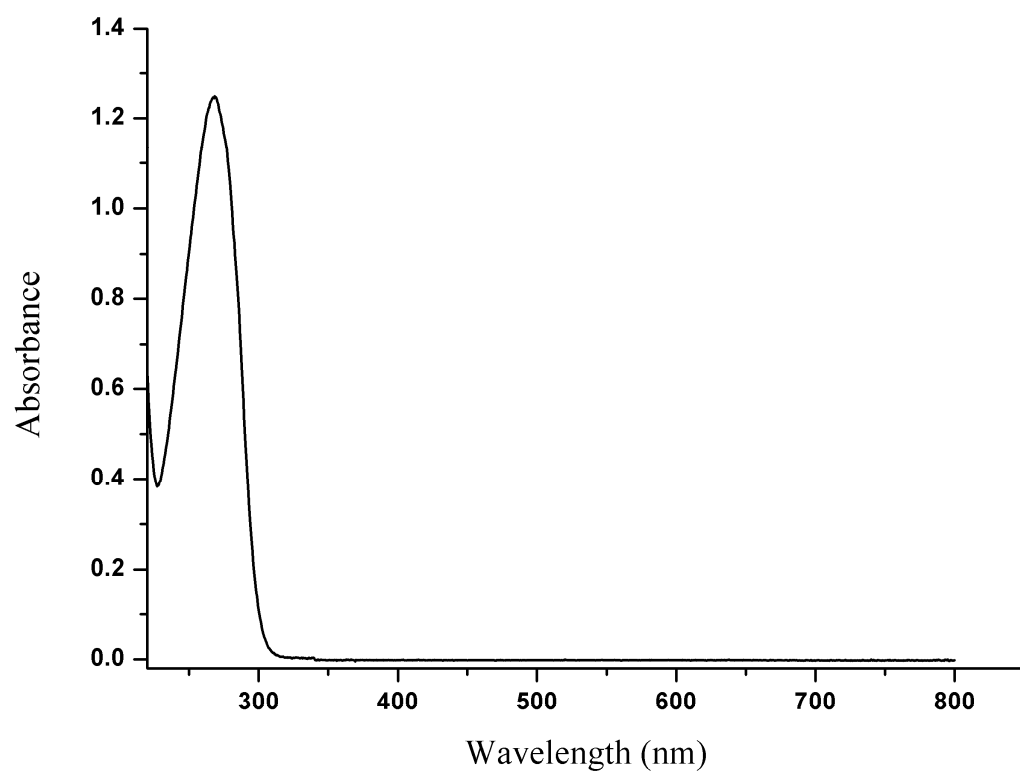


Figure S1. UV-VIS spectrum of **2** in methanol solution.

Orientation of the calculated dipole moment of the free molecule

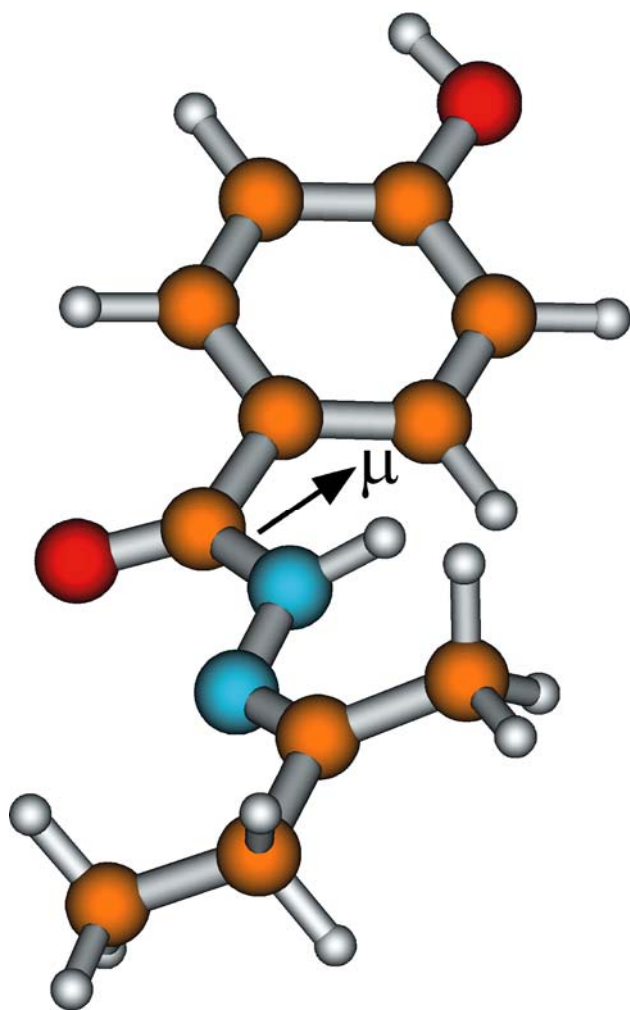


Fig. S2. Calculated dipole moment of 1.

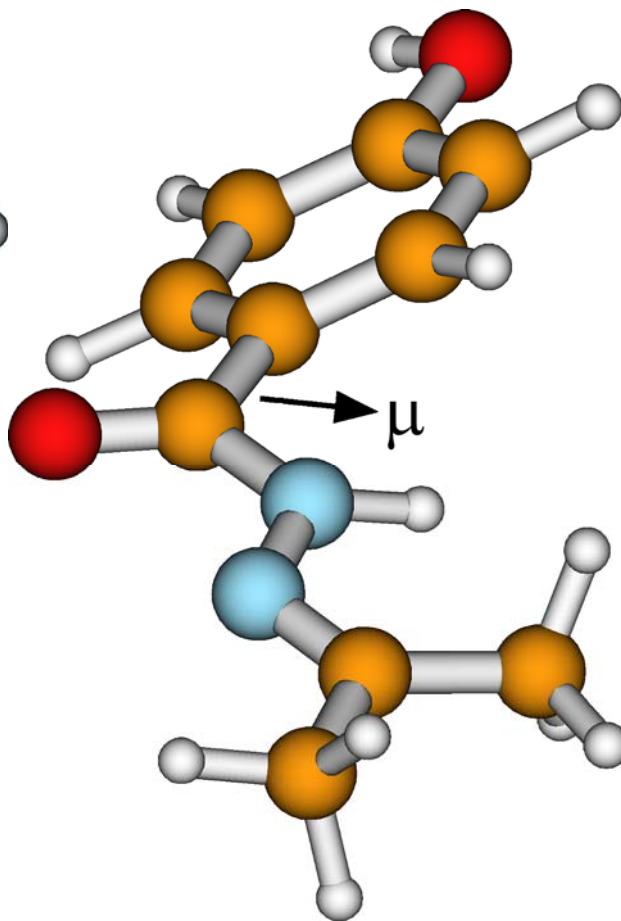


Fig. S3. Calculated dipole moment of 2.

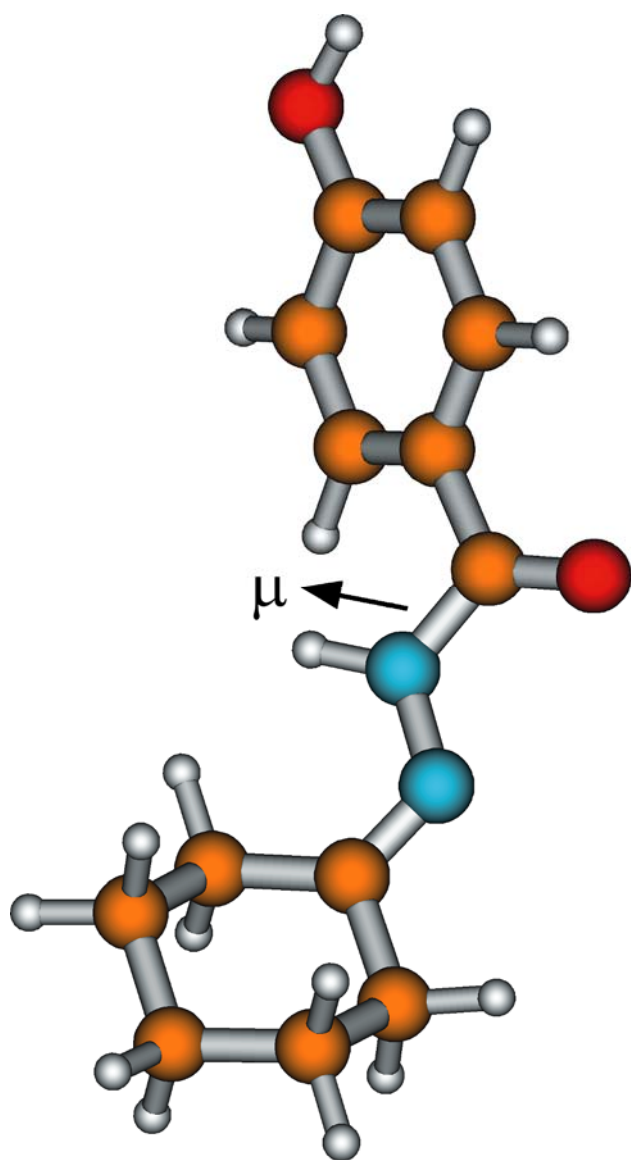


Fig. S4. Calculated dipole moment of **3**.

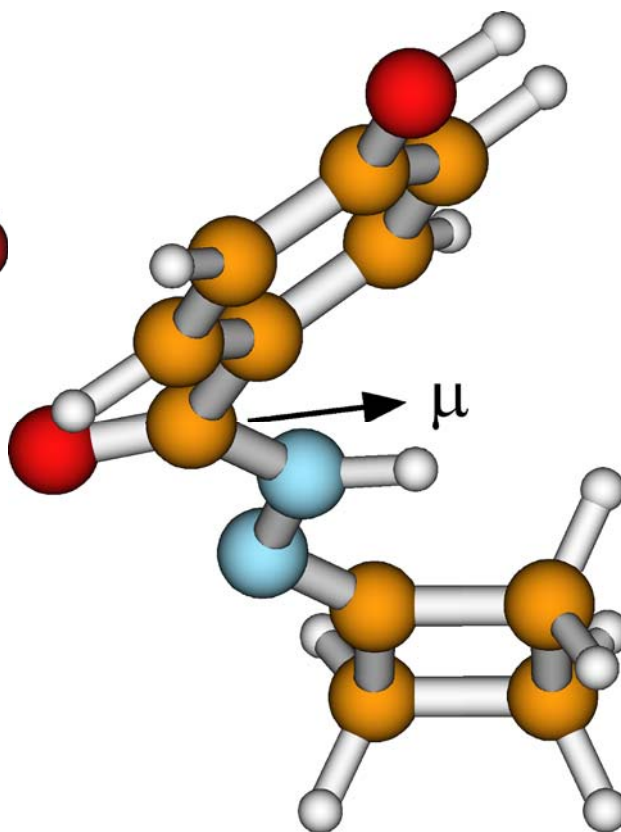


Fig. S5. Calculated dipole moment of **4**.

Table S2

1		2 (phase I)		3		4	
μ (D)	θ (°)	μ (D)	θ (°)	μ (D)	θ (°)	μ (D)	θ (°)
4.10	74.9	4.50	66.1	3.86	77.2	6.77	77.1

μ = calculated ground state dipole moment of the molecule (see Experimental Part of the typescript);

θ = angle between μ vector and LM axis (see the typescript for the definition of LM axis).

Comparison of the molecular structure of **2** in the three polymorphs.

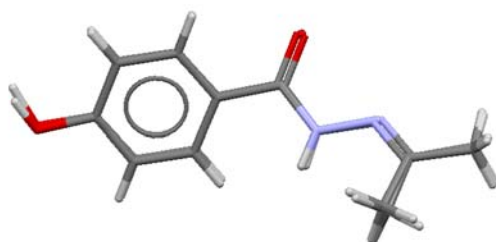


Figure S6. Superposition of molecular structures of **2** in phases I and II. Front view.

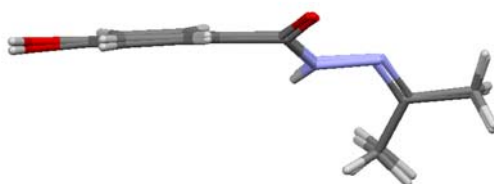


Figure S7. Superposition of molecular structures of **2** in phases I and II. Edge view.

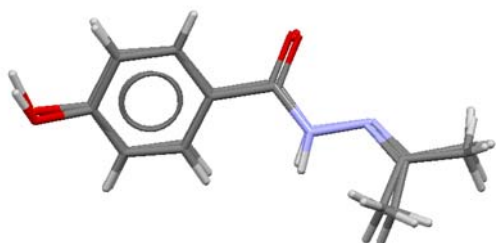


Figure S8. Superposition of molecular structures of **2** in phases I and III. Front view.

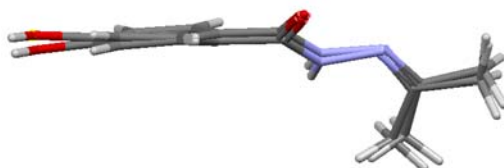


Figure S9. Superposition of molecular structures of **2** in phases I and III. Edge view.

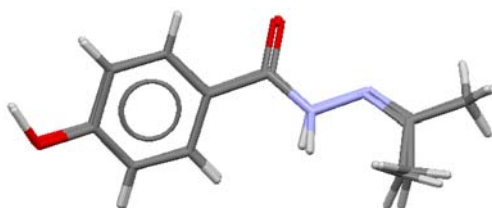


Figure S10. Superposition of molecular structures of **2** in phases II and III. Front view.



Figure S11. Superposition of molecular structures of **2** in phases II and III. Edge view.

Appendix

Discussion of H bonding in the crystal phases of **1**, **2**, **3** and **4**

The O–H···N(*sp*²) hydrogen bond, which is present in our compounds (see Fig. 2(b) of the typescript), has been extensively studied in the literature, with particular focus on the charge transfer along the bridge O–H···N in adducts between phenols and pyridines.¹ In the three crystal phases of **2**, as well as in the crystal structures of **1**, **3** and **4**, the C–OH phenol bond length is always close to 1.36 Å and this indicates that no relevant charge transfer is present.^{1b} With reference to the H bonding patterns described in Fig. 2(b) of the typescript, we must acknowledge that the structure of the molecules is such that O₁–H may act as donor both to N₂ and to O₂ (bifurcated acceptor), so this H bond could be also described as a bifurcated H bond, with O₁–H···N₂ as the major component and O₁–H···O₂ as the minor one.²

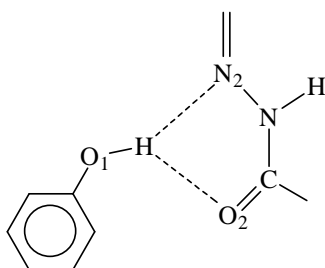


Figure S12. Particular of the three-center H bonding involving the OH group.

The relevant bond distances are, of course, O₁–H, H···N₂ and H···O₂ which, unfortunately, are not determined accurately in X-ray analysis, and the distances O₁···N₂ and O₁···O₂. All those distances, as obtained by X-ray structure refinements, are reported in Table S3 for the three polymorphs of **2**, and in Table S4 for **1**, **3** and **4**. Because of the solid state polymorphism of **2**, X-ray data for phases I and III of **2** were also collected at 173 K.

Table S3. Geometric parameters (Å, °) of the H bonding involving O–H in **2**.

	O1–H	H···N2	H···O2	O1···N2	O1···O2	∠O1HN2	∠O1HO2
I (293 K) (i)	0.84(3)	1.99(3)	2.58(3)	2.804(3)	3.145(3)	164(3)	126(2)
I (173 K) (ii)	0.87(2)	1.93(2)	2.62(2)	2.782(2)	3.180(2)	166(2)	123(2)
II (368 K) (i)	1.03(7)	1.86(7)	2.42(7)	2.877(7)	2.970(7)	173(6)	112(5)
III (293 K) (i)	1.03(3)	1.85(3)	2.44(3)	2.865(3)	3.030(3)	171(3)	116(2)
III (173 K) (iii)	1.01(3)	1.92(3)	2.28(3)	2.855(3)	3.034(3)	153(3)	130(2)

(i) = -x, 2-y, -1/2+z; (ii) = 1-x, 1-y, -1/2+z; (iii) = 2-x, 2-y, -1/2+z.

From Table S3 we find that in comparing I with III or I with II the distance O1···O2 is reduced, on average, by 0.15 Å, while the distance O1···N2 is increased by approximately half this figure (i.e. about 0.06 Å). The comparison between structural data of the same polymorph (I or III) at different temperatures is also informative, suggesting that the contact O1···N2 is attractive both in phase I and III, while the contact O1···O2, which is repulsive in I, becomes non repulsive or perhaps even attractive in phase III; the trend is even more evident if bond lengths involving H are considered. On the other hand, by comparing phases II and III with each other, the differences are by far less evident and on the border of statistical significance. In conclusion, it can be inferred that the description of the H bonding involving the phenol O–H group as a bifurcated H bonding is reasonable. The analysis of more subtle effects suggested by the X-ray data, such as the relative strength of the two components of the bifurcated H bond in the three polymorphs of **2**, as well as the reliability of the apparent O–H bond lengthening in phases II and III of **2**, would require, of course, low temperature neutron diffraction data. These effects could have a role in the polymorphism of **2**.

Table S4. Geometric parameters (Å) of the H bonding involving OH in **1**, **3** and **4**.

	O1–H	H···N2	H···O2	O1···N2	O1···O2	∠O1HN2	∠O1HO2
1 (i)	1.00(3)	1.98(3)	2.25(3)	2.919(4)	2.948(4)	157(3)	126(2)
3 (i)	0.83(4)	1.99(4)	2.70(5)	2.815(4)	3.085(5)	175(4)	110(3)
4 (ii)	0.77(5)	2.45(5)	2.55(5)	3.221(4)	2.955(3)	177(5)	115(4)

(i) = -x, 2-y, -1/2+z; (ii) = -1+x, y, -1+z.

Table S5. Geometric parameters (Å, °) of the H bonding involving N–H in **2**.

	N1–H	H···O2	N1···O2	∠(N1, H, O2)
I (25 °C) (i)	0.80(3)	2.27(3)	3.051(3)	168(2)
I (-100 °C) (i)	0.79(2)	2.21(2)	2.990(2)	171(2)
II (95 °C) (i)	0.86(7)	2.33(7)	3.167(6)	165(6)
III (25 °C) (i)	0.88(3)	2.09(3)	2.959(2)	169(2)
III (-100 °C) (ii)	0.87(3)	2.05(3)	2.913(2)	178(3)

(i) = 1/2+x, 1.5-y, z; (ii) = -1/2+x, 1/2-y, z; (ii) = -1/2+x, 1.5-y, z

Table S6. Geometric parameters (Å, °) of the H bonding involving N–H in **1**, **3** and **4**.

	N1–H	H···O2	N1···O2	∠(N1, H, O2)
1 (i)	0.85(3)	2.14(3)	2.986(4)	175(3)
3 (i)	0.87(4)	2.13(4)	2.996(4)	175(4)
4 (ii)	0.78(4)	2.44(4)	3.216(4)	172(4)

(i) = -1/2+x, 1.5-y, z; (ii) = x, -y, -1/2+z.

Comments to the movies

Movie1. A microcrystalline sample of **2** in phase I is heated up to 147 °C under the polarizing microscope, and the transition from I to II is observed (heating rate 10 K/min). The "burst" is particularly evident if the larger crystals are spotted during the reproduction.

Movie2. A large single crystal of **2** in phase I is heated on a heating plate (covered with black paper in order to increase the contrast) up to 147 °C and the transition from I to II takes place. After sudden movements and leaps, the single crystal explodes and only two fragments, that are single crystals of the phase II, are left on the plate. The others are found off the plate, on the desk, even at 1 m from the plate.

Movie3. A well shaped single crystal fragment of **2** in phase III (obtained after burst on the heating plate of a large single crystal of phase I, see comment to Movie 2) is heated under the polarizing microscope up to 88 °C and the topotactic transition from III to II is observed; the crystal is then cooled, and the reversed transition is observed. It has to be noted that the same crystal had already undergone two times the transition from II to III before that featured in movie3.

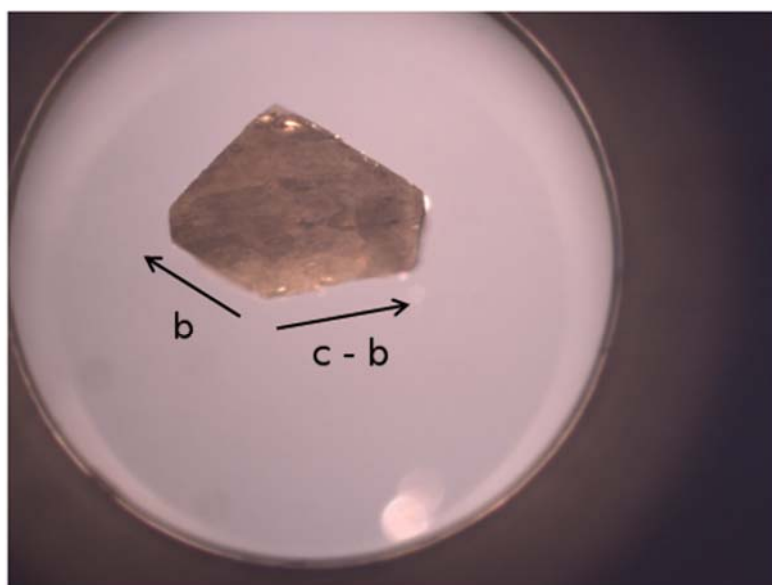


Figure S13. The crystal of movie3 with some axis indication.

References

- (1) (a) A. L. Llamas-Saiz, C. Foces-Foces, O. Mo, M. Yañez and J. Elguero, *Acta Crystallogr.*, 1992, **B48**, 700. (b) I. Majerz, Z. Malarski and L. Sobczyk, *Chem. Phys. Lett.*, 1997, **274**, 361. (c) T. Steiner, I. Majerz and C. C. Wilson, *Angew. Chem. Int. Ed.*, 2001, **40**, 2651.
- (2) (a) G. A. Jeffrey, *Cryst. Rev.*, 1995, **4**, 213. (b) T. Steiner, *Angew. Chem. Int. Ed.*, 2002, **41**, 48.