Discussion of the disorder in 1ort, 1mon and 2

In the three structures, the X-ray diffraction pattern, even if collected at low temperature (173 K) up to $\vartheta = 25°$, showed few observed reflections at $\vartheta \geq 20°$ ($\lambda/2\sin\vartheta \leq 1.04$ Å with MoKα), this suggesting static disorder involving a significant portion of the molecule. That hypothesis was confirmed in the structure solution and refinement. In fact, in all the investigated crystal structures, the 3-methylcyclopentylidene group is involved in static disorder and the careful inspection of the Fourier maps evidenced two (for **2**) or four (for **1**ort and **1**mon) split positions for the disordered group. Two split positions correspond to the *cis* (Z) and *trans* (E) isomers with respect to the double bond C=N, and it is known that *cis* and *trans* imines can interconvert in solution or in the melt.[1,2] Moreover, in the case of the racemic crystals (**1**ort and **1**mon) superposition of *R* and *S* enantiomers in the same site is also observed. The disorder is severe because:

1) It involves a large fraction of the total molecular electronic density (about 40 %);

2) Several atoms of the split positions are close to each other (less than 0.5 Å so well below the actual resolution at $\vartheta = 20°$).

During the refinements, that severe disorder was handled by introducing some restraints on bond lengths and displacement parameters of C atoms of the disordered groups. In the case of **1**ort and **1**mon, C atoms of the disordered groups were given isotropic displacement parameters because of point 2) discussed above. The occupancy factor of the split positions was also refined, and it came out that all the positions are significantly populated.

In the case of **1**mon the four positions of the disordered 3-methylcyclopentylidene group, named A, B, C and D correspond, respectively, to (*R*)-*trans*, (*R*)-*cis*, (*S*)-*trans* and (*S*)-*cis* stereoisomers. The two *trans* positions (A and C) are almost overlapped, but for the position of the C10 atom, which corresponds to the flap of the envelope conformation of the ring; owing to the different configuration of C10A and C10C, the two methyl groups (C13A and C13C) are almost overlapped too, see Fig. S1; the same circumstance holds for the two *cis* positions (B and D).
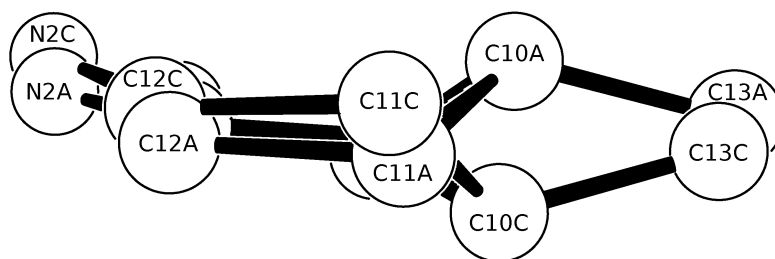
Fig. S1. The two orientations of the *trans*-3-methylcyclopentylidene group in **1**mon. H atoms are

not shown.

In view of that, two refinement strategies were considered.

In the first strategy, the coordinates of the atoms of the four positions were considered free to refine; restraints were introduced only for bond lengths within the cycle and for isotropic displacement parameters; the latter were considered equal for corresponding atoms of the two overlapping positions (A with C and B with D).

In the second strategy, all corresponding atoms of the two overlapping images (for instance C11A/C11C, C12A/C12C, N2A/N2C, *etc.*) were considered exactly coincident, both in coordinates and in ADP, with exception for C10A, C10C, C10B and C10D, which were considered free to refine. Restraints for bond lengths within the ring were introduced.

In both cases, a satisfactory agreement was finally reached in terms of *R* indices and residual electronic density. Surprisingly, the calculated powder diffraction pattern proved sensible to the refinement strategy used. In particular, the powder diffraction pattern calculated with the model obtained by the first refinement procedure was almost coincident with the experimental one, while in the other case some differences were present. So, the first refinement procedure was retained and adopted also for **1**ort.

Population of stereoisomers and melting behaviour of 1mon and 2

As we have stated before, the occupancy factors of the split positions of the disordered 3-methylcyclopentylidene groups were refined, and the population of the various stereoisomers was determined.

Crystals of **1**ort contain four stereoisomers: (*R*)-*trans*, (*R*)-*cis*, (*S*)-*trans* and (*S*)-*cis* with the total amount of *trans* stereoisomers being 43 % and *cis* 57 %.

Crystals of **1**mon also contain four stereoisomers: (*R*)-*trans*, (*R*)-*cis*, (*S*)-*trans* and (*S*)-*cis*; the total amount of *trans* stereoisomers is 57 %, while *cis* is 43 %.

Crystals of **2** contain two stereoisomers: (*R*)-*trans* (60 %) and (*R*)-*cis* (40 %).

In the case of **1**ort and **1**mon, each lattice point can be occupied by one of the four stereoisomers, so there is a contribution to the configurational entropy of the crystal equal to $R \ln 4$ (in the simplifying assumption that the four events are equiprobable). Upon melting, *cis* and *trans* isomers become interconvertible, so the contribution to the configurational entropy of the melt is only due to mixing of the *R* and *S* enantiomers, and it is $R \ln 2$.[3] The configurational melting entropy can be estimated as $\Delta S_m = R \ln 2 - R \ln 4 = -R \ln 2$.

In the case of **2**, each molecular site can be occupied by the *trans* or *cis* isomer, so the contribution to the configurational entropy of the crystal is $R \ln 2$ (again in the simplifying assumption that the two cases are equiprobable). Upon melting, *cis* and *trans* isomers become interconvertible, so there is no contribution to the configurational entropy of the liquid any more. The configurational melting entropy of **2** can be estimated as $\Delta S_m = 0 - R \ln 2 = -R \ln 2$, which is equal to **1**ort and **1**mon.

Now, let us consider, in particular, **1**mon and **2**. They have the same crystal packing and almost the same population of *cis* and *trans* isomers; therefore, an almost equal melting enthalpy, ΔH_m, is expected, as experimentally found by DSC measurements. The additional experimental finding that they have also the same melting temperature, T_m, can be fully understood on account of the basic

thermodynamic relation $T_m = \dfrac{\Delta H_m}{\Delta S_m}$ considering that, as we have shown above, the configurational

melting entropy is equal for **1**mon and **2**.

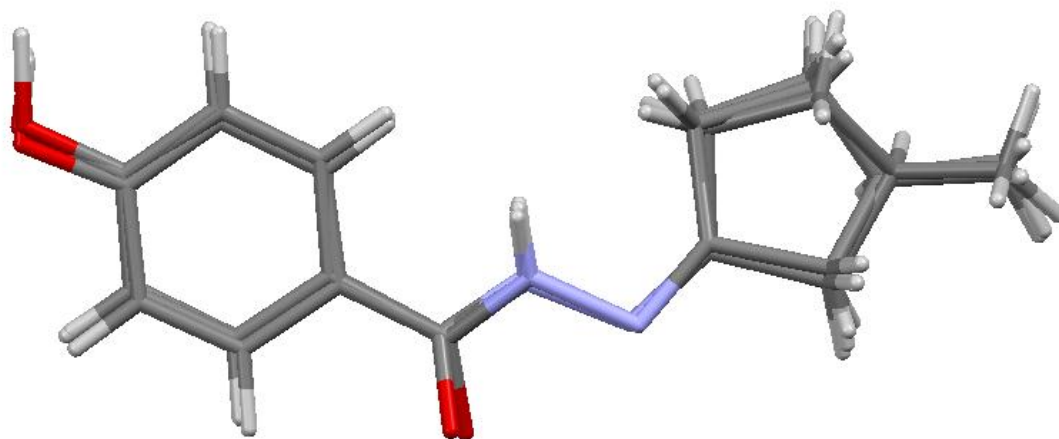**Comparison of the molecular conformation in the crystal structures** (only (*R*)-*trans* isomers are

shown).

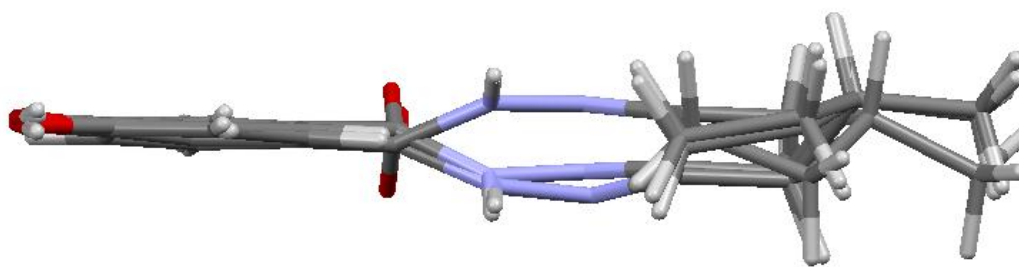Fig. S2. Superposition of (*R*)-trans molecules of **1**mon and **2**. Face view.

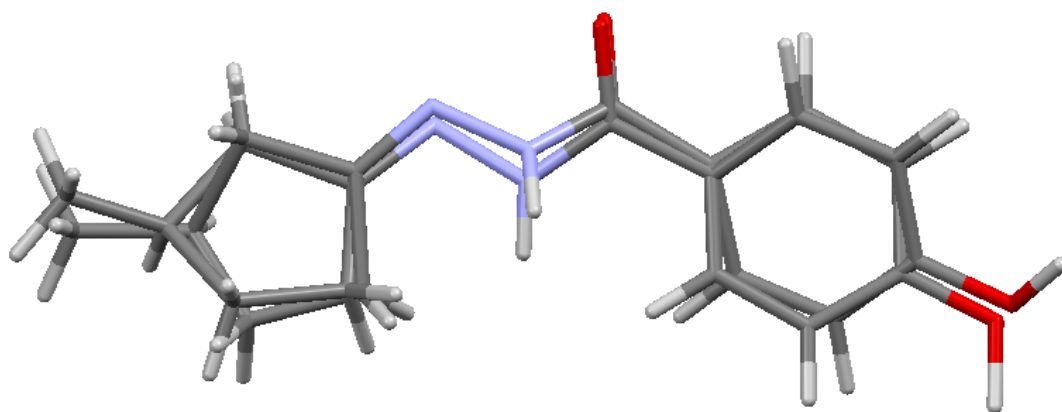Fig. S3. Superposition of (*R*)-trans molecules of **1**mon and **2**. Edge view.

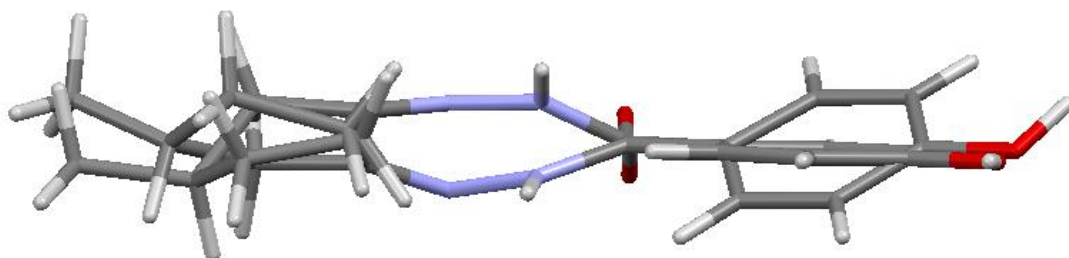Fig. S4. Superposition of (*R*)-trans molecules of **1**ort and **1**mon. Face view.

Fig. S5. Superposition of (*R*)-trans molecules of **1**ort and **1**mon. Edge view.
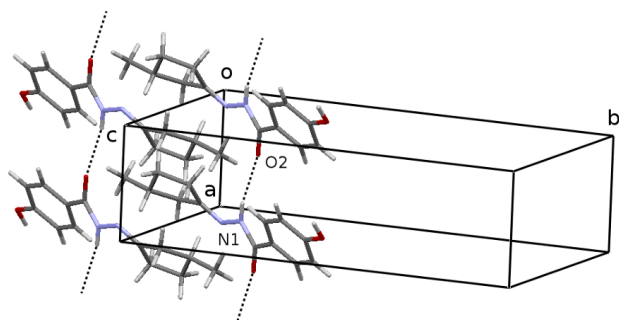
Packing diagrams of 1mon.

Fig. S6. H bonded chains in **1**mon. N1^i–H^i···O2: 0.935, 2.211, 3.120(4) Å, 163.9°, i = 1+x, y, z. Only one orientation of the disordered 3-methylcyclopentylidene group is shown. This figure should be compared with Fig. 5(a) of the typescript.
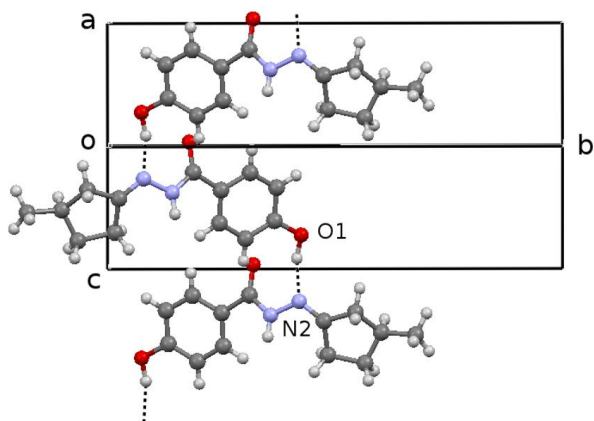

Fig. S7. H bonded chains in **1**mon. O1–H···N2A^i: 0.841, 2.05, 2.86(2) Å, 162.5°, i = -0.5+x, 0.5-y, 0.5+z. Only one orientation of the disordered 3-methylcyclopentylidene group is shown. This Figure should be compared with Fig. 5(b) of the typescript.
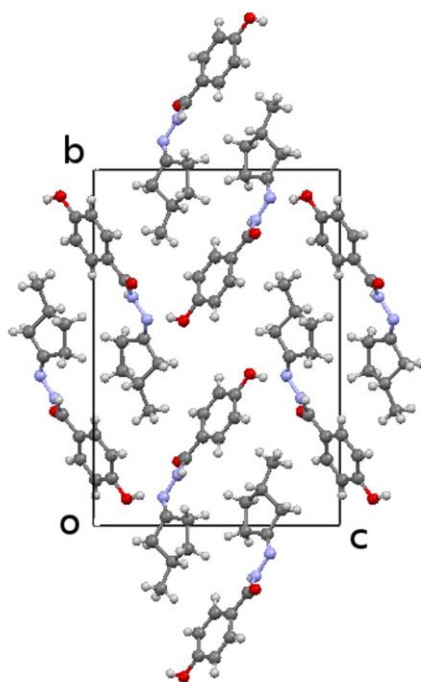
Fig. S7. Crystal packing of **1**mon viewed down **a**. Only one orientation of the disordered 3-methylcyclopentylidene group is shown. This Figure should be compared with Fig. 6 of the typescript.

References

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3 C. P. Brock, W. B. Schweizer and J. D. Dunitz, *J. Am. Chem. Soc.*, 1991, **113**, 9811-9820.