Electronic Supplementary Information

Polymorphism of the azobenzene dye compound methyl yellow

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Table S1: Solvents used for the recrystallisation of methyl yellow (DAB) and various crystallisation conditions.

Number	Solvent 1	Solvent 2	Crystallisation conditions	Product
1	Ethanol	-	[a], [b]	Form I
2	Ethanol	Water	[a], [b], [c]	Form I
3	Methanol	-	[a], [b]	Form I
4	Methanol	Chloroform	[a], [b], [c]	Form I
5	THF	-	[a], [b]	Form I and Form II
6	THF	Water	[a], [d]	Form I
7	THF	Trichloroethylene	[a], [b], [c]	Form I
8	Toluene	-	[a], [b]	Form I
9	Acetone	-	[a], [b]	Form I
10	Acetone	Water	[a], [b], [c]	Form I
11	Acetonitrile	-	[a], [b]	Form I
12	Acetonitrile	Dichloromethane	[a], [b], [c], [e]	Form I
13	Ethyl acetate	-	[a], [b]	Form I
14	Isopropanol	-	[a], [b]	Form I
15	Isopropanol	Water	[a], [b], [c]	Form I
16	Dichloromethane	-	[a], [b]	Form I
17	Dichloromethane	Hexane	[a], [b], [c], [e]	Form I
18	o-xylene	-	[a], [b]	Form I
19	m-xylene	-	[a], [b]	Form I
20	p-xylene	-	[a], [b]	Form I

*The solubility of DAB in several other solvents was limited.

[a] Solutions were left to crystallise at 4 °C, 23 °C and 60 °C

[b] Solutions were prepared in small, medium and large vials.

[c] Different percentages of each solvent were used.

[d] A layering method was used.

[e] A vapour diffusion method was used.

Hirshfeld surface analysis for the DAB polymorphs.

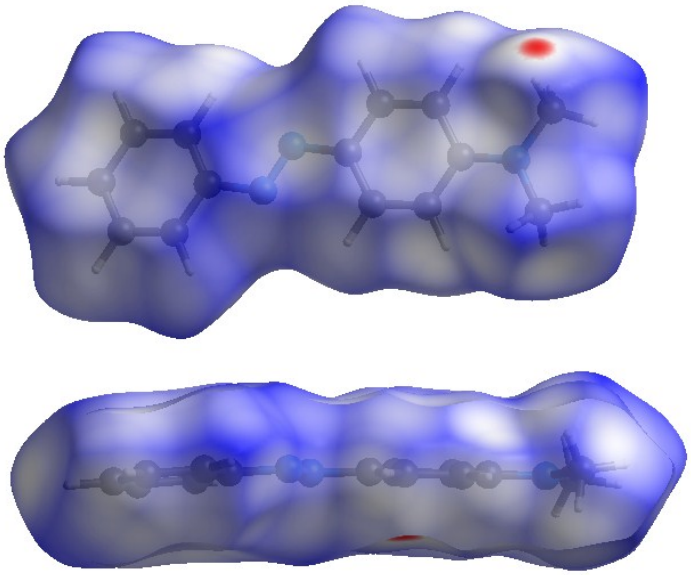

Figure S1 (a). DAB Form I, head-on (top) and side view (bottom) illustrating the short intermolecular contact regions in red. The overall, rounded Hirshfeld surface, supports the layered packing arrangement that is seen for this polymorph.[1]

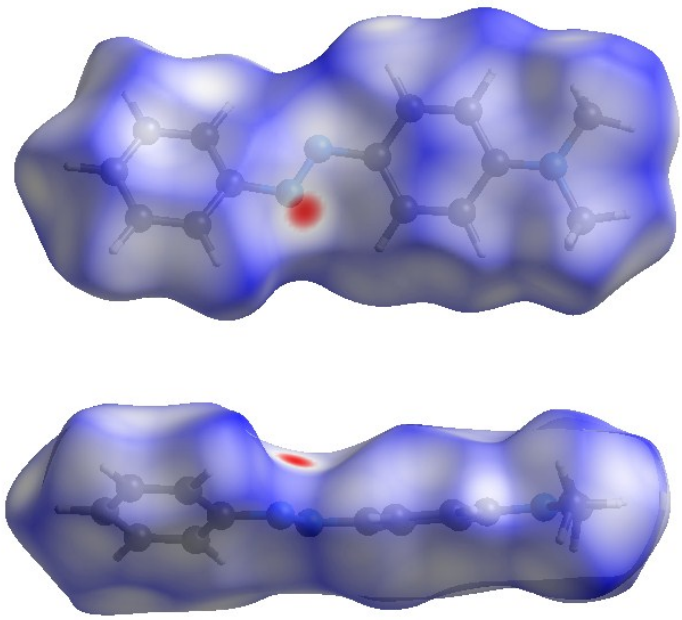

Figure S1 (b). DAB Form II, head-on (top) and side view (bottom) illustrating the short intermolecular contact regions in red, which are seen over the azo region. The sharper more curved, Hirshfeld surface around the azo group, supports the herringbone packing arrangement that is seen for this polymorph.[1]

Powder X-ray Diffraction

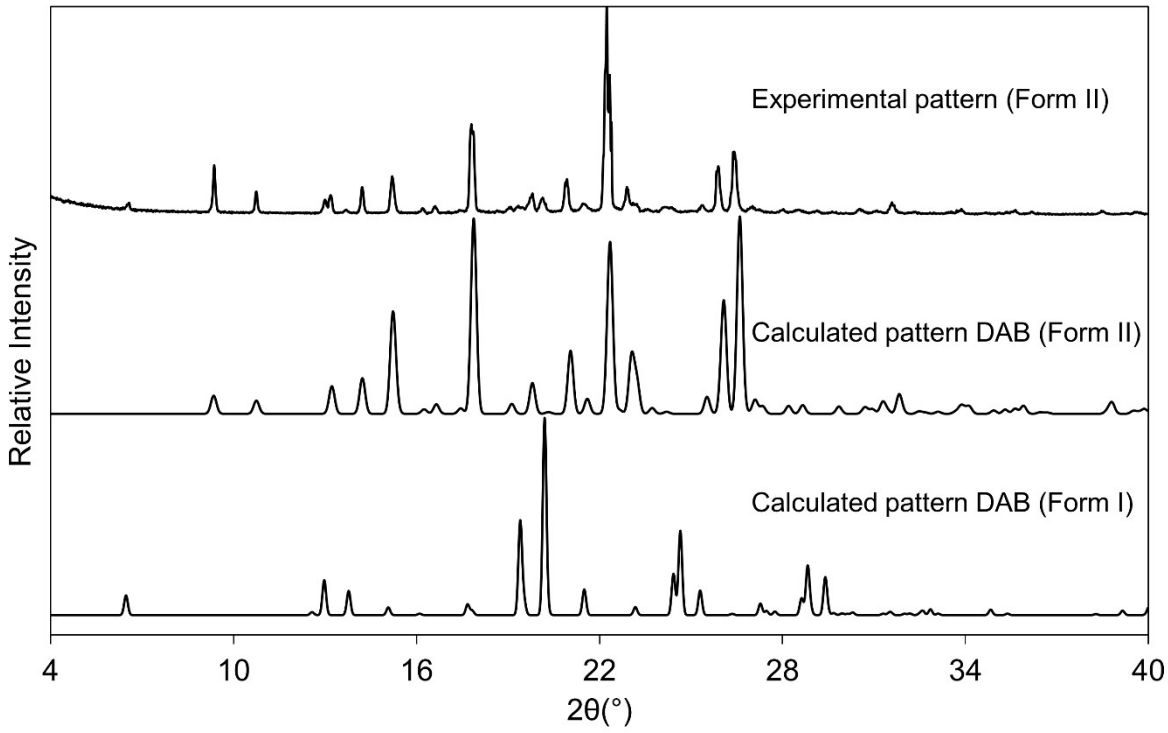

Figure S2. PXRD analysis showing the small amount of Form I present in the bulk sample used for DSC analysis.

Reference

1. M. A. Spackman and D. Jayatilaka, *CrystEngComm*, 2009, **11**, 19-32.