Mechanically induced reactions in organic solids. Liquid eutectics or solid-state processes?

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Experimental Details

The starting materials o-vanillin (**oV**, 99 wt. % purity) and p-toluidine (**pT,** 99 wt. % purity) were purchased from Sigma-Aldrich Co.

Room temperature experiments: The mixture of **oV** and **pT** taken in a 1:1 molar ratio was ground with an agate pestle in an agate mortar at room temperature. The formation of an orange liquid was observed immediately. Further grinding led to the crystallization of the liquid and the formation of the orange solid condensation product. The liquid also formed if **oV** and **pT** were ground separately using a mortar and a pestle, and then mixed together by spatula at room temperature. The crystallization of the final product occurred also in this case. Water formed during the condensation reaction could not be visually observed.

Low temperature experiments: An ice-water bath was used for the preparation of the ice-cold mixture (in 1:1 molar ratio). The starting materials, spatula, mortar, and pestle were cooled down to ~0°C prior to their use. Next, the equimolar mixture of cold **oV** and **pT** was ground. No phase or color changes occurred when materials were processed at 0°C (the low temperature) for 5 min. The grinding of **oV** and **pT** below 10°C for one hour concluded in a color change without a noticeable formation of a liquid phase. No liquid formation was also observed during warming up of the processed sample to room temperature. Water formed during the condensation reaction could not be visually observed.

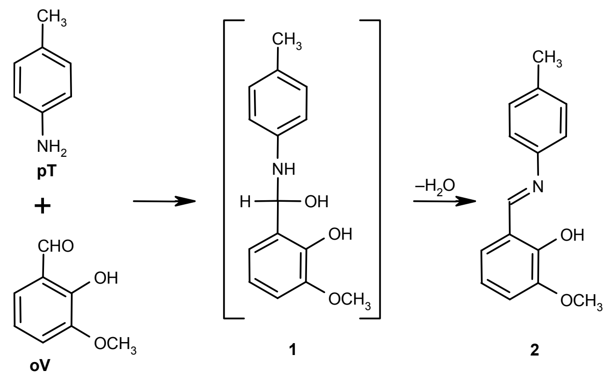

Figure S1. The reaction between o-vanillin (**oV**) and p-toluidine (**pT)**

NMR measurements

The ^{1}H and, ^{13}C NMR experiments were performed using the Varian Infinity 400 spectrometer, equipped with a doubly tuned 5 mm probe. Acetone-d$_6$ (Aldrich) and 5 mm NMR tubes were used for obtaining the reference spectra in solution. The ^{1}H and ^{13}C Bloch decay spectra were recorded in acetone-d$_6$ at 25 °C. All chemical shifts are referred to TMS as standard (0 ppm).

Sample preparation: **oV** and **pT**, a spatula, 5 mm glass NMR tubes, an agate mortar and pestle were cooled down to ~0 °C using an ice-water bath. The cold mixture of **oV** and **pT**, taken in a 1:1 molar ratio was ground in the mortar, than quickly transferred into the tube, sealed, and placed in liquid nitrogen. No changes in the material were observed during this preparation step.

Room temperature measurements: the sample prepared at ~0°C was loaded into the probe preheated to 25 °C and kept at this temperature during the course of NMR measurements. The ^{1}H spectra (4 scans, 1 s repetition rate) were recorded every 4 seconds starting at the 30th second form insertion into the probe (Fig. S2).

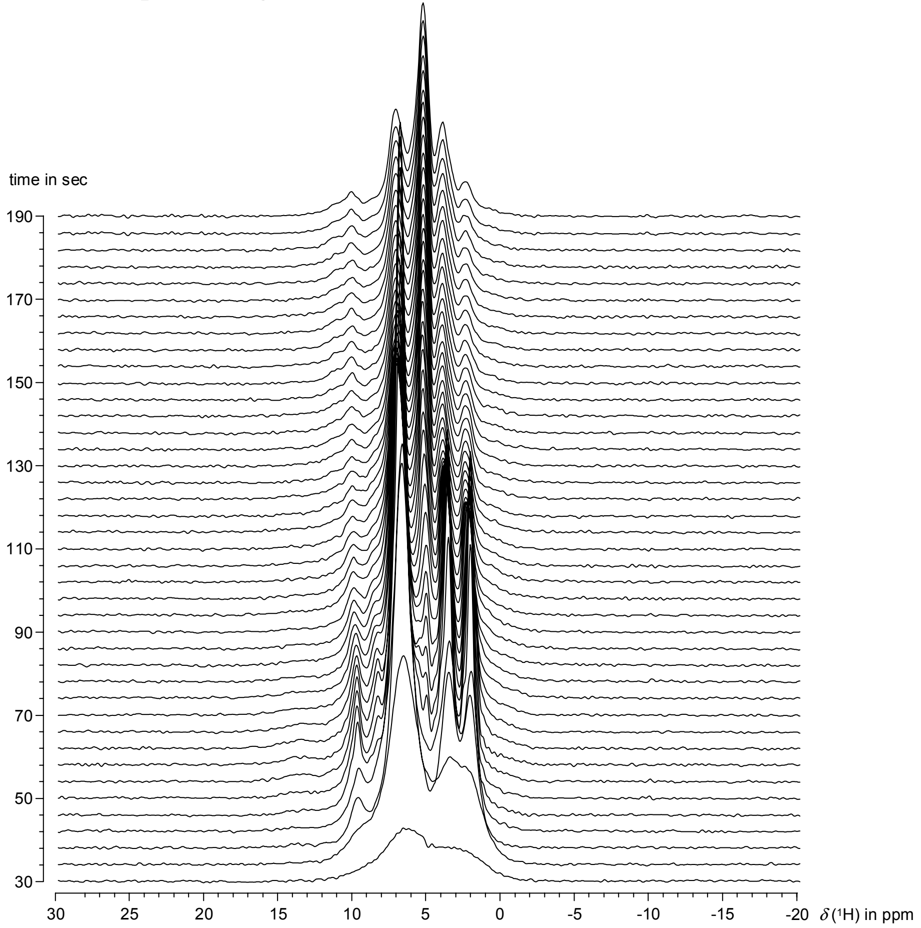

Figure S2. ^{1}H spectra of the mixture of **oV** and **pT** ground at 0 °C for 5 min and quickly warmed up to room temperature in the solid state NMR probe. The melting of the sample becomes apparent after 34 seconds at room temperature. The scale on the left side represents time in seconds from insertion of the sample into the probe.

For the ^{13}C measurements, the fresh ice-cold solid mixture of **oV** and **pT** was prepared and handled similarly. The spectra were recorded for 6 min. The ^{13}C chemical shifts (Fig. S3 and Table S1) were assigned according to literature data.[1-3]

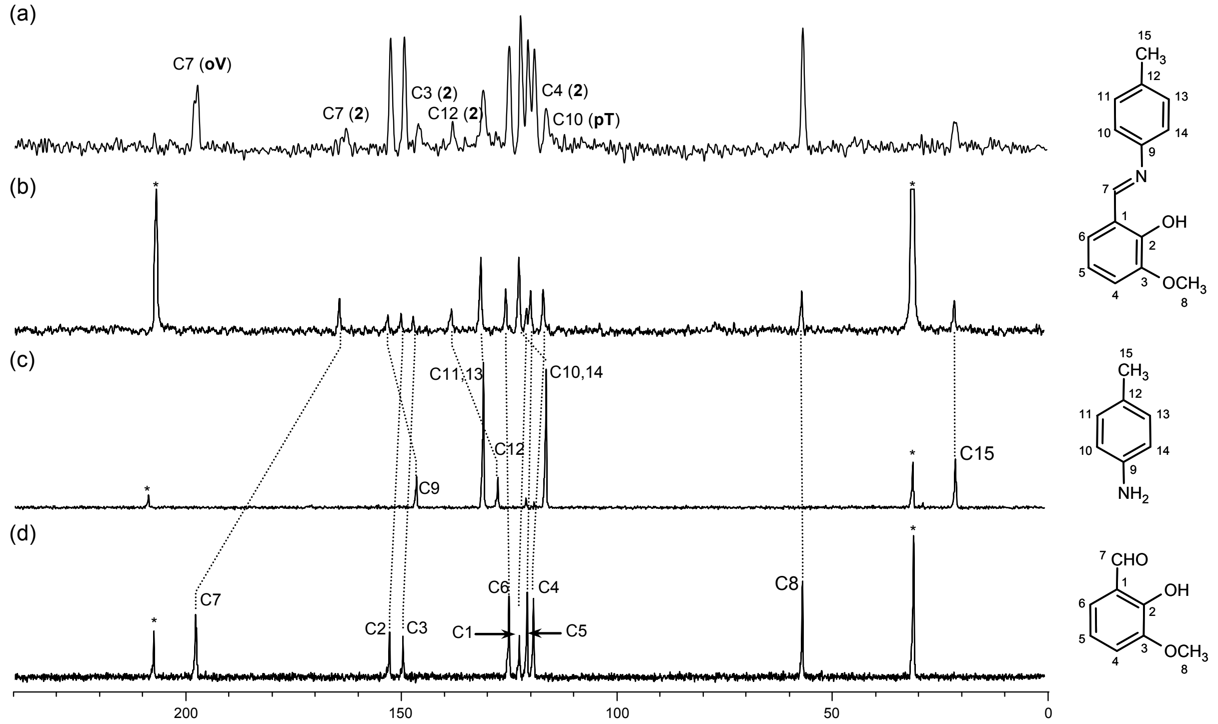

Figure S3. ^{13}C spectra recorded for (a) reaction mixture, (b) product **2,** (c) **pT**, and (d) **oV**. Resonances representing solvent are marked with asterisks. Signal assignment as indicated in the right hand inset.

Table S1. ^{13}C Chemical shifts for ***o*V**, ***p*T**, **2**, and reaction mixture.

position[a]	***o*V**		***p*T**		**2**		mixture
	this work	ref. [1]	this work	ref. [2]	this work	ref. [3]	
C1	121.7	120.7			120.0	119.6	120.3
C2	151.8	151.5			149.1	148.9	149.0
C3	148.7	148.1			146.3	145.8	145.7
C4	118.4	118.0			116.1	115.0	116.0
C5	119.9	119.5			119.0	118.9	118.8
C6	124.2	124.4			124.8	124.1	124.6
C7	196.8	200.2			163.4	162.0	197.0 162.4
C8	56.1	56.2			56.2	56.8	56.6
C9			145.6	144.4	152.2	151.9	152.2

C10,14			115.6	115.4	121.7	121.4	122.0
C11,13			130.1	130.0	130.6	130.4	130.7
C12			126.7	126.4	137.4	137.4	137.7
C15			20.6	20.6	20.8	21.5	21.3

[a] See Fig. S3 for atom numbering.

X-ray investigation

The X-ray powder diffraction experiments were carried out at room temperature on a PANalytical powder diffractometer using Cu Kα_1 radiation with a 0.02° 2θ step in the range of Bragg angles 2θ from 5° to 70°.

The orange sample prepared by grinding **oV** and **pT** at room temperature was analyzed after its complete crystallization and an additional pulverization.

The analysis of the product of the low temperature reaction was carried out using the sample ground below 10^{o}C for one hour and slowly warmed up to room temperature. The sample changed color to orange and retained solid appearance throughout the entire process. The XRD trace, taken shortly after the sample was warmed up to room temperature, containes peaks of the starting materials and the final product (**2**). The diffraction peaks of starting materials disappear after one hour at room temperature without an apparent formation of a liquid phase (Fig. S4).

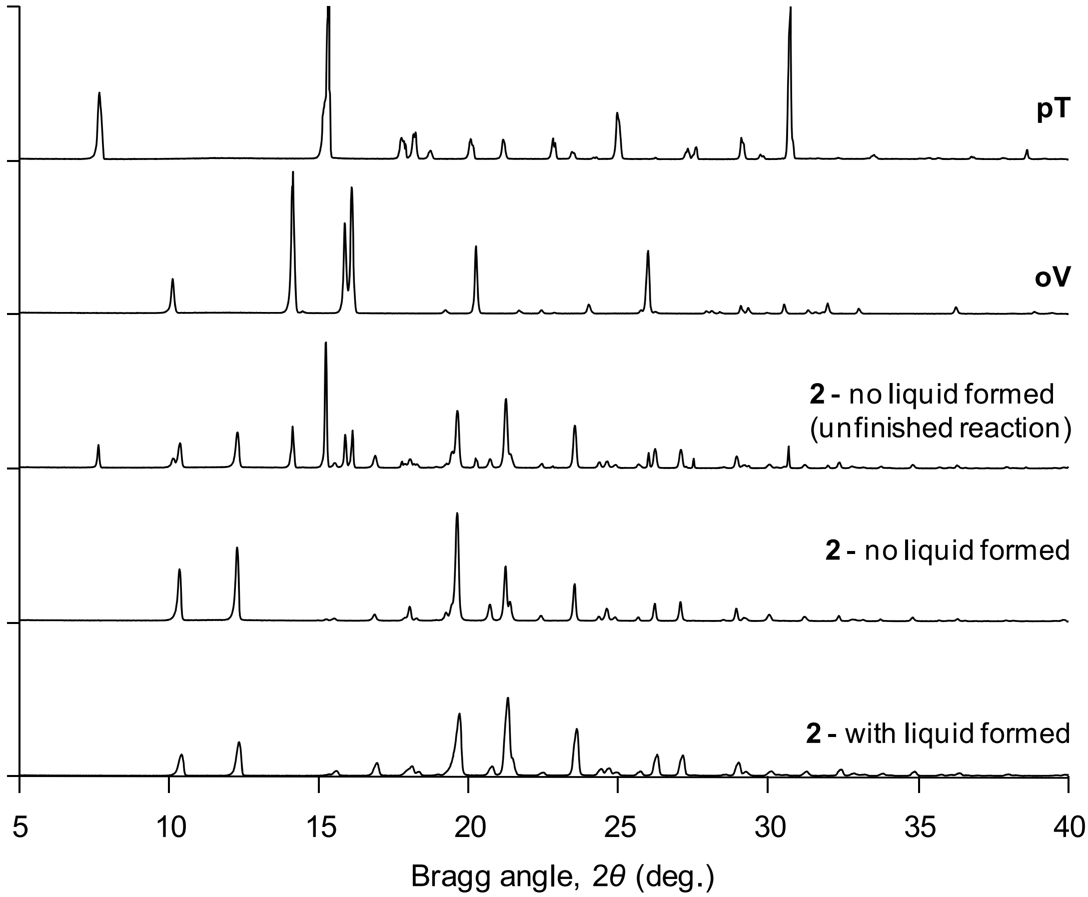

Figure S4. X-ray powder diffraction patterns of o-vanillin (**oV**), p-toluidine (**pT**), and the mechanochemically prepared azomethine **2.**

DSC measurements

The DSC experiments were performed using the PERKIN ELMER Differential Scanning Calorimeter "Pyris 1". The measurements were executed with a heating rate of 10°C/min. Approximately 8 mg of the investigated material was sealed in the aluminum sample holder, placed in a refrigerator, which maintained the temperature of -20°C. The dry ice cooling was used during transferring the sample from the refrigerator to the DSC equipment. The measurements of the baseline using the empty sample holder in the same temperature interval and with the same heating rate were performed before every run.

References

1. A. Pelter, R. S. Ward, T. I. Gray, *J. Chem. Soc., Perkin Trans. 1,* **1976**, 2475.
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