Nature of the multicomponent crystal of salicylic acid and 1,2-phenylenediamine

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Tables

Figures

Table S1. DSC of the neat coformers, physical mixtures and cocrystals.

Comp.	Endotherms (°C)			
	(i)	*(ii)*	*(iii)*	*(iv)*
SA	161	-	-	-
Phen	102	-	-	-
SA···Phen (1:1)	90	100	119	152
SA···Phen (1:2)	89	100	118	163
SA···Phen (2:1)	91	-	117	166
SA···Phen (LAG)[a]	91	101	-	160
SA···Phen (Sol.)[b]	89	-	-	-

[a]Solid obtained by liquid assisted grinding. [b]Solid obtained by slow evaporation of solvent.

Table S2. FTIR data of **SA···Phen** obtained from LAG and slow evaporation of solvent methods.

Bands (λ cm^{-1})	SA	Bands (λ cm^{-1})	Phen	Bands (λ cm^{-1})	SA···Phen	
					LAG	Solution
OH	3239	NH	3385	NH	3429	3429
OH	3007	NH	3364	NH	3361	3360
C=O	1658	-	-	C=O	1635	1635

Table S3. Experimental and calculated ^{1}H and ^{13}C NMR chemical shifts.

Function	**Atom Label**	δ_{exp} **/ ppm**	δ_{calc} **/ ppm (*)**	$\delta_{exp} - \delta_{calc}$ **/ ppm**
		Carbon		
COO^{-} (SA)	C7	175.87	174.35	1.52
C-OH (SA)	C6	160.75	162.81	-2.06
C-NH$_2$ (Phen)	C13	137.76	137.62	0.14
C-H (SA)	C4	134.48	135.42	-0.94
C-H (SA)	C2	128.93	128.99	-0.06
C-H (SA)	C11	127.14	126.08	1.06
C-H (Phen)	C9	123.10	122.77	0.33
C-H (Phen)	C12	121.20	120.28	0.92
C-H (SA)	C3	119.54	119.53	0.01
C-H (Phen)	C10	118.06	119.30	-1.24
C-NH$_3^+$ (Phen)	C8	117.48	117.57	-0.09
C-H (SA)	C5	117.28	117.20	0.08
C-COO^{-} (SA)	C1	116.68	116.33	0.35
		Hydrogen		
O**H** (SA)	H1’	11.78	11.97	-0.19
N**H**$_3^+$···$^{-}$OOC (Phen)	H2’-H4’	10.32	10.29	0.03
C-**H** (Phen)	H7’-H10’	7.67	7.48	0.19
C-**H** (Phen)	H7’-H10’	7.12	6.96	0.16
N**H**$_2$···O=C (Phen)	H5’	4.95	4.98	-0.03
N**H**$_2$···O-H (Phen)	H6’	3.4	3.57	-0.17
		Nitrogen		
NH$_3^+$	-	-337.80	-321.06	-16.74
NH$_2$	-	-331.80	-312.96	-18.84

(*) ^{13}C/^{1}H chemical shifts calculated according to Eq. 1; ^{15}N chemical shifts determined using a calculated reference value for the isotropic absolute shielding of neat nitromethane found in refs. [41,42]

Table S4. Selected bond lengths [Å] and angles [°] for SA···Phen.

Bond distances		Bond angles	
N(1)-C(1A)	1.4591(16)	C(6)-C(1)-C(11)	120.45(11)
O(2)-C(11)	1.2672(14)	C(2)-C(1)-C(11)	121.24(10)
O(1)-C(11)	1.2559(15)	(6A)-C(1A)-N(1)	119.53(10)
C(1)-C(11)	1.4855(15)	C(2A)-C(1A)-N(1)	118.57(10)
C(2)-O(3)	1.3514(17)	O(3)-C(2)-C(3)	118.25(13)
C(2A)-N(2)	1.3945(18)	O(3)-C(2)-C(1)	121.80(12)
N(1)-H(1)	0.944(16)	C(3A)-C(2A)-N(2)	122.17(11)
N(1)-H(3)	0.941(16)	N(2)-C(2A)-C(1A)	121.10(12)
N(1)-H(2)	0.946(16)	O(1)-C(11)-O(2)	122.58(11)
O(3)-H(3A)	0.928(19)	O(1)-C(11)-C(1)	119.48(10)
N(2)-H(2B)	0.931(19)	O(2)-C(11)-C(1)	117.93(11)
N(2)-H(2A)	0.86(2)	C(1A)-N(1)-H(1)	111.4(9)
		C(1A)-N(1)-H(3)	110.8(9)
		H(1)-N(1)-H(3)	107.8(13)
		C(1A)-N(1)-H(2)	109.1(9)
		H(1)-N(1)-H(2)	109.6(13)
		H(3)-N(1)-H(2)	108.0(13)
		C(2)-O(3)-H(3A)	103.0(12)
		C(2A)-N(2)-H(2B)	119.1(11)
		C(2A)-N(2)-H(2A)	114.7(12)
		H(2B)-N(2)-H(2A)	111.0(16)

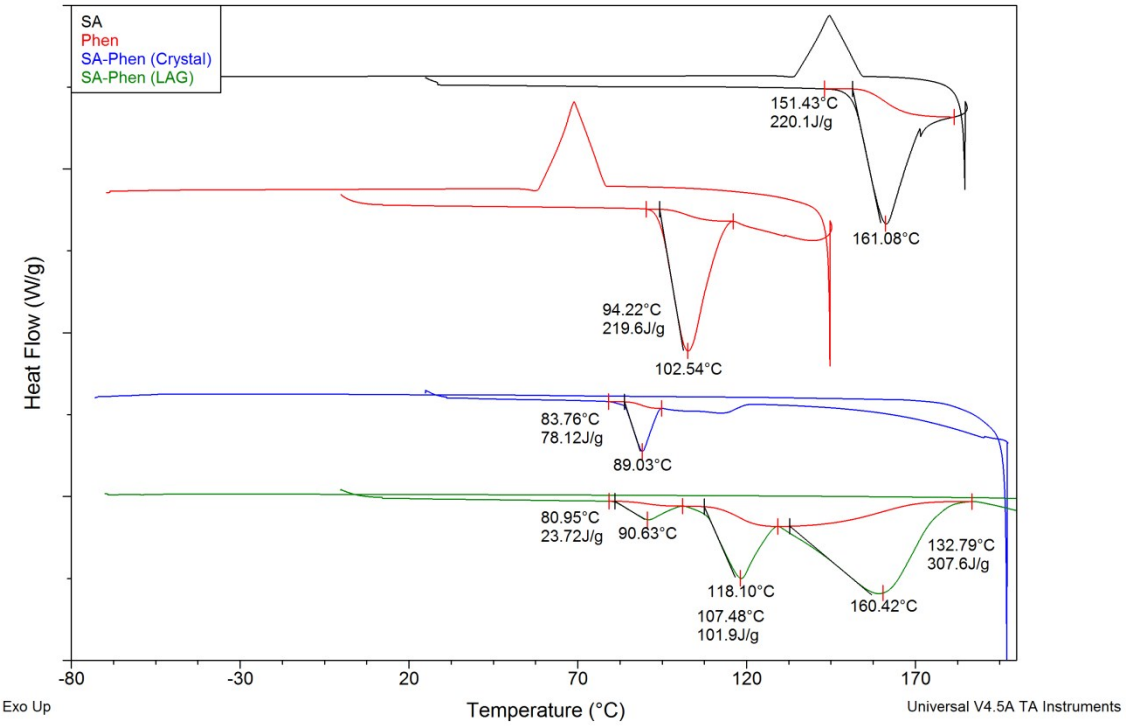

Figure S1. DSC curves of salicylic acid (**black**), 1,2-phenylenediamine (**red**) and crystal SA···Phen obtained from slow evaporation of the solvent (**blue**) and mixture of SA···Phen obtained by LAG (**green**).

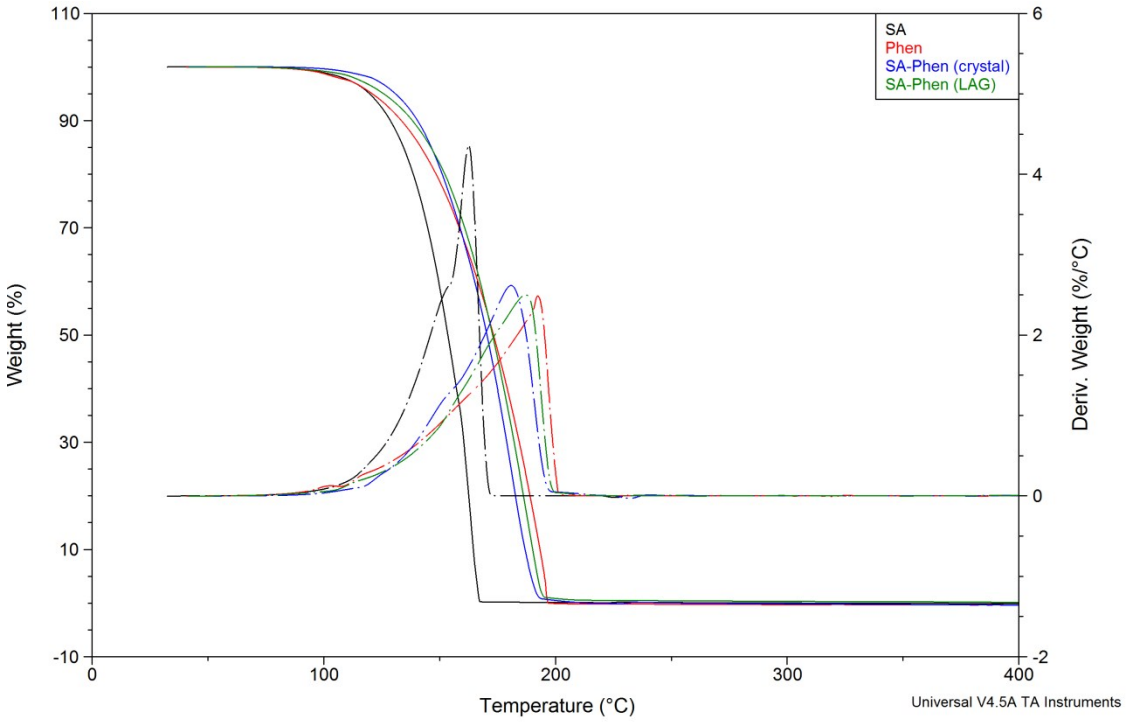

Figure S2. TGA traces of salicylic acid (**black**), 1,2-phenylenediamine (**red**) and crystal SA···Phen obtained from slow evaporation of the solvent (**blue**) and mixture of SA···Phen obtained by LAG (**green**).

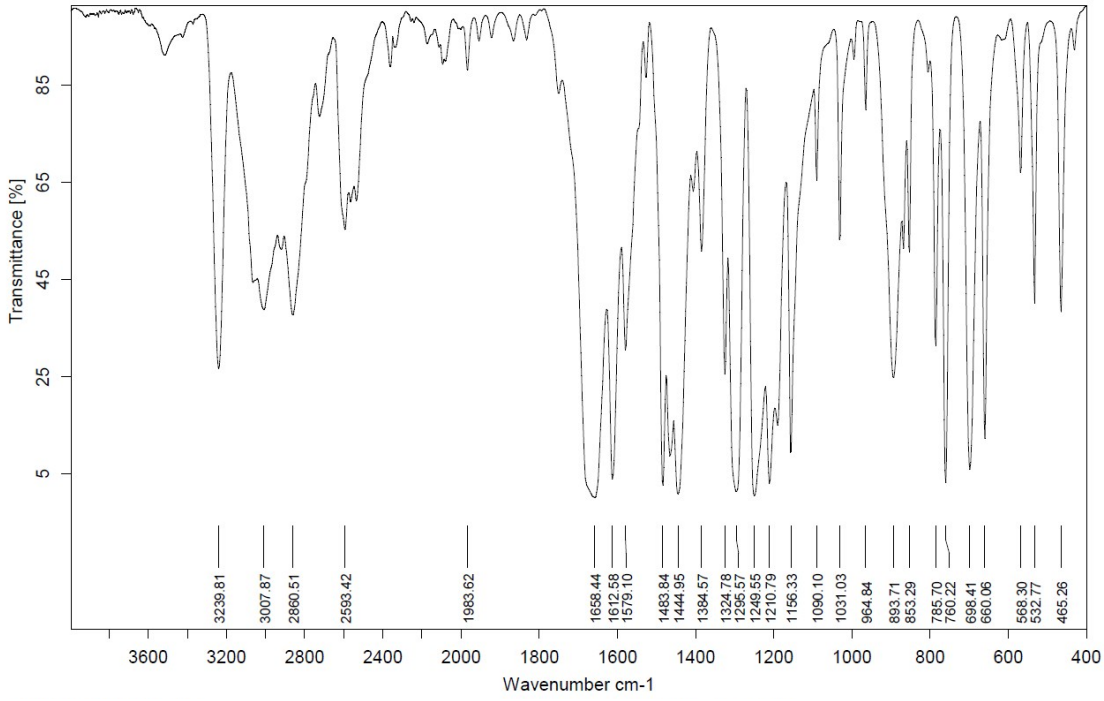

Figure S3. FTIR spectra of salicylic acid.

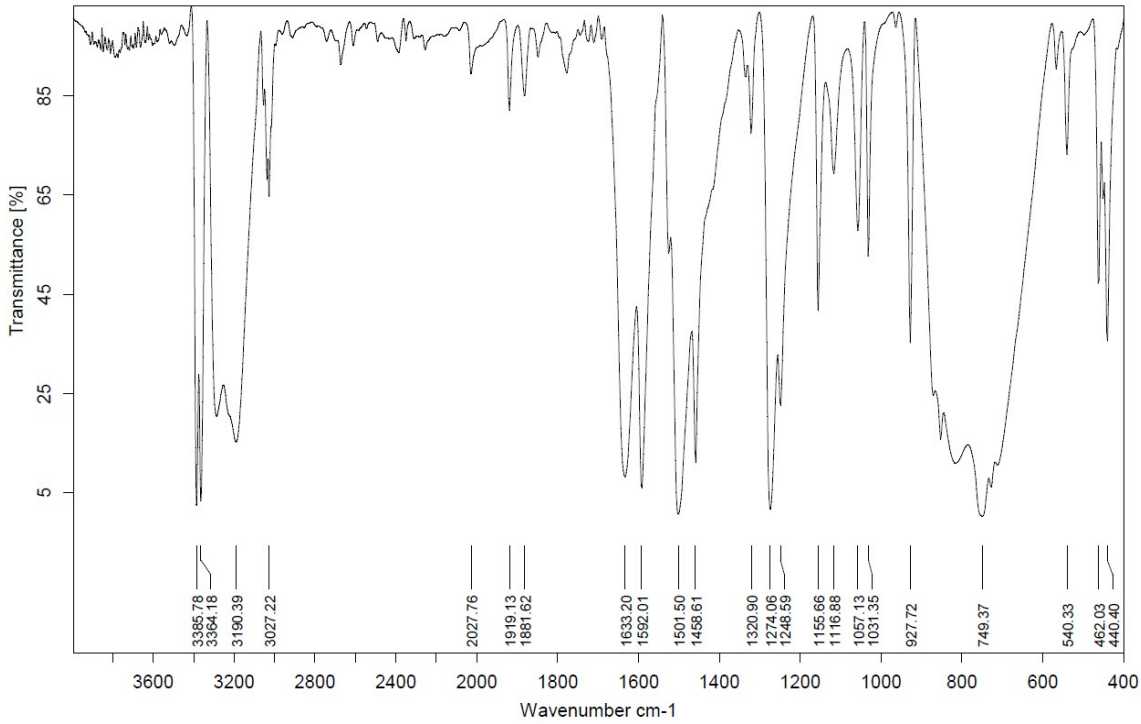

Figure S4. FTIR spectra of 1,2-phenylendiamine.

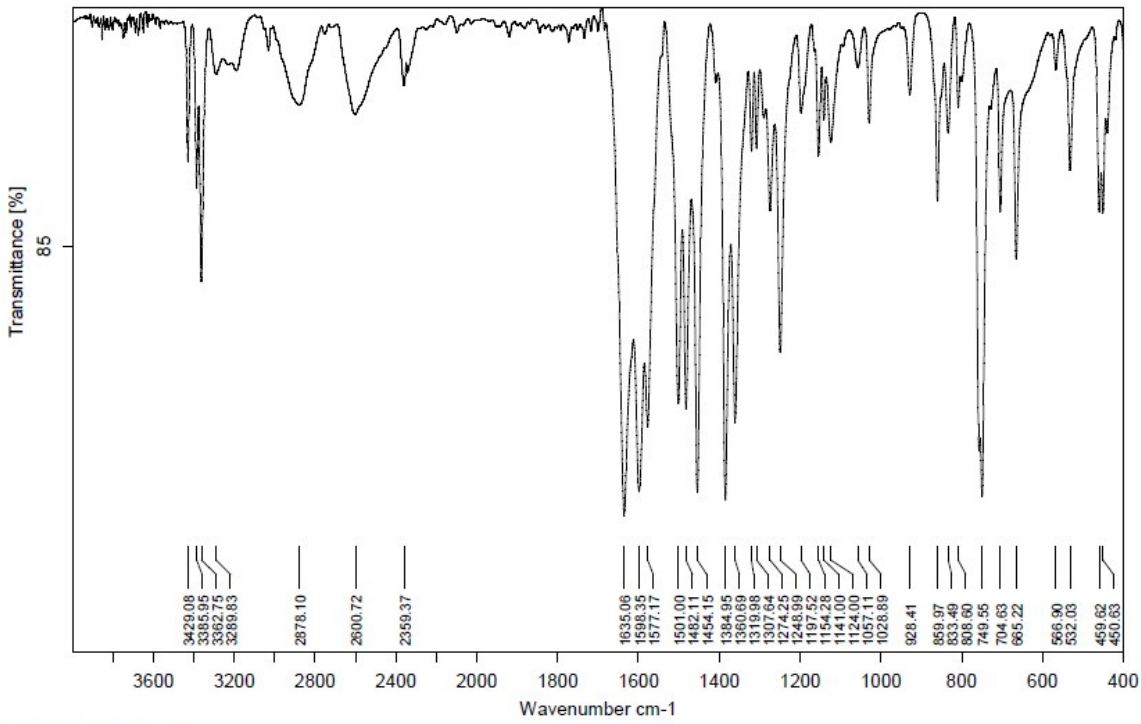

Figure S5. FTIR spectra of **SA···Phen** obtained by LAG method.

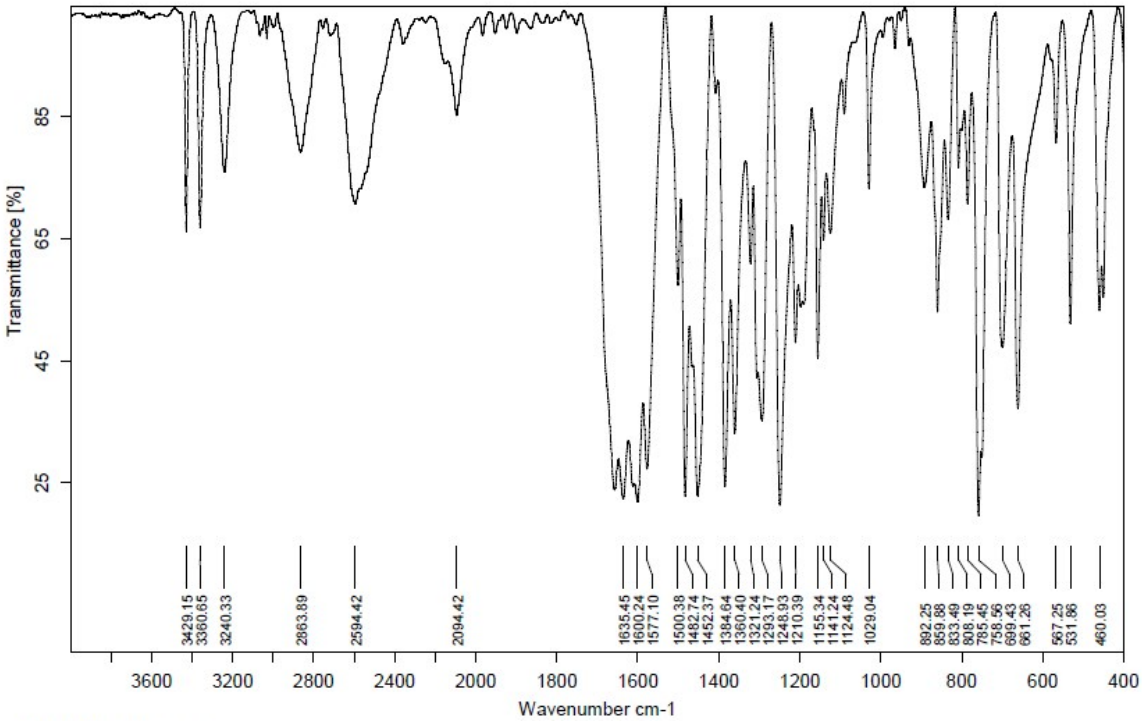

Figure S6. FTIR spectra of **SA···Phen** obtained by slow evaporation of solvent method.

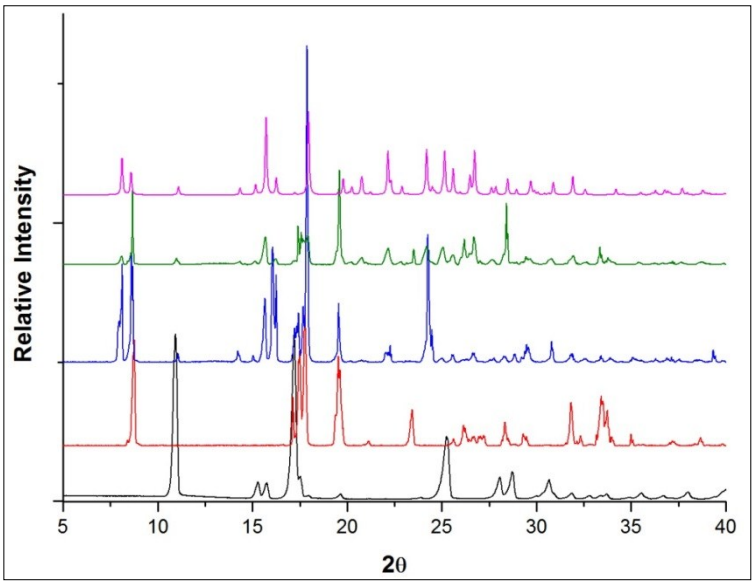

Figure S7. PXRD patterns of salicylic acid (**black**), 1,2-phenylendiamine (**red**) and the **SA···Phen** obtained by slow evaporation of solvent (**blue**) and LAG (green) and **SA···Phen** pattern simulated from SCXRD data using the package program Mercury® (**magenta**).