Electronic Supplementary Material (ESI) for CrystEngComm

SUPPLEMENTARY INFORMATION: *COMPLEXITIES OF MECHANOCHEMISTRY: ELUCIDATION OF PROCESSES OCCURRING IN MECHANICAL ACTIVATORS VIA IMPLEMENTATION OF A SIMPLE ORGANIC SYSTEM*

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THEORETICAL XRPD PATTERNS OF KNOWN COMPONENTS

Theoretical XRPD patterns for the known reactants, glycine and malonic acid (MA), and the known product, glycinium semi-malonate salt (GSM) phase, were prepared using Mercury, **Figures 1-3,** respectively.

Fig 1: *Theoretical XRPD of α-Glycine (GLYCIN29)*

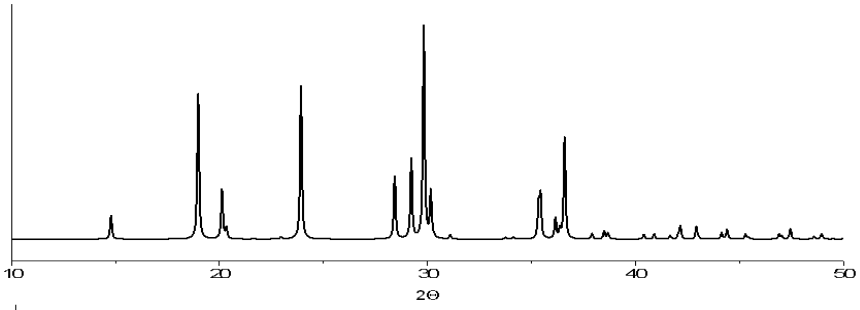


Fig 2: *Theoretical XRPD of β-Malonic Acid (MALNAC06)*

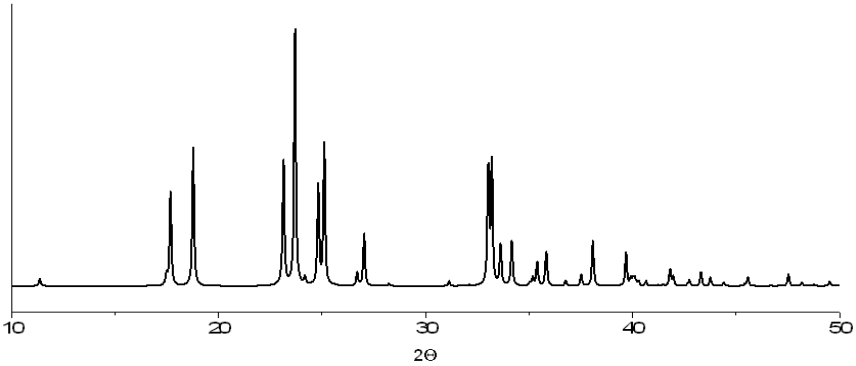
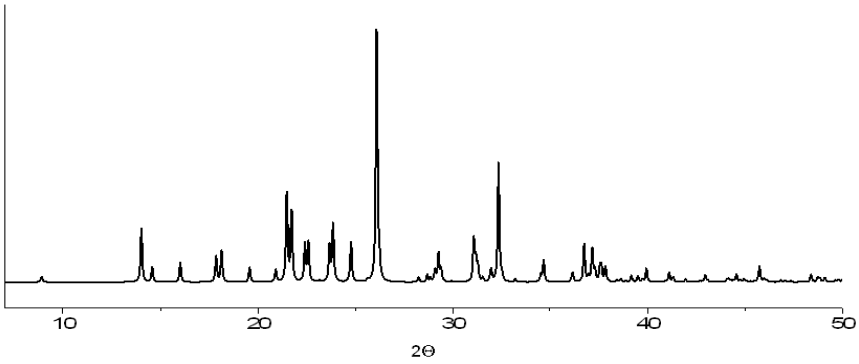


Fig 3: *Theoretical XRPD of Glycinium Semi-Malonate (AWIHIY).*



XRPD PATTERNS OF MECHANICALLY TREATED REACTANT AND KNOWN PRODUCT PHASES

To ensure that the novel phase was not simply a mechanically induced polymorphic transition of one of the reactant components, or the GSM salt, mechanical treatment was performed on the individual components. The reactant components were treated by milling at 24 Hz for 90 minutes (demonstrated to consistently induce formation of the novel phase). As mentioned in the main text, large quantities of GSM salt was unattainable, and as such pure GSM salt was submitted to 120 minutes impact treatment (observed to consistently induce formation of the novel phase). A comparison of experimentally obtained XRPD pattern for the un-treated and treated components is shown in **Figure 4**. It does not appear that mechanical treatment of individual components can induce formation of this novel phase.

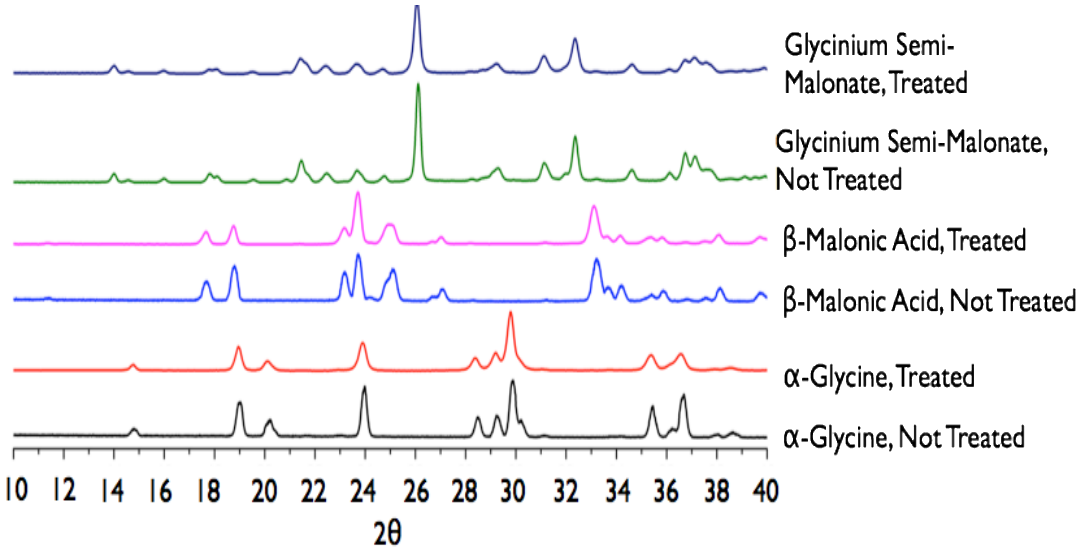


Fig 4: *Experimentally obtained XRPD patterns for treated and un-treated reactant and known product components.*

IMPACT TREATMENT OF EQUIMOLAR MIXTURES OF α-GLYCINE + β-MALONIC ACID

XRPD of an equimolar α-glycine +β-MA mixture was submitted for impact treatment, **Figure 5**. Separate samples were submitted for 60 min and 120 min to assess the suitability of this composition for further study. While both products were obtainable from this treatment method, the novel product could not be obtained in isolation, even after 120 min treatment (the maximum treatment time capable by the mechanoreactor). Of further consideration, as discussed in the main article, the simple process of manual mixing of the equimolar components was observed to already yield GSM product. As such equimolar mixtures were not used for further study. This being said, the trend of subsequent products (GSM followed by novel phase) remains consistent between the equimolar mixture and the 3:1 Gly/MA mixture discussed in the main paper.

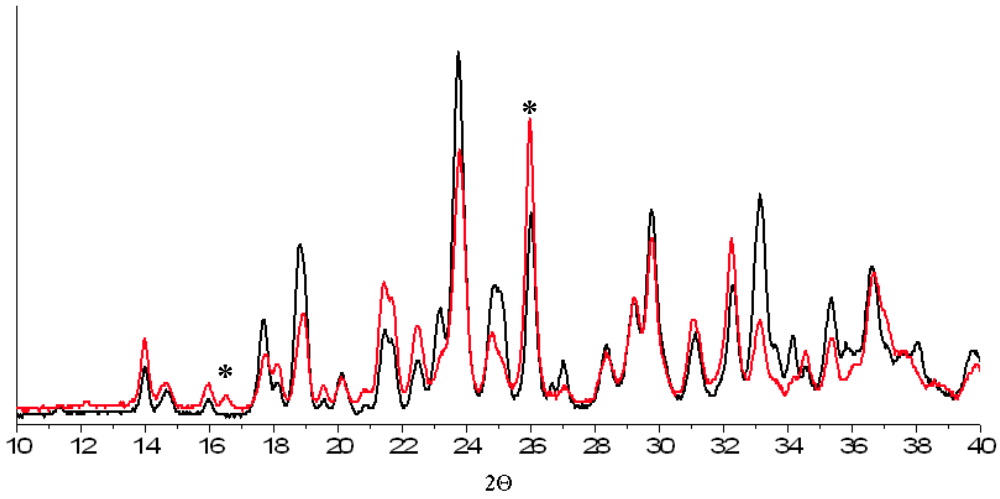


Fig 5: *XRPD of equimolar mixtures submitted to impact treatment for 60 min (black) and 120 min (red). For clarity, the product phases can be monitored by their major peaks at 16.5° (novel phase) and 26° (GSM).*

MILLING STUDIES OF MIXTURES 75 MOL% α-GLYCINE + 25 MOL% β-MALONIC ACID

Mixtures composed of 75 mol% α-glycine + 25 mol% β-MA (3:1 mixture) were also submitted for milling treatment at 24 Hz, **Figure 6**. The trend of successive products, transitioning from GSM to the novel phase after sufficient treatment, is consistent with that observed by treatment of the equimolar mixtures, discussed in the main paper. Of note, however, is the difference in treatment time required to obtain each phase, with the 3:1 mixture requiring less treatment for transition from GSM to the novel phase. Resulting from smaller amounts of MA in the mixture, the observation of the novel product phase was more difficult to observe; as such, the equimolar mixture was chosen for deeper investigation.

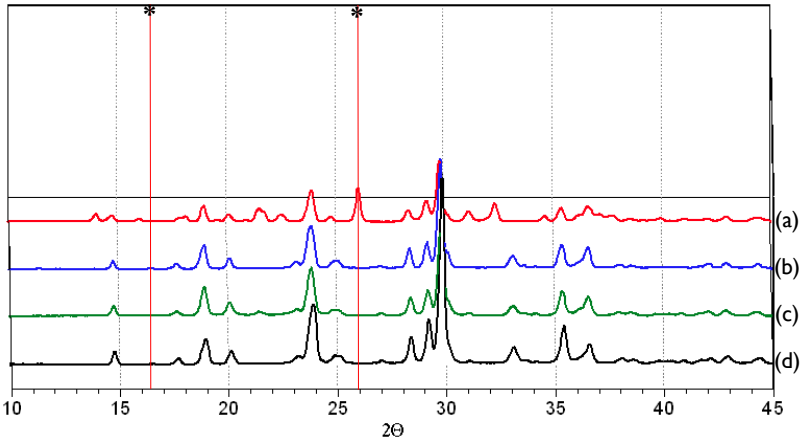


Fig 6: *Milling at 24 Hz of a 3:1 α-Glycine + β-MA mixture: (a) 30 min, (b) 45 min, (c) 60 min, and (d) 90 min) For clarity, the reaction products can be monitored by means of their most intense peaks, 26° (GSM) and 16.5° (novel product), as indicated by (*).*

FURTHER SUPPORT FOR UNIQUE REACTION ZONES WITHIN A MILLING JAR

Milling (24 Hz) was repeated with both equimolar and 3:1 mixtures, sampling from both the milling jar ends (purple) and walls (blue), **Figures 7-11**. For clarity, the products can be followed by monitoring their major peaks at 26° (GSM) and 16.5° (novel phase), labelled by (*). The low intensity of the novel product peak is discussed in the main paper. The hump observed from *ca.* 10-23° is taken to be the result of X-ray refraction by the sample holder; this effect is observed due to the small amounts of powder obtainable from the milling jar walls. A definite differentiation between observed products is noticeable in all cases.

Fig 7: *75 mol% α-glycine + 25 mol% β-MA milled 24 H 3 x 20 minutes with no intermittent mixing.*

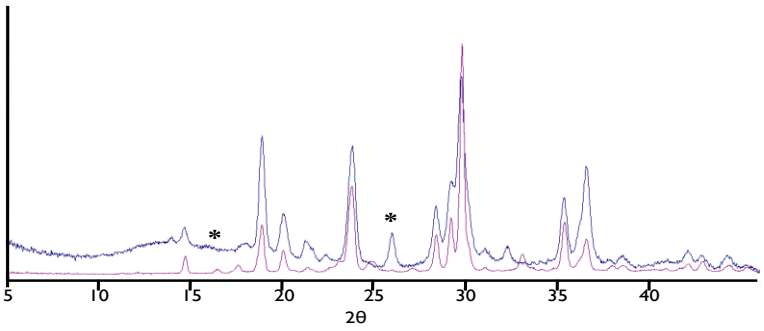
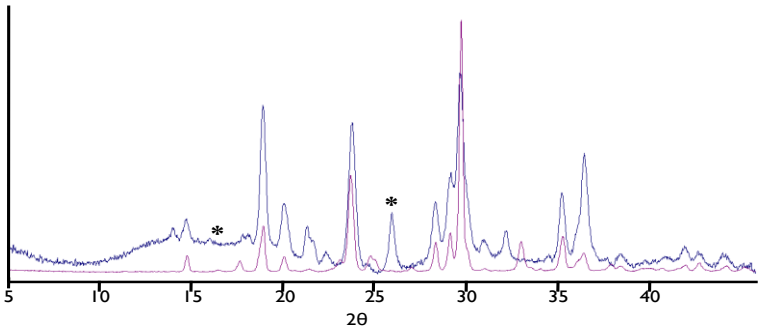


Fig 8: *75 mol% α-glycine + 25 mol% β-MA milled 24 H 3 x 20 minutes with no intermittent mixing.*



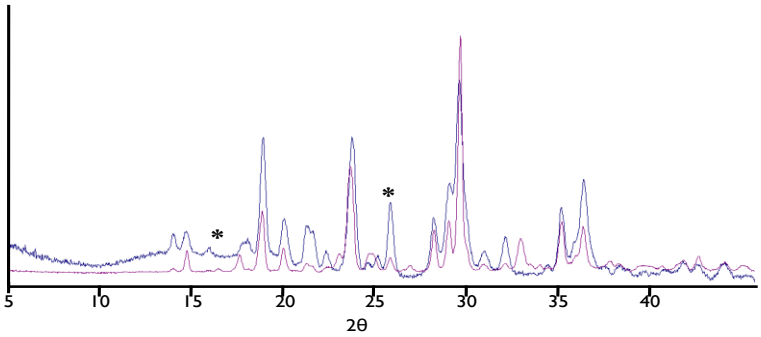


Fig 9: *75 mol% α-glycine + 25 mol% β-MA milled 24 H 3 x 20 minutes with no intermittent mixing.*

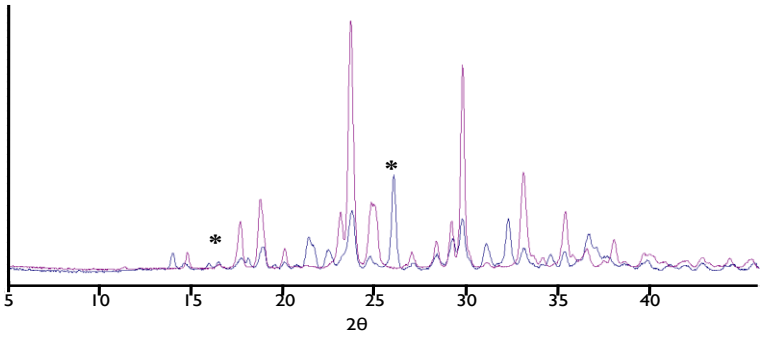


Fig 10: *50 mol% α-glycine + 50 mol% β-MA milled 24 H 3 x 20 minutes with no intermittent mixing.*

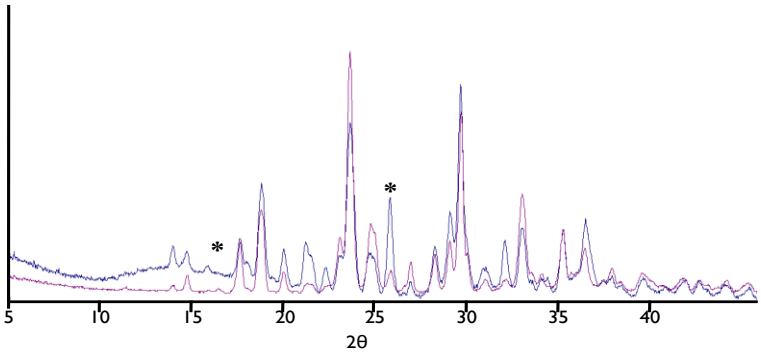


Fig 11: *50 mol% α-glycine + 50 mol% β-MA milled 24 H 3 x 20 minutes with no intermittent mixing.*