Electronic Supplementary Material (ESI) for CrystEngComm.

Mechanics of Twisted Hippuric Acid Crystals Untwisting as they Grow

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Electronic Supplementary Information

Fig. S1 Relationship between twist period (2*P*, mm) and the smallest size in a cross section (*h*, μm) fitted with by the power law, $P = kh^n$, and the linear function, $P = k_0 + k_1h$.

Fig. S2 Correlation between twist intensity (*r*/*P*) and temperature at the bench, T_{bench} (a) and the substrate, *T* (b).

Supplementary information text. Reformulating of discrete untwisting models in terms of continuous growth.

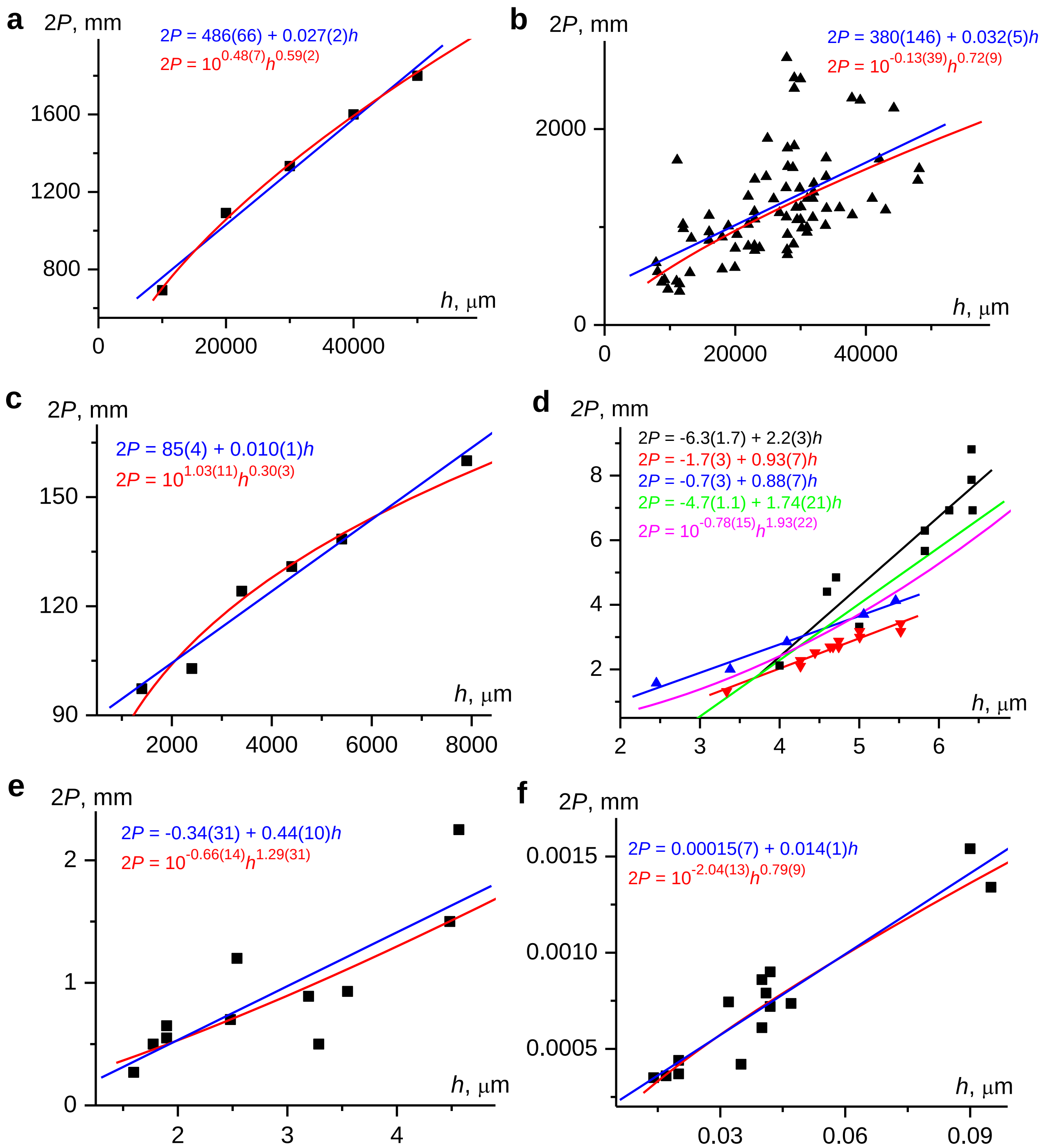

Fig. S1 Relationship between twist period (2P, mm) and the smallest size in a cross section (h, μm) fitted with by the power law, $P = kh^n$, and the linear function, $P = k_0 + k_1h$. (a) Natural quartz, data from ref. 7; (b) Natural quartz, data from ref. 6; (c) Oxalic acid dihydrate, data from ref. 7; (d) Melt grown hippuric acid; separate fittings for three crystals and simultaneous fitting, data from ref. 12; (e) (1,4-bis[2-(pyrene-1-yl) vinyl]-2,5-dimethylbenzene)IBr_2, data from ref. 11; (f) Poly(m-phenylene isophthalamide), data from ref. 14.

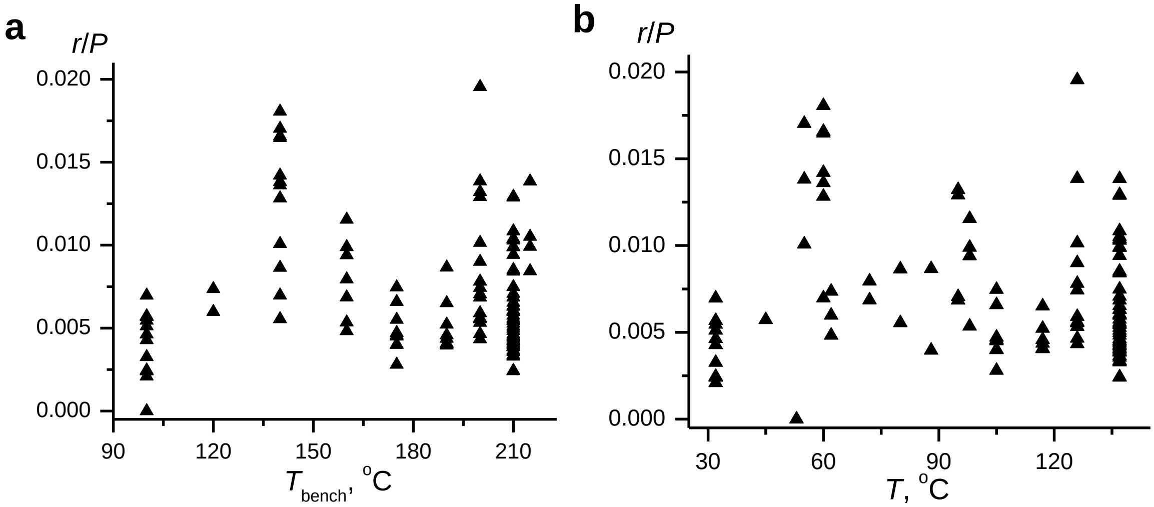

Fig. S2 Correlation between twist intensity (*r*/*P*) and temperature at the bench, T_{bench} (a) and the substrate, *T* (b). In order to minimize the effect of crystal size the twist intensity, 1/*P*, is multiplied by the crystal radius, *r*.

Supplementary information text

Reformulating of discrete untwisting models in terms of continuous growth

It should not be a big error to replace growth by discrete layers of thickness Δr = 0.7 nm with continuous growth by infinitesimal layers, since experimentally observed Δr is much less than the minimal observed crystal size r_0 > 50 nm. The equation (8) can be rewritten as

$$\theta_{T(N)} r_N^4 = \theta_{p,0} r_0^4 + \sum_{i=1}^{N} \theta_{p,i} \left(r_i^4 - r_{i-1}^4 \right), \tag{S1}$$

where summation can be replaced by integration

$$\theta_{T(N)} r_N^4 = \theta_{p,0} r_0^4 + \int_{r_0}^{r_N} \theta_p(r) dr^4 = \theta_{p,0} r_0^4 + 4\int_{r_0}^{r_N} \theta_p(r) r^3 dr\ . \tag{S2}$$

The condition (7) can be rewritten as $\gamma_{p,i} = \theta_{p,i} r_i = \theta_{p,i-1} r_{i-1} \alpha = \gamma_{p,i-1} \alpha$. Then the difference in shear strain $\Delta\gamma_{p,i} = \gamma_{p,i} - \gamma_{p,i-1} = \gamma_{p,i-1}\alpha$ in a continuous form is

$$\frac{d\gamma}{dr} \Delta r = \gamma(\alpha - 1) \tag{S3}$$

Solution to eq. (S3) gives $\gamma_p = \gamma_{p,0} \exp\left([\alpha - 1] \frac{r - r_0}{\Delta r} \right)$ or in terms of twist intensity

$$\theta_p = \theta_{p,0} \frac{r_0}{r} \exp\left([\alpha - 1] \frac{r - r_0}{\Delta r} \right). \tag{S4}$$

The final expression is obtained by combining eqs. (S2) and (S4)

$$\frac{\theta_{T(N)} r_N^4}{\theta_{p,0} r_0^4} = 1 + \frac{4}{r_0^3} \int_{r_0}^{r_N} r^2 \exp\left([\alpha - 1] \frac{r - r_0}{\Delta r} \right) dr\ . \tag{S5}$$

This integral can be solved straightforwardly to give

$$\frac{P_0 r_N^4}{P_N r_0^4} = 1 + \frac{4}{r_0^3} \left[\left(\frac{r_N^2}{k} - \frac{2r_N}{k^2} + \frac{2}{k^3} \right) \exp\left(k[r_N - r_0] \right) - \left(\frac{r_0^2}{k} - \frac{2r_0}{k^2} + \frac{2}{k^3} \right) \right], \tag{S6}$$

where $k = (\alpha - 1)/\Delta r$. Eq. (9) cannot be directly obtained from eq. (S6) because of the zero denominator, k = 0, but it can be obtained easily by soling eq. (S5) with α = 1.