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# Mechanically induced molecular migrations in molecular crystals

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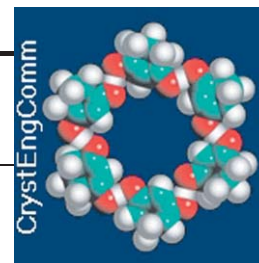


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Received 3rd March 2005, Accepted 10th June 2005

First published as an Advance Article on the web 21st June 2005

The action of mechanical pressure on organic molecular crystals is studied by the new technique of nanoscratching at various faces in different directions in order to induce far-reaching anisotropic long-range molecular migrations. Three-dimensionally interlocked packing as in the chemically unreactive crystals of 2-benzylidenecyclopentanone (**1**) or *cis*-1,2-dibenzoylthene (**2**) cannot experience molecular migrations and only abrasion (sometimes shift of debris in front) is detected upon scratching in any direction. Conversely, chemically reactive crystals of thiohydantoin (**3**), anthracene (**4**), thiourea (**5**), tetraphenylethene (**6**), and ninhydrin (**7**) experience mechanically induced anisotropic long-range molecular migrations within the crystal, because they exhibit cleavage planes between mono-, or bi-layers, along which migration occurs. This is shown by detailed analyses of the respective crystal packing. Flat parallel layers give no molecular migrations under pyramidal horizontally advancing tips but abrasion and/or shift of layered segments. Skew cleavage planes give either migration to both sides and in front, or only to the right, or only to the left, or no molecular migration but abrasion, depending on the orientation of the scratching. Vertical cleavage planes give either molecular migrations to both sides and in front, or shift of material in front (probably of extended molecular layer segments for nearly planar molecules), or abrasion. But three-dimensional extended molecules require a push by the tip from their side in order to migrate either to the right or to the left in competition with abrasion if there is some interlocking within the cleavage plane. Polar axes in crystals result in different appearance of the migrations in forward or reverse scratching. The results are discussed in terms of crystal packing.

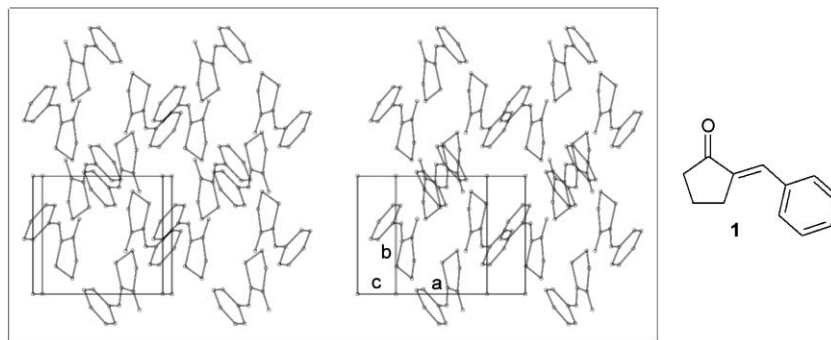
## 1. Introduction

Long-range molecular migrations are the basics for environmentally benign solid-state syntheses with 100% yield that have been realized in more than one thousand cases and mechanistically studied.<sup>1–3</sup> Their importance for waste-free production also on a larger scale has been appreciated for the gas–solid and the solid–solid version and compared with less efficient solvent-free syntheses.<sup>4</sup> The application of a small amount of solvent followed by kneading has recently been advertised.<sup>5</sup> However, this is neither “solid-state” nor “solvent-free” and the term “mechanochemical” should be restricted to mechanical breaking of covalent bonds (in polymers, infinitely covalent crystals, explosives, and with Bridgman’s anvil) rather than on mechanical agitation or milling that cannot break normal covalent bonds. The reason for anisotropic molecular migrations is the urgent need for release of internal pressure as imposed by chemical reaction with change of molecular geometry. Conversely, previous theories claiming minimal atomic and molecular movements (at most 4.2 → 1.5 Å) in solid-state reactions (Schmidt’s topochemistry hypothesis denies molecular migrations both for homogeneous and heterogeneous solid-state reactions) found access in textbooks. Therefore, the overwhelming evidence for long-range anisotropic migrations (that are strictly related to the molecular packing) by atomic force and near-field optical microscopy (AFM and SNOM)<sup>1,2</sup> and grazing incidence diffraction (GID)<sup>6</sup> should be supplemented by mechanical induction of far-reaching molecular migrations without chemical transformation. A suitable means for that purpose are nanoscratching experiments that evaluate the molecular packing on various faces in different directions by the AFM determination of the molecular migrations, because these provide more detailed information than indentation experiments.<sup>7</sup> We report here on

various characteristic cases and correlate them with the crystal packing. If far-reaching molecular migration is observed the crystalline material will be ready for suitable solid-state chemical reactions, a fact that is important if X-ray crystal data are not available. Thus, this endeavor has predictive power.

## 2. Experimental

The single crystals of compounds **1–7** [2-benzylidenecyclopentanone (**1**), *cis*-1,2-dibenzoylthene (**2**), thiohydantoin (**3**), anthracene (**4**), thiourea (**5**), tetraphenylethene (**6**), and ninhydrin (**7**)] were obtained from solutions in hexane, acetone, acetone, 1,2-dichloroethane [**4**: both plates for (001) and prisms for {110}], methanol, dichloromethane, and water, respectively, by slow evaporation, filtration, rapid suction with solvent to remove mother liquor and drying in a vacuum. The natural surfaces were studied without further treatment after gluing horizontally to a magnetic plate. The cleavage plane of **3** was isolated by touching the crystal with a fine needle and gluing the cleaved crystal with (10–2) horizontally by additionally putting some material in the gap between the skew face and the support surface. Crystal data were obtained from Cambridge Crystallographic Data Base and primary literature. They were imaged and analyzed with Schakal software (E. Keller, University of Freiburg, Germany). Crystal faces were identified by X-ray diffraction using the crystal parameters, which also confirmed the correct polymorph. The AFM imaging used a Digital Instruments Nanoscope III scanning probe microscope. The magnetic support with the crystal was placed on the magnetic table of a Hysitron-Triboscope with 2D-transducer, aligned horizontally with a leveling system under the vertical tip (better than 1° in *x* and *y*



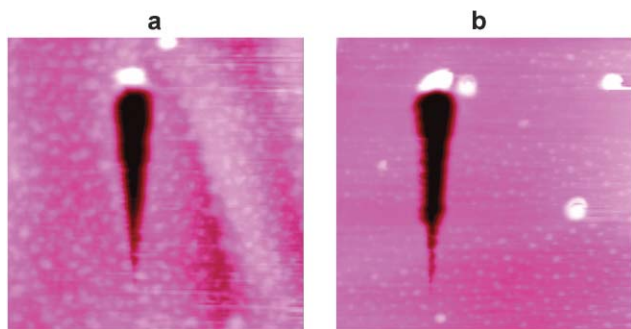
**Fig. 1** Stereoscopic view of the crystal packing of 2-benzylidenecyclopentanone (**1**) ( $P2_1/n$ )<sup>12</sup> on (001) showing severe 3D-interlocking (hydrogens omitted for clarity).

as detected by AFM scans with plane fit off) and scratched with a calibrated cube corner indenter or Berkovich indenter (the latter for Fig. 4) at the experimental settings indicated for best performance. There were no significant differences if the scratches were performed in 30 or 60 s. The three-sided pyramidal tips were aligned with the sharp edge in front unless indicated differently. The differentiation between piled-up debris and migrated material is quite easy: piled-up debris does not reveal a significant hardness and elasticity upon nanoindentation,<sup>7</sup> whereas anisotropically migrated material exhibits nanoindentation hardness and elasticity modulus values very close to the ones of the original material.

### 3. Crystals with three dimensionally interlocked packing

Molecular crystals exhibit small crystal energies, as there are only intermolecular forces between the distinctly shaped molecules or at best hydrogen bonds, which are comparatively weak. The crystal packing of anisotropic molecules may be three dimensionally (3D) interlocked so that the molecules are not able to migrate along easy paths within the crystal. That means: it is not possible to achieve thermal or photochemical solid-state reactivity in these cases, if the pressure induced by the intended chemical change cannot be released within the crystal lattice. Exceptions are shrinking upon reaction,<sup>8</sup> the presence of nearby holes in the crystal lattice<sup>9</sup> and topotactic conversions if the geometric change stays below 4% overall,<sup>10,11</sup> when no molecular migrations are required. 2-Benzylidenecyclopentanone (**1**) is an example of non-reactivity despite the very short distance between the double bonds ( $d = 4.10 \text{ \AA}$ ) due to its 3D-interlocking (Fig. 1).

Also scratching cannot induce molecular migrations in the cases of 3D-interlocking. The only choice is abrasion at all faces in all directions. This is shown in Fig. 2.



**Fig. 2** 15  $\mu\text{m}$  AFM topography (Z range 600 nm) of 3D-interlocked 2-benzylidenecyclopentanone (**1**) on (010) after ramp scratching with a cube corner indenter at 0–150  $\mu\text{N}$  in parallel (a) and orthogonal (b) directions with respect to the long crystal edge [010], showing only abrasion and some debris collection in front.

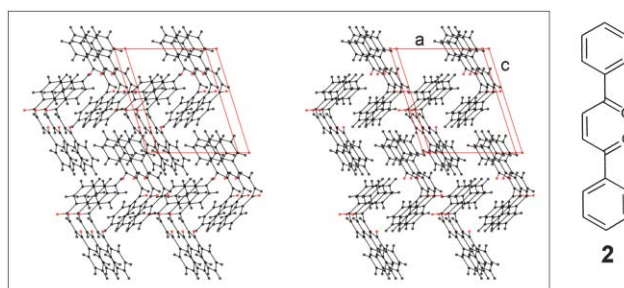
It should be noted that there might be limiting cases of layered structures with weak hydrogen bonds or counter ions between the layers that may permit molecular migrations and thus chemical reactivity.

Similarly, crystals of *cis*-1,2-dibenzoyl ethene (**2**) are photo-stable, because their packing is 3D-interlocked and molecules cannot migrate in the crystal (Fig. 3)

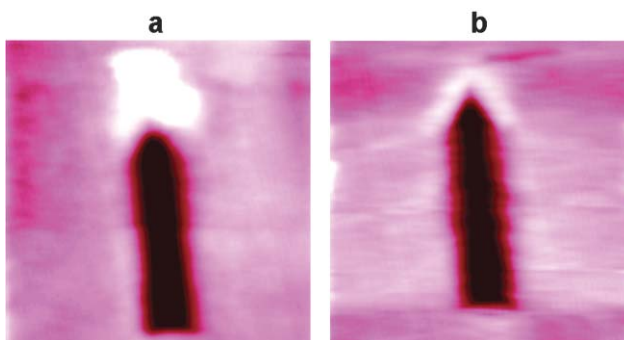
Again, the nanoscratching in all different directions does not lead to molecular migrations but only to abrasion and shift of debris in front. This is clearly shown in Fig. 4 for the orientations of  $0^\circ$  and  $90^\circ$  to the long crystal axis. The same is true for  $180^\circ$  and  $270^\circ$  (not shown here). The crystal anisotropy decides the ratio of materials loss and pile-up of debris in front of the advancing tip.

### 4. Skew layers

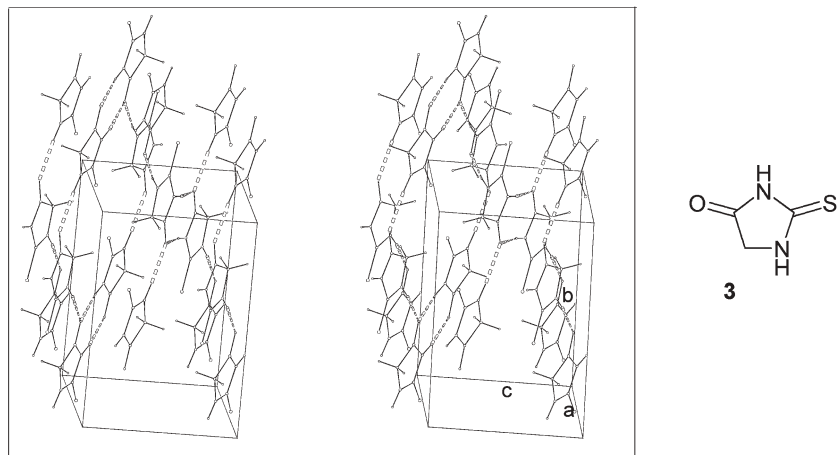
Many organic molecular crystals crystallize in layers and are thus highly anisotropic. Mono- or bi-layers may be internally connected by hydrogen bonds or only by van der Waals



**Fig. 3** Stereoscopic view of the crystal packing of *cis*-1,2-dibenzoyl ethene (**2**) ( $P2_1$ )<sup>13</sup> on (010) with (001) on top showing severe 3D-interlocking.



**Fig. 4** Nanoscratching with a Berkovich indenter at 200  $\mu\text{N}$  load of *cis*-1,2-dibenzoyl ethene (**2**) on (001); (a) at  $0^\circ$ , (b) at  $90^\circ$  to the long crystal axis [010], showing shift of debris in front (a) and almost exclusive abrasion with loss of the excavated material (b) but no molecular migration.



**Fig. 5** Stereoscopic view of the crystal packing on (110) of thiohydantoin (**3**) ( $P2_1/c$ )<sup>15</sup> showing skew monolayers with highlighted hydrogen bridging exclusively within the layers but not between them.

interactions. Thiohydantoin (**3**) is an almost planar heterocyclic compound. It contains many heteroatoms, is thus dipolar, and forms hydrogen bonds. Furthermore, it crystallizes in monolayer sheets that are  $66^\circ$  skew under the natural (110) face with cleavage planes between them (Fig. 5), because all hydrogen bonds are within the layers but not connecting them.<sup>7</sup> Such structural anisotropy must cause anisotropic nanoscratching and this should become visible at various orientations of the scratching direction. Previous work<sup>14</sup> showed the anisotropies with ramp scratches to rather high forces (up to 1 mN) and the same relationship between lateral and normal force as with much harder inorganic crystals. As expected, constant normal force nanoscratching leads also to molecular migrations in the proper directions even at lower load (Fig. 6).

Four different appearances are observed upon nanoscratching at different orthogonal directions in Fig. 6. Every angle has its own characteristics. At  $0^\circ$  (along the long crystal edge [001]) there is molecular migration to both sides and in front (a); the fissures indicate the direction of the cleavage planes (the more inclined fissure is exceptional and must derive from a crystal fault). At  $90^\circ$  molecules migrate only to the right hand side (b). Only abrasion is detected at  $180^\circ$  (c). At  $270^\circ$  molecules migrate only to the left hand side (d). The migrated materials have about the same hardness and elasticity as the initial crystal.<sup>7</sup> The unusual piling-up of material only at one side of the scratch (Fig. 6b, d) must be caused by the skew cleavage plane under the (110)-face. The geometric arrangement in that experiment is such that the cleavage planes are open to the right side and blocked to the left side and *vice versa* as the scratching tip advances down in (b) and (d), respectively. The sketch in Fig. 7 visualizes this situation more clearly. At  $90^\circ$  nanoscratching molecules migrate upward in the gaps to the right, at  $270^\circ$  to the left.

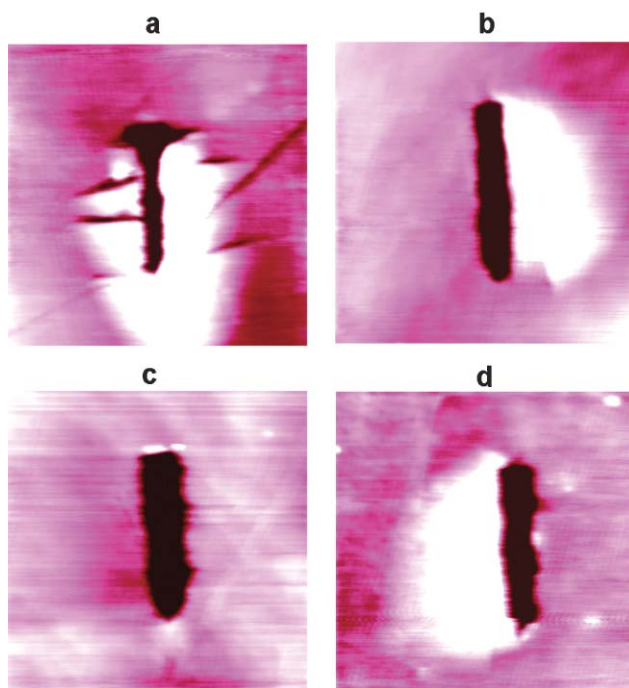
Furthermore, it is easily comprehended that the migration to both sides and in front in Fig. 6a occurs at the  $0^\circ$  scratching, as the cleavage planes are open for release of molecules under pressure. It is also clear that there is formation of orthogonal fissures along the cleavage plane direction in that instance. Conversely, scratching in Fig. 6c at  $180^\circ$  is against the skew monolayers and this must give abrasion.<sup>7</sup> As there are multiple hydrogen bonds between the thiohydantoin molecules within a layer it cannot be claimed that only single molecules migrate. Rather it appears likely that small molecular aggregates such as almost planar hexamers that are present in the crystal structure as cyclic entities (Fig. 5) may be small enough for the migration. Anisotropic effects are most frequently encountered with organic molecular crystals if these contain cleavage planes. The orientation of the cleavage planes can also be demonstrated

with a micrograph of a larger crystal (long edge 4.5 mm) in Fig. 8.

The importance of the unprecedented molecular migrations within the crystals just by application of mechanical stress requires verification also with further examples. It is of interest if skew layers of hydrocarbon crystals without hydrogen bonding behave similarly. Anthracene (**4**) is a planar hydrocarbon. Fig. 9 shows the skew layers of anthracene (**4**) under its natural (110) face in its prism type crystals.

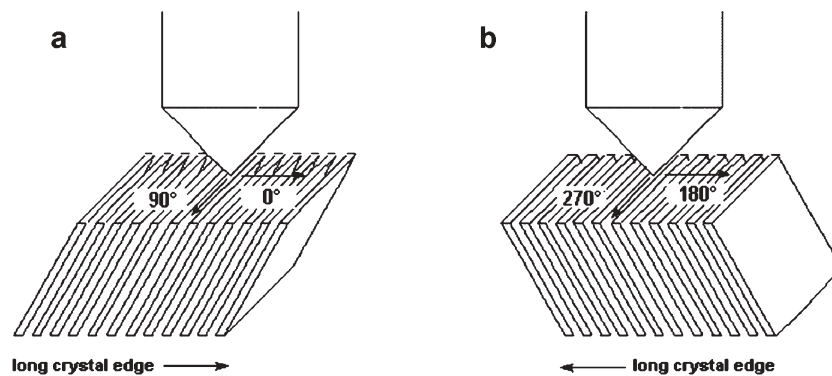
Molecular migrations similar to the ones of thiohydantoin do indeed occur with **4** on (110) as shown in Fig. 10.

The volumes of migrated molecules (a, b, c) and ditch, as measured with AFM, correspond closely as do hardness and elasticity values of migrated material and original (110) surface ( $H$  0.30 GPa,  $E_r$  11.3 GPa at 250  $\mu\text{N}$ ; standard technique). Conversely, the debris in front of the scratch in (d) are loosely piled up. Thus, a similar analysis as with thiohydantoin (**3**)

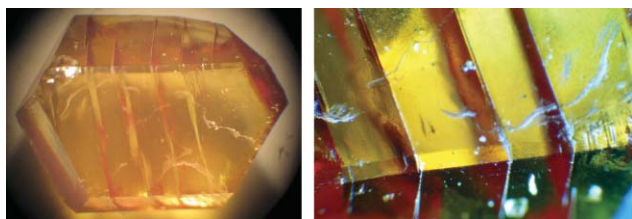


**Fig. 6** AFM topographies (10  $\mu\text{m}$ , Z range 200 nm) of 5  $\mu\text{m}$  nano-scratches on the (110) face of thiohydantoin (**3**) with a cube corner at 250  $\mu\text{N}$  (for a, b, and d), or 200  $\mu\text{N}$  (for c) in 60 s; (a):  $0^\circ$ , (b):  $90^\circ$ , (c):  $180^\circ$ , (d):  $270^\circ$  orientation (by clockwise turning of the crystal) with respect to the long crystal edge [001], which is cut by the skew cleavage planes between the monolayers at an angle of  $90^\circ + 16^\circ$  according to the crystal packing.





**Fig. 7** Scheme of the geometric conditions for nanoscratching by the vertical pyramidal tip under load to a surface with skew cleavage planes ending there [for example the (110) face of thiohydantoin (**3**)]; (a) skew sheets/cleavage gaps sloping to the right; (b) same crystal model turned by 180° with sloping to the left, the various scratch directions are indicated; the different directions are obtained by turning the crystal under the fixed route before indentation and advancing of the tip.



**Fig. 8** Microscopic image of an unusually large crystal of thiohydantoin (**3**) with (110) in front (left, 20 × microscopic enlargement); detail with illumination from the side (right, 32 × microscopic enlargement) showing cleavages along (10–2) that are skew (66°) under the face and cut the long edge [001] at an angle of 106° in accord with the crystal structure.

holds true. The single organic molecules of **4** experience only van der Waals interactions and are therefore not efficiently aggregated while they migrate.

## 5. Flat layers

Scratching on flat layers is different from chemical reactions, which show molecular migrations with upward penetration and forming volcanoes in those cases.<sup>1,2</sup> Pyramidal tips efficiently obstruct upward migrations upon scratching. The only choice is abrasion or shift of whole layer segments. This can be experimentally verified. For example, the crystal packing on the cleaved (10–2) surface (*cf.* Fig. 8) of thiohydantoin (**3**) (Fig. 11) is totally different from Fig. 5. It has the monolayers parallel to that surface. There is no possibility for molecular migrations upon scratching in any direction on that surface but only abrasion and some shifting of fragments of the anisotropic monolayers in front of the tip that may depend on the direction.

The expectations of Fig. 11 have been experimentally verified. This is shown in Fig. 12a, b. The ramp scratches were at right angles (a) or along the long crystal edge (b) on the (10–2) cleavage face of thiohydantoin (**3**). The slight frontal

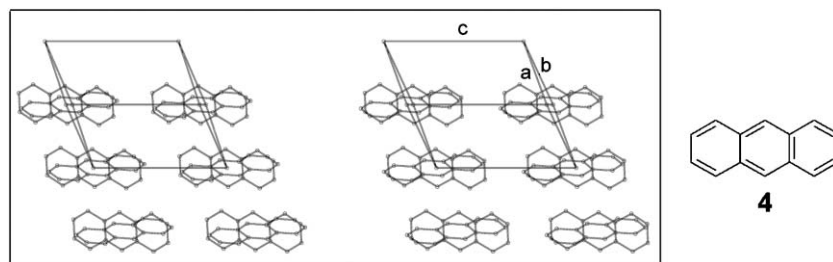
pileup in Fig. 12a is loose debris as detected by indentation, which does not reveal significant hardness values.<sup>7</sup>

Again it is important to also study the behavior of flat layers of a hydrocarbon. Actually, in the more easily obtained scales of anthracene (**4**) the (001) face is very prominent. The molecules are inclined under that face but form monolayers that are separated by the parallel cleavage planes. Fig. 13 depicts views from two different directions. The skew arrangement of the single molecules within the layer array does not alter the nanoscratching on these layers. Molecular migrations by nanoscratching are impossible under that face. Therefore, only abrasion and some apparent shift of layers in front of the indenter occur in any direction as shown for two in Fig. 14. The looseness of the debris in front was secured by indentation, which did not give reasonable hardness or elasticity values, while these values on the (001) face are measured as  $H = 0.35$  GPa and  $E_r = 14.8$  GPa (150 μN) according to the standard technique.

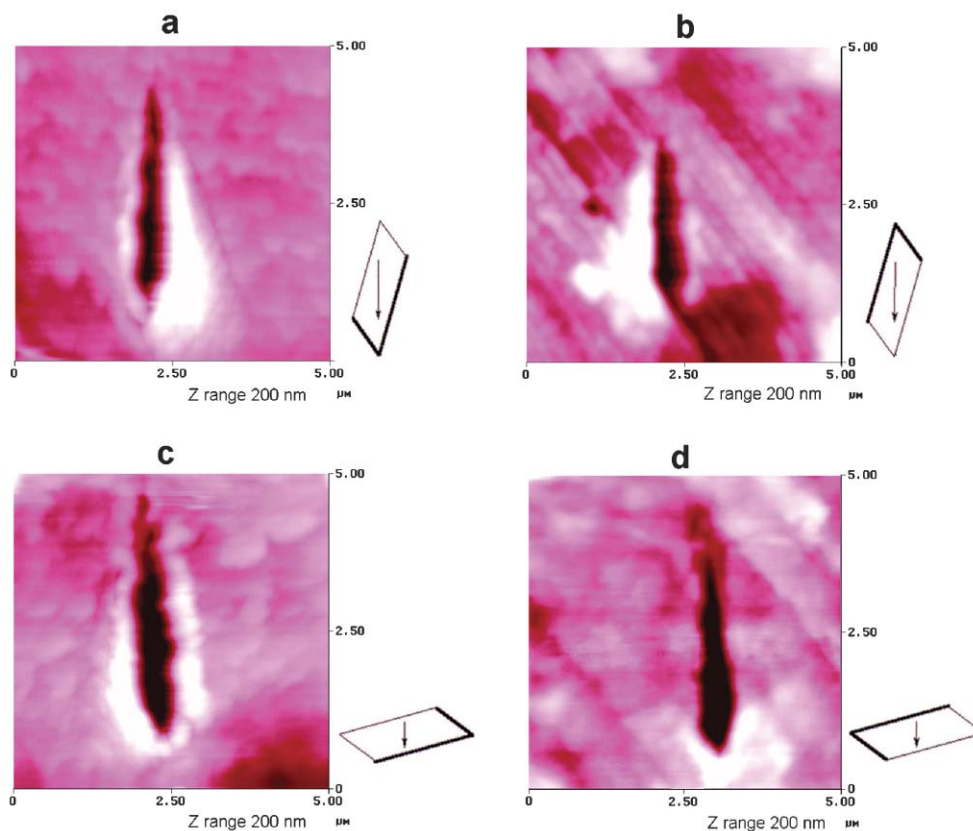
## 6. Vertical layers

A different situation is encountered if crystals with vertical layers and cleavage planes are scratched. Thiourea crystals (**5**) on (100) offer the possibility to study planar hydrogen bonded molecules with vertical cleavage plane arrangement. The crystal packing in Fig. 15 shows slightly zigzagged monolayer sheets. Most interesting are scratches along or across the direction of the sheets. Fig. 16a shows molecular migrations to both sides and in front if the scratching is performed in the [010]-direction, which is crossing the layers. Conversely, scratching along the sheets in the [001]-direction in Fig. 16b shifts the vertical layers in front of the tip. This is an excellent example for a slip mechanism in nanoscratching.

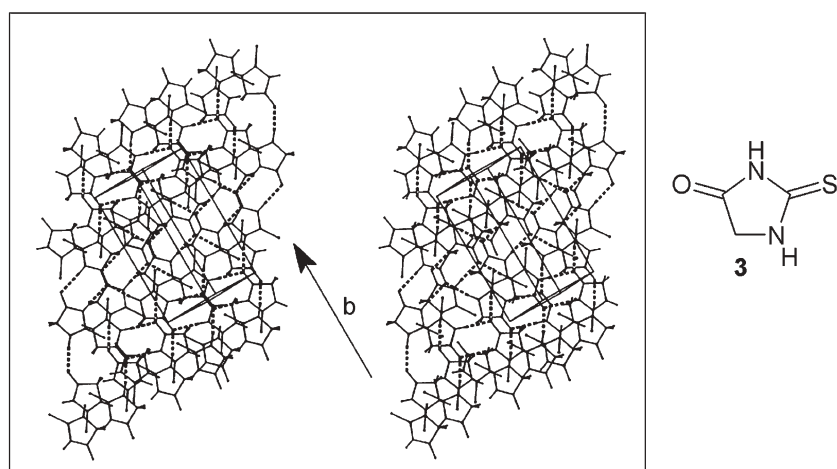
A still different situation is encountered if a crystal exhibits vertical monolayers of bulky three-dimensional molecules without hydrogen bonds such as in the case of tetraphenyl-ethene (**6**). The most prominent face is (10–1) and the plane of the layers is (010) extended along the large crystal axes. The



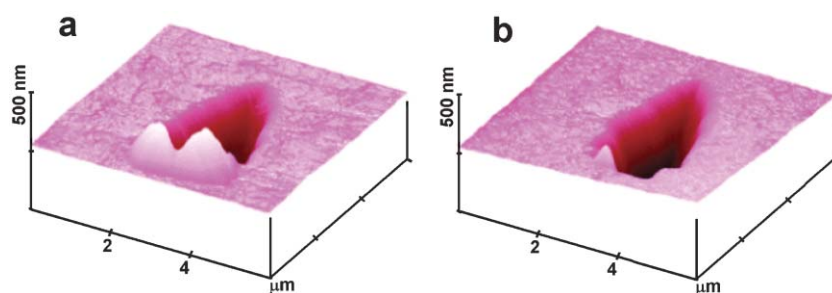
**Fig. 9** Stereoscopic view of the crystal packing of anthracene (**4**) ( $P2_1/a$ )<sup>16</sup> along  $[-1\ 1\ 0]$  with (110) on top, showing the skew cleavage plane under the surface (hydrogens omitted for clarity).



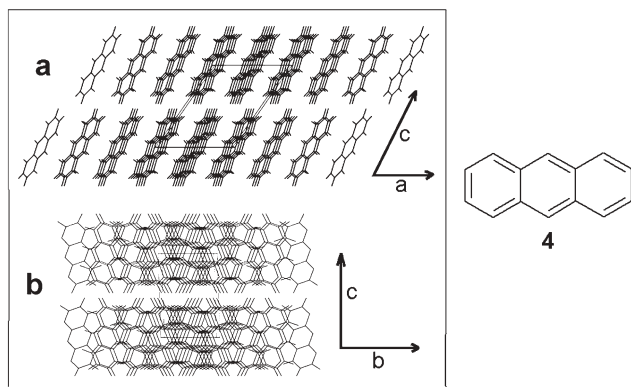
**Fig. 10** Nanoscratching on (110) of anthracene (**4**) showing anisotropic molecular migrations (a, b, c) and abrasion with some debris in front (d), depending on the direction due to skew cleavage planes.



**Fig. 11** Stereoscopic representation of the crystal packing of thiohydantoin (**3**) ( $P2_1/c$ )<sup>15</sup> under the (10–2) face, which is in front, showing the infinitely hydrogen bonded flat monolayers with the flat cleavage planes between them.



**Fig. 12** AFM topographies of ramp scratches on (10–2) of thiohydantoin (**3**) at right angles (a) or along (b) the longest crystal edge [001] with a cube corner at forces from 0–1000  $\mu\text{N}$ .



**Fig. 13** Crystal packing of anthracene (**4**) ( $P2_1/a$ )<sup>16</sup> with (001) on top: (a) along [010], (b) along [100]; both images are turned around  $y$  by  $1^\circ$  showing inclined monolayers that are parallel under the surface.

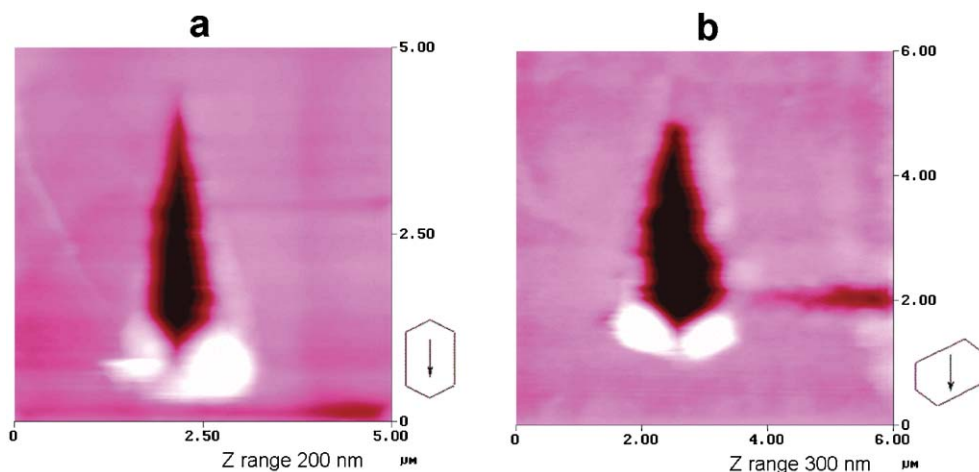
vertical cleavage planes separating the monolayers are rather poor for migrations of molecules as there is apparent interlocking (Fig. 17).

Due to the considerable interlocking it is not possible to shift material in front of the tip when scratching along the layer direction ( $0^\circ$ , Fig. 18c). Also the  $90^\circ$  scratching at right angles to the plane direction does not push the molecules in one of the cleavage plane directions for upward migration and only abrasion is observed (Fig. 18d). However, if the crystal is turned under the scratch direction as in Figs. 18a, b molecular migrations only to the right or only to the left side are observed in considerable amounts in addition to some abrasion. Clearly,

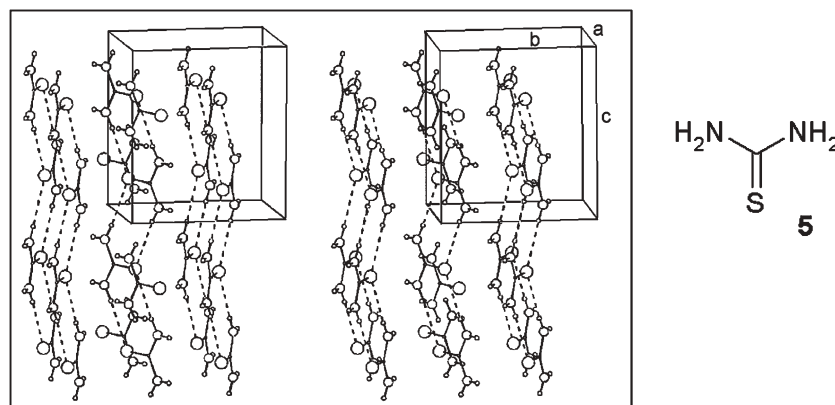
the molecules must get both a push from their sides to leave the layer and then also a push in the direction of the open cleavage plane for the anisotropic upward migration as observed. The efficiency of these pushes in competition with the abrasion is only partly successful and the anisotropic molecular migrations occur in the ranges of  $30^\circ$ – $80^\circ$  (right),  $100^\circ$ – $150^\circ$  (left),  $210^\circ$ – $260^\circ$  (right) and  $280^\circ$ – $330^\circ$  (left). The asymmetry in the ranges means that the push to the molecule from the side (out of the layer) is more important than the push for guiding along the cleavage plane direction and that there are wide ranges without migration.

## 7. Crystals with polar axes

The high sensitivity of the new analysis technique for the elucidation of mechanical properties of crystals allows differentiation between the back and forward direction in the case of a polar axis. For example, the occurrence of a polar axis in the crystals of ninhydrin (**7**) [cleavage plane (100), H-bridging within double layers] must lead to different nano-scratching responses in the forward and back directions. Fig. 19 shows the differences in both vertical directions. Clearly, the marked differences in Fig. 20a, b and c, d derive from the polar packing as tip shape effects have been excluded by exploring either edge- or side-in-front scratching with a cube corner for both directions. It appears that the scratching from top to bottom (in the orientation of Fig. 19) makes the flatter lying molecules penetrate through the steeper ones that are thus pushed aside (Fig. 20b, d) in competition with abrasion. On the other hand, scratching in an upward direction (in the

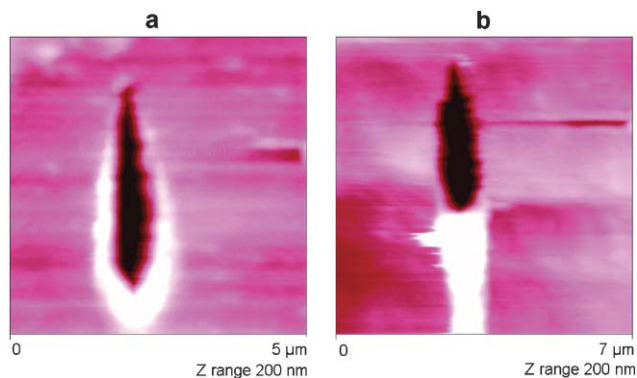


**Fig. 14** Nanoscratching (0–150  $\mu\text{N}$ ) on the cleavage plane of anthracene (001) that separates monolayers, showing complete abrasion and loose pileup at the end of the scratch both in the scratch directions (a) and (b).



**Fig. 15** Crystal packing of thiourea (**5**) on (100) ( $Pbnm$ )<sup>17</sup> (image rotated by  $10^\circ$  around  $x$  and  $y$  for a better view) showing vertical monolayer sheets separated by cleavage planes under (100) and (001).



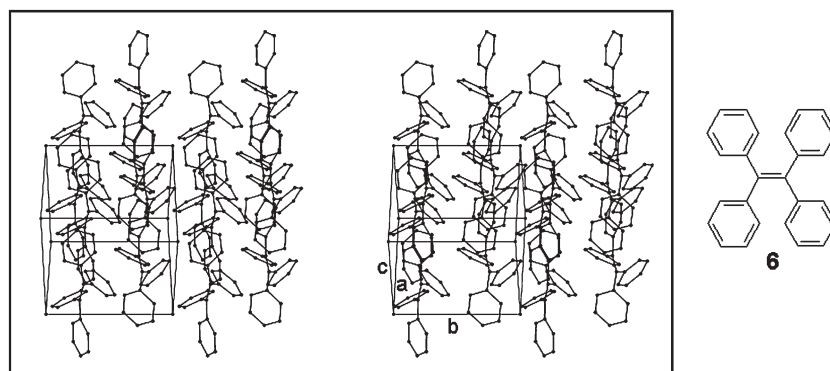


**Fig. 16** AFM topographies on (100) of thiourea (**5**) after cube corner scratching (4  $\mu\text{m}$ ); (a) along [010], (b) along [001] at 0–150  $\mu\text{N}$  load showing (a) molecular migrations to both sides and in front, (b) material shift in front of the indenter.

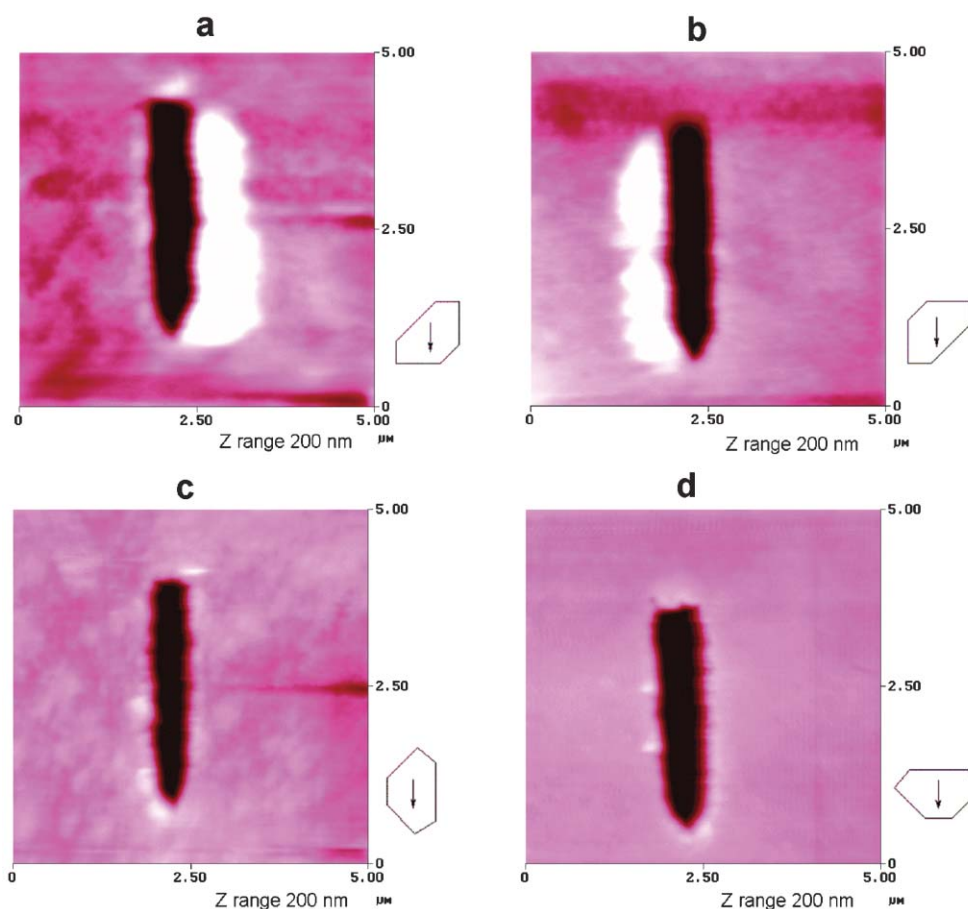
orientation of Fig. 19) finds the flatter lying molecules connected by hydrogen bonding with the steeper ones in the next row and they have to go with the OH groups in front. This process would appear very unfavorable and indeed complete abrasion is observed (Fig. 20a, c). Thus very detailed analyses are possible with the powerful nanoscratching tool.

## 8. Conclusions

There are important relations between solid-state chemical reactivity of molecular crystals and nanoscratching results. In solid-state chemistry the local pressure is produced by change of the molecular shape in the bulk of the crystal. Such pressure must be released from the start by molecular migration along cleavage planes or channels or to nearby voids of the crystal. Schmidt's topochemistry principle did not take into account that necessity. Rather Schmidt postulated minimal atomic and

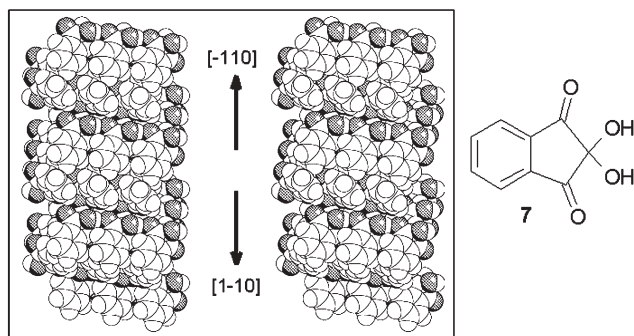


**Fig. 17** Stereoscopic representation of the crystal packing of tetraphenylethene (**6**) ( $P2_1$ )<sup>18</sup> on the natural (10–1) face showing poor cleavage planes between monolayers, which extend on (010) despite the bulky molecular shape (hydrogens are omitted for clarity).

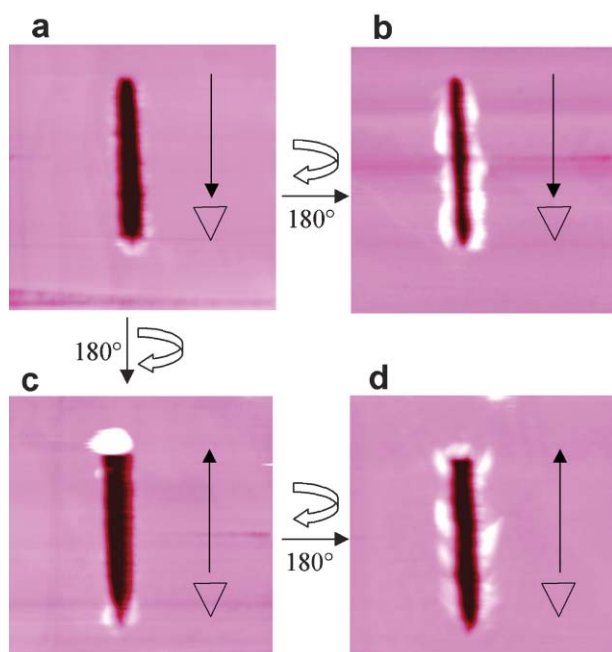


**Fig. 18** Nanoscratches on (10–1) of tetraphenylethene (**6**) in various directions showing complete abrasion in (c) and (d) and molecular migration to the right in (a) or to the left in (b), due to vertical cleavage plane and bulkiness of the molecules.





**Fig. 19** Stereoscopic space filling crystal face model of ninhydrin (7) ( $P2_1$ )<sup>19</sup> with (110) in front, showing the polar character in the vertical  $[1-10]$  and  $[-110]$  directions; oxygen atoms are highlighted.



**Fig. 20** Cube corner nanoscratching on (110) of ninhydrin (7) along the polar  $[1-10]$  axis: (a), (b) edge in front forward and reverse after a turn of the crystal; (c), (d) side in front forward and reverse after the proper turns of the crystal as indicated.

molecular movements,<sup>20</sup> and succeeded in finding immediate inclusion of his undue hypothesis in textbooks. A recent review tries to appreciate molecular migrations in crystals but unduly excludes them for solid-state cycloadditions,<sup>5</sup> despite the experimental evidence securing their occurrence also for these reaction types.<sup>1,2,10</sup> Thus, the enthusiasm expressed in ref. 5 lacks appreciation of the reason for long-range anisotropic migrations.<sup>1,2,10</sup> The cited authors<sup>5</sup> and all the others who still claim “topochemical behavior” do not acknowledge molecular migrations for their reactions and definitely assume “minimal atomic and molecular movements”. This implies that the experimental evidence by supermicroscopy<sup>1,2,10</sup> and GID<sup>6</sup> is largely not acknowledged. It was therefore of highest importance to complement the vast evidence for the experimental solid-state mechanism (phase rebuilding, phase transformation, crystal disintegration)<sup>1,2,6,10</sup> by purely mechanical induction of anisotropic molecular migrations. As expected, the complete correspondence with the crystal packing (not just distance and relative orientation) is also demonstrated with the action of mechanical pressure by pyramidal tips in nanoscratching experiments. Again the long-range anisotropic molecular migrations (without chemical transformation) strictly choose

cleavage planes. The various cases for the orientation of cleavage planes have been elucidated and discussed with the mechanical effects at polar molecules (3, 5, and 7, all with intralayer hydrogen bonds) and hydrocarbons (4 and 6). Both mono- and bi-layered structures have been selected. Even effects of interlocking of three-dimensional molecules in the cleavage planes and crystals with polar axis correspond with the expectations. The mechanical treatment of the molecular crystals is less complicated than the chemical reactions that imply change in molecular shape.

Due to the shape of the horizontally advancing indented pyramidal tip there is a difference in chemical reaction and nanoscratching with crystals on faces with flat lying layers. Chemically, these give volcano-like features by upward migrations with penetration of the mono- (easy) or bi-layers (more difficult),<sup>1,2,10</sup> however, molecular migrations in that direction are (of course) impeded in the mechanical experiment. Molecular migrations in nanoscratching are differentiated from piling up of debris by hardness and elasticity measurements with local nanoindentation. Piled-up debris does not provide significant values (they are easily removed upon repeated AFM scans in most cases), while migrated material gives hardness and elasticity modulus values closely similar to the original material on the same surface (and it withstands repeated AFM scans).

There is a concern with regard to single molecule or small molecular aggregate migrations. The bending of the cleavage planes by the pressure of the nanoindenter tip does not allow for migration of larger aggregates unless cleavage planes are horizontal or unless vertical cleavage planes stay precisely in the direction of the scratching. It is therefore very unlikely that the hydrocarbons 4 and 6 migrate as aggregates, but the multiply intralayer hydrogen bonded flat molecules might migrate as small aggregates [for example thiohydantoin (3) perhaps as cyclic hexamers; Fig. 5].

The results allow for very detailed analyses of the mechanical properties of molecular crystals under mechanical stress at the nanoscale and open up a new field for investigation and use of anisotropic crystal packing also for nanoscopic modeling of surfaces by nanoscratching.

The experimental proof of mechanically induced anisotropic molecular migrations supports the experimentally secured phase rebuilding mechanism in molecular solid-state chemistry.<sup>1-3,10</sup> If these far-reaching migrations occur, one can safely predict that the same crystals will be reactive in suitable gas-solid, solid-solid or internal thermal or photochemical solid-state reactions, depending on the chemical functionality. If molecules cannot migrate there will be no solid-state reactivity (rare special cases have been specified and listed in Section 3). These firm predictions relate to the phase rebuilding stage (relief of internal pressure by anisotropic migration). Any difficulties with phase transformation or crystal disintegration can be engineered if they occur. The possibility for mechanically or chemically induced molecular migrations is safely judged from the hitherto neglected molecular crystal packing (contemporary “topochemistry” still neglects the packing<sup>5,20</sup>). This has been demonstrated with crystals of 1–7 in this work: 1 and 2 do not give mechanically induced anisotropic migration and are not solid-state reactive. Conversely, crystals of 3–7 exhibit both anisotropic migration by mechanical stress and solid-state chemical reactivity with formation of characteristic surface features.<sup>1-3</sup> For example, crystals of 3 on (110) react with gaseous methylamine giving ring opening. By doing so they form submicroscopic ridges and valleys along the cleavage direction with different slopes to both sides (26° and 41°).<sup>21</sup> The nanoscratching result (Fig. 6b, d and Fig. 7a, b) along the cleavage direction with molecular migration either to the right or to the left is completely compatible. The reasons for the anisotropic migrations are internal pressure, as applied either chemically or mechanically.

Finally, it can also be concluded that all of the reactive crystals in ref. 3 with about 1000 successful reactions could be used for surface modeling by nanoscratching at the appropriate faces.

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