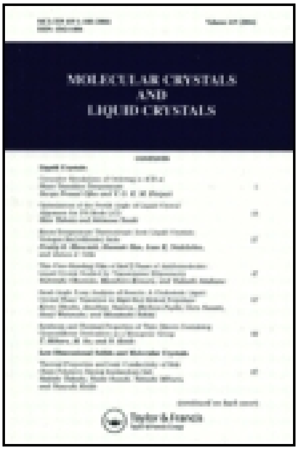

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Atomic Force Microscopy on Photoreactive Organic Solids: Nanostructures

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ATOMIC FORCE MICROSCOPY ON PHOTOREACTIVE ORGANIC SOLIDS: NANOSTRUCTURES

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Abstract The formation of regular nanostructures by photolysis of chemically reactive crystals is investigated by atomic force microscopy (AFM) in relation to known crystal structures where available and with respect to different crystal faces. Thus, upon photodimerization of 2,5-dibenzylidenecyclopentanone **1** three products form stereoselectively though with far-reaching molecular transports along gliding planes giving both nanostructured trenches and volcanoes. [4+4]-Photodimerization of 9-chloroanthracene **5** provides exceptionally regular and stable floes and volcanoes on different faces, respectively, indicating the influence of bulk crystal structure to the formation of the nanostructures. The photoelimination of nitrogen from crystalline 3,6-diphenyltetrazine **7** yields nanostructures in the form of very regularly shaped craters, even though the product benzonitrile is a liquid.

Keywords: atomic force microscopy, AFM, nanostructures, bulk structure, crystal face, 2,5-dibenzylidenecyclopentanone, 9-chloro-anthracene, 3,6-diphenyltetrazine, cycloaddition, elimination, photochemistry

INTRODUCTION

Atomic force microscopy (AFM) is a versatile tool for the study of individual atoms and molecules,[1] of chemical reactions of solids,[2] and of nanostructures.[3] The results on non-conducting surfaces cannot be obtained by any other technic with similar resolution in space. There are no problems with depth of focus, and therefore even applications of AFM on the scale of 125 μ and more are of high interest.

Nanostructures are an active field of research, e.g.

for information storage devices. Thus, AFM and more frequently STM have been used to create nanostructures by application of increased force or bias voltage.[3] On the other hand, it turned out now, that photoreactions of solids may create very well organized nanostructures on solid surfaces. This was unforeseen and could only be investigated by AFM. There are unprecedented far-reaching transport phenomena which are connected to necessary solid phase transformations in the surface region, where the light is absorbed. These are dictated by the bulk structure of organic solids (crystals in most cases) and the difference in molecular shapes of the starting and product molecules. The nanostructures are easily depicted by perspective computer drawings, the size and shape of the features accurately measured. At present there are eight very distinct phase transformation mechanisms known already. In this paper we describe the formation of particularly regular nanostructures which form upon photoreaction of crystals and whose appearance is primarily dictated by the bulk crystal structure.

EXPERIMENTAL

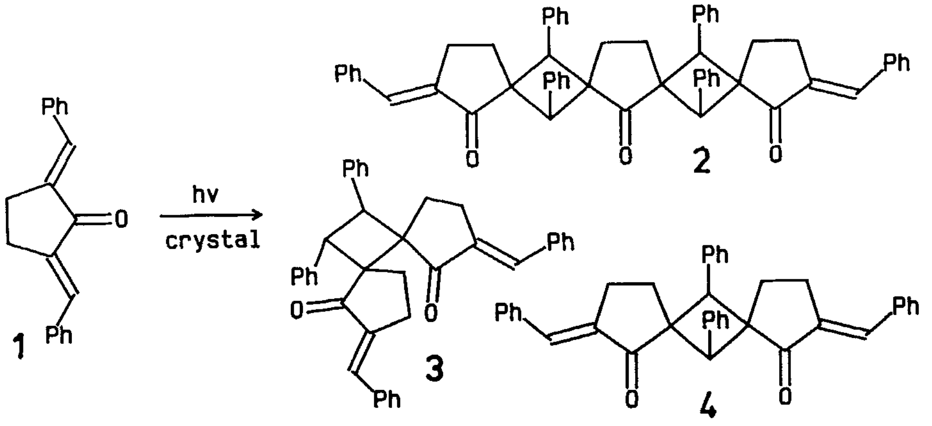
A Digital Instruments NanoScope II version 5 was used with commercial Si_3N_4 cantilevers and tips. The forces were set to 10 - 30 nN attractive throughout.[2] For colour imaging NanoScope III software was used in mixed mode by adding some colour coding for height to illuminated perspective pictures, for best appearance. Those pictures were printed on a Mitsubishi CP-200 E (H) videoprinter though in parallel mode. The large colour transparencies obtained were photographed for glossy black and white prints. Crystal packing drawings were generated from published X-ray data by using SCHAKAL 92 (AIX-UNIX version, E. Keller, Universitaet Freiburg) at an IBM RS 6000 32 H workstation.

Single crystals were obtained as described[2,4c] (**7** from benzene) and irradiated on the AFM stage directly from 5 cm distance with a Hanau 150 W high pressure mercury lamp through a water-cooled Solidex filter.

RESULTS AND DISCUSSION

The recently reported[2] formation of nanostructures along mono-, bi-, tri-, and tetramolecular steps via photolysis of anthracene (chainy hills up to 50 nm high) does not lead to very regular surface features, mainly because the initial steps are not uniformly arranged. Therefore this will be a matter of nanostructuring via ploughing molecular furrows at enhanced force with the AFM on flat surfaces of anthracene, followed by irradiation, if regular structures are desired. Likewise, the appearance of the floes from photodimerization of 9-cyanoanthracene depends strongly on the accidental number of steps which may be 50 - 200 nm high. Thus, for any practical applications which come to mind, one would prefer more uniformly generated nanostructures which may be formed on flat or moderately rough surfaces. Such possibilities have been recently described with gas/solid-reactions,[4,5] and they occur also with photoreactions.

2,5-Dibenzylidenecyclopentanone **1** crystallizes in the chiral space group $C222_1$[6] and provides three products, **2**, **3**, **4**, upon photolysis, one of them being asymmetric. Interestingly, the products form in an X-ray amorphous form,[6] but nevertheless there are beautiful nanostructures formed on the initial (001) surface (Figure 1). These consist of almost parallel furrows at 3 to 5 µ distance and of volcanoes on the heights in between. The mean height of the volcanoes is 6 - 7 nm, the valleys are 40 - 70 nm deep, the slopes 15 to 20° steep. Clearly two of the basic phase transformation mechanisms occur at the same time here. There are no grooves around the volcanoes (amorphous solid) and the structures are very stable.[4c] Thus, doubling the irradiation time keeps the valleys and decreases the volcanoes only slightly. The almost parallel furrows cut the a-axis at right angles and this is clearly predetermined by



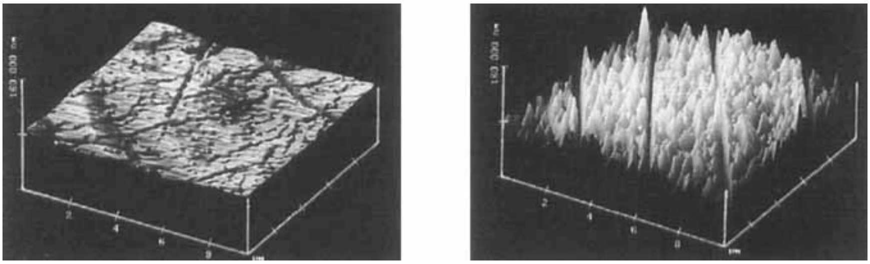


FIGURE 1 AFM surfaces (001) of 1 before and after 7 min irradiation

the original crystal structure which shows hardly interlocked layers parallel to the b-axis. Thus, the furrows form along these gliding planes.

The nanostructures formed prove, that far-reaching molecular transports occur upon the photodimerizations and it is of high interest that those proceed nevertheless stereo- and regioselectively. It has been repeatedly shown that the cyclotrimer **2**, the head-to-head-anti-dimer **3** and the head-to-tail-syn-dimer **4** form,[4c, 6, 8] but not the known head-to-tail-anti-dimer.[6] The possibility that **3** might be formed enantioselectively from enantiomorphous crystals of **1** in terms of (absolute) asymmetric synthesis[7] is being studied.

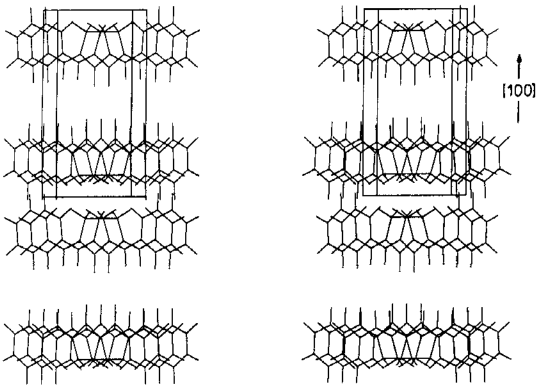
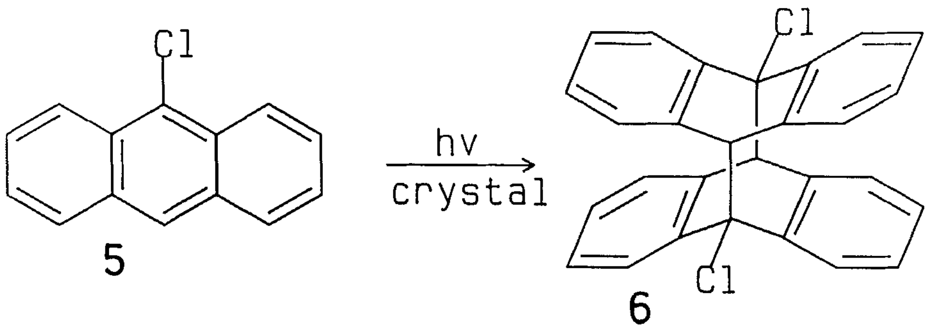


FIGURE 2 Stereoscopic view of the molecular packing of **1** on (001) ($C222_1$, a = 11.803, b = 5.698, c = 20.872)[6]

The stereoselectivities and the oriented AFM-features show, that the bulk crystal structure (Figure 2) controls the events of transport and phase rebuilding. Thus, for the formations of the volcanoes, the molecules will have to use the free space between the layers for making their initial partial turns for dimerization into the three different products (**2** : 26 %, **3** : 8 %, **4** : 38 %).[8] Then they stand up and slide upward for several nm in [001]-direction (initially they cut the a/b-plane at an angle of 40°) while forming valcanoes. There is so much restriction by the crystal lattice that stereospecifity is retained in the regioisomers **3** and **4** despite the long-range transports.

9-Chloroanthracene **5** photodimerizes to give the head-to-tail-[4+4]-dimer **6** in the solid state as had been predicted by topochemical considerations.[9] It turns out, that again unexpectedly, distinct nanostructures are formed and that this involves far-reaching well-directed molecular transports which are dictated undoubtedly by the bulk crystal structure. Unfortunately, the crystal structure of **5** is not known yet. Two modifications have been described ($P2_12_12_1$ and $P2_1/c$).[9] Our crystals (laths from $ClCH_2CH_2Cl$ or hexane) were about 3 to 4 times as broad as they were high.



Both the main- and the side-face were investigated separately. If the largest face, which is rather smooth on crystals from hexane, is irradiated, regular floes are obtained. Those stand almost perpendicular on it and extend almost parallel to each other with heights of up to 100 nm and slope angles of 15 to 35° (Fig.3, top). If on the other

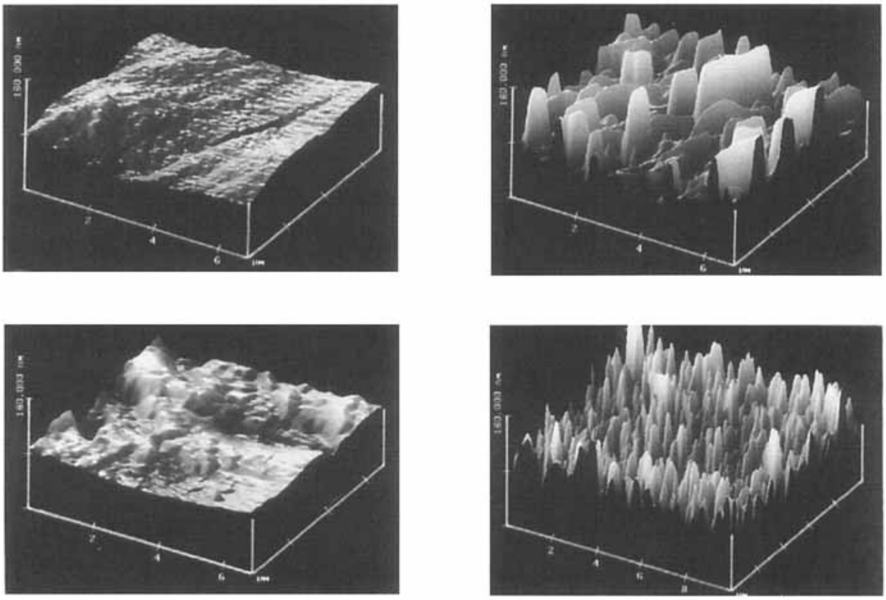


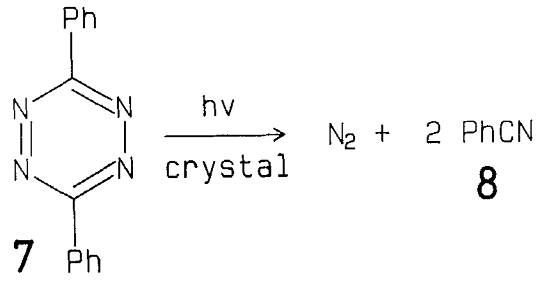
FIGURE 3 AFM surfaces of 5; morphologically dominant face (top) and long side-face (bottom), both before and after 15 min irradiation

hand the long side-face is irradiated, very uniform volcanoes form on a previously rather rough surface (Figure 3, bottom). These beautiful nanostructures are about 90 nm high, their slope angle varies from 15 to 25°. At shorter irradiation times the features are well developed too, though smaller. Thus, the volcanoes will be 45 nm high (slope angle 8 - 15°) and the floes are more uniform in height (55 nm, slope angle 15 - 30°) if the irradiations of the respective surfaces are stopped after 1 min or 5 min.

A detailed molecular interpretation must await the X-ray crystal structure determination. However, it is apparent from the different nanostructures on different crystal faces, that the packing of the molecules in the bulk of the crystal is decisive. For practical applications it appears important, that both types of nanostructures stick tightly to the original crystal and are very stable even against light. This should facilitate all uses in nanotechnology.

Cinnamic acid (α- and ß-modification) has been described to provide nanostructures (craters, volcanoes, trenches, flat covers, floes).[2] However, those appear not stable enough for nanotechnical applications because they suffer from collapsing upon further irradiation and from thermal phase transformations. Even the layered plates of 100 nm thickness[2] will not easily be suitable, because they are moisture sensitive and only loosely bound to the original crystal surface.

3,6-Diphenyltetrazine **7** yields nitrogen and benzonitrile **8** upon photolysis of its crystals. Even though the product **8** is a liquid, there are no signs for liquid material[4b] on the irradiated surface (Figure 4). Stable nanostructures are formed with the shape of round craters which are up to 16 nm deep (slope angle 6°). Apparently mixed crystals containing **7** and **8** form and keep the surface solid at this point of conversion. It may be argued that the craters will help in releasing the nitrogen which is formed inside the crystal, though still in the surface region where the light



7

8

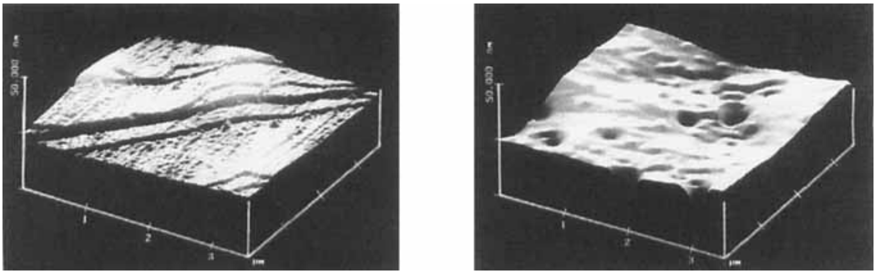


FIGURE 4 AFM surfaces (100) of **7** before (image rotated by 270°) and after 30 min irradiation

is absorbed. A precise molecular explanation appears difficult in this situation. However the molecular packing on (100) as depicted from the X-ray data[10] suggests convincingly, why **7** forms its terraces (Figure 4) so easily. The molecules cut the (100) face at an angle of 54° and the horizontal layers of tilted molecules interlock slightly (1 Å on both sides). The effective height of the layers is 5.4 Å. Thus, the steps in Figure 4 (left), which are 1 to 4 nm high consist of 2 to 8 molecular layers. The zigzag framework of inclined molecules on (100) of Figure 5 is indicative for the formation of round craters, as the product molecules **8** are shorter and as the effects of shrinking[2,4b] will be faster close to the surface than in the deeper layers. The craters of Figure 5 differ considerably from tip-generated holes with their flat bottoms.[4b]

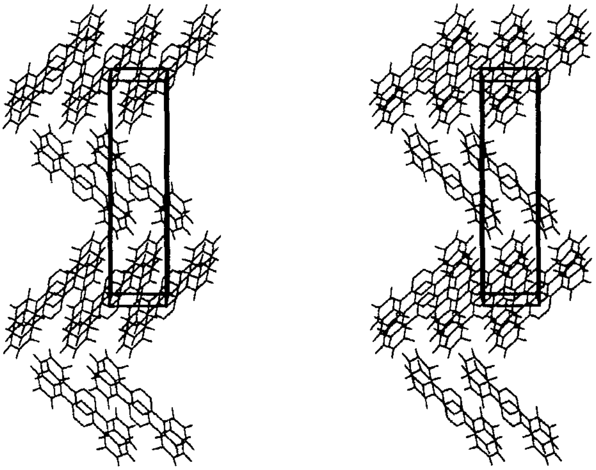


FIGURE 5 Stereoscopic view of the molecular packing of 7 on (100) ($P2_1/c$, a = 5.415, b = 5.183, c = 20.603 Å, ß = 101.50°)[10]

CONCLUSIONS

The nanostructures of this paper are generated by a new and unforeseen technic, which uses organic crystal structure properties as they influence the phase transformations in solid state photoreactions. Previously, the topochemical principle assumed "reaction cavities" in the bulk of the crystal for the chemical transformation to occur. Thus, any change in the surface region, where the light is absorbed in all preparatively useful applications, was generally not investigated.[2] Also, X-ray powder diagrams, by necessity at very late stages of transformation, seemed to indicate complete absence of orientation of crystalline photoproducts in topochemically allowed reactions.[11] Therefore any influence of bulk crystal structure on phase transformations and unforeseen far-reaching molecular transports on the nm-scale in the surface region was never thought of before. Only AFM is able to detect the new phenomena of well-directed molecular transports and to show the quality of the nanostructures formed. The foremost advantage of the photochemical technic in generating nanostructures is the large area that may be evenly covered with them at the same time, the only limitation being the size of the crystals. The heights of the nanostructures are clearly on the level of some to several molecules. Their shape has been worked out by larger magnification in z-direction in the perspective images as usual. There are ample means of influencing these shapes which will be of interest for nanotechnological applications.

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REFERENCES

1. J. Frommer, Angew. Chem. Int. Ed. Engl., 31, 1298 (1992).
2. a) G. Kaupp, Angew. Chem. Int. Ed. Engl., 31, 592; 595 (1992); b) GIT Fachz. Labor., 37, 284; 581 (1993).
3. A survey is given in the numerous papers which were presented at the STM 91 Conference in Interlaken, August 12 - 16, 1991 and which are collected in two proceedings volumes in Ultramicroscopy, 42 - 44 (1992) on 1717 pages; more recent results have been collected on the NANO II Conference at Moskow, August 2 - 6, 1993 and will be published in its proceedings.
4. a) G. Kaupp, J. Schmeyers, Angew. Chem. Int. Ed. Engl., in press; b) G. Kaupp, Mol. Cryst. Liq. Cryst., in press; c) G. Kaupp, J. Microscopy, in press.
5. G. Kaupp, Mol. Cryst. Liq. Cryst., 211, 1 (1992).
6. C. R. Theocharis, W. Jones, J. M. Thomas, M. Motevalli, and M. B. Hursthouse, J. C. S. Perkin Trans. II, 1984, 71; H. Frey, G. Behmann, and G. Kaupp, Chem. Ber., 120, 387 (1987).
7. G. Kaupp, M. Haak, Angew. Chem. Int. Ed. Engl., 32, 694 (1993).
8. G. Kaupp, I. Zimmermann, Angew. Chem. Int. Ed. Engl., 20, 1018 (1981). 2 replaces the previous spirooxepane.
9. E. Heller, G. M. J. Schmidt, Isr. J. Chem., 9, 449 (1971).
10. N. A. Ahmed, A. I. Kitaigorodsky, Acta Cryst., B28, 739 (1972).
11. M. D. Cohen, G. M. J. Schmidt, F. I. Sonntag, J. Chem. Soc., 1964, 2000; 2014.