Sergeants-and-soldiers principle in chiral columnar stacks of disc-shaped molecules with C3 symmetry

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A fragment of this sample was clamped to the sample holder with a small vice. The images were obtained under ultrahigh vacuum after an outgassing procedure of several hours at about 400 K with a combined atomic force/scanning tunneling microscope (Omicron Vakuumphysik GmbH). The AFM measurements were carried out in the contact mode immediately after transfer with single crystal silicon cantilevers (Nanosensors) and constant loading forces in the range 25 nN–50 nN[17].

Experimental Section

The Ba/SiO/C glass was made under argon atmosphere by melting a mixture of BaCO₃, SiO₂, and SiC in a high frequency furnace in a BN crucible placed in a carbon crucible to ensure inductive coupling. The melt was held at 1650°C for 30 min and after switching off the furnace cooled down in a strong stream of argon. The average cooling rate from maximum temperature to around 300°C was about 10 K s⁻¹. The cation ratio Ba:Si in the starting mixture was 37.63 with 3 atom% carbon in form of SiC.

At larger distances further peaks clearly indicate a medium-range order in the investigated glass. However, a definite assignment has yet to be done. The appearance of the 0.77 nm peak both in AFM and diffraction measurements is particularly remarkable, since this is a lattice constant of crystalline barium disilicate.

Two possible problems arise with the direct imaging of fracture surfaces of amorphous solids by atomic force microscopy, if one wants to resolve the bulk structure of glasses. First, the structures on the fracture surface might undergo a relaxation and therefore not correspond exactly to the position of the atoms in the bulk. Second, as the fracture will take place predominantly at the weaker bonds in the glass, these areas will dominate the images. However, since the relaxation in glasses with a highly developed network and low crystallization tendency will only result in displacements and not in re-constructions one can expect that the principles (repetition of structures, ring dimension, residues of translational symmetry) of medium- and long-range order will be preserved and reproduced in the image. In the case of the Ba/SiO/C glass the justification for this assumption is proved by the good agreement of the AFM results with data obtained from completely independent measurements.

Atomic force microscopy is superior to all other methods of studying solids without translational symmetry in that it allows direct imaging of the atomic structure and therefore can be used to develop a reliable model of the structure of glasses. In this paper the classical controversy concerning the structure of glass between the hypothesis of Zachariasen (“network hypothesis”) and that of Lebedew (“crystallite theory”) can be settled. The AFM images show unambiguously that the barium silicate glass consists of a tetrahedral network.

**Communications**

| Table I. Comparison of interatomic distances [nm] and their assignment extracted from pair distribution functions of the Ba/SiO/C glass with those in crystalline Ba₅Si₃O₁₂ and amorphous barium disilicate. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| From AFM of Ba/SiO/C glass | From electron diffraction of Ba/SiO/C glass[13] | From neutron and X-ray diffraction of Ba₅Si₃O₁₂[14] | In crystalline Ba₅Si₃O₁₂ | Assignment |
| – | 0.165 | 0.16 | 0.16 | Si–O |
| 0.21 | 0.27 | 0.27 | 0.26 | C–O (? ) |
| 0.27 | – | – | 0.27 | Ba–O |
| – | – | 0.30 | 0.35 | Si–Si |
| 0.34 | – | 0.34 | 0.4 | Ba–Si |
| 0.41 | 0.424 | 0.415 | 0.4 | Ba–O |
| 0.44 | – | 0.45 | 0.4 | Ba–Ba |
| 0.48 | 0.50 | 0.494 | 0.48 | mro |
| 0.57 | – | 0.53 | – | mro |
| 0.6 | – | – | 0.6 | mro |
| 0.68 | – | 0.78 | 0.77 | mro |
| 0.77 | – | – | – | – |

[a] Distances above 0.45 nm are not assigned to a certain atomic distance pair and are attributed to medium range order effects (mro).

Keywords: amorphous materials • atomic force microscopy • glasses • structure elucidation

Sergeants-and-Soldiers Principle in Chiral Columnar Stacks of Disc-Shaped Molecules with C₃ Symmetry


Seminal studies by Green and co-workers to understand the underlying principles of chirality in stiff helical polymers such as the polyisocyanates have led to observations referred to as the “Majority Rule” and the “Sergeants-and-Soldiers Principle.” Poly(n-alkyl isocyanates) adopt an extended helical conformation in which long stretches of one helical sense, Por “Majority Rule,” are attributed to medium range order effects (mro).” Poly(n-alkyl isocyanates) adopt an extended helical conformation in which long stretches of one helical sense, Por “Majority Rule,”
helical sense, it is only required to add a small portion of chiral units (sergeants) to the achiral units (soldiers) or to have a slight majority of \( R \) over \( S \) units in the polymer. Recently, it was shown that these effects are operative in other polymers with stiff helical backbones.\(^2\) This is in sharp contrast to the behavior in small molecules where, for example, the optical rotation of a mixture of two enantiomers varies linearly with their ratio. Also in liquid crystals the induction of chirality is complex but seems to be predominantly linear or additive.\(^3\) The more chiral molecules added to a nematic liquid crystal, the shorter the helical pitch of the induced cholesteric phase.\(^3\) In this communication we describe our results on the stereochemical issues of the associates of disc-shaped molecules \( 1 \) in diluted alkane solutions \((10^{-4} - 10^{-6} \text{ mol L}^{-1})\). The molecules are stacked in highly ordered chiral columns, with a strong, cooperative response to chiral information. This amplification in chirality furnishes the first example in which the sergeants-and-soldiers principle is operative in dynamic structures of molecular aggregates.

Extended-core disc-shaped molecules are of interest, because they show liquid-crystalline properties within a broad temperature regime, and the stability of the molecular stacks is guaranteed by many secondary interactions.\(^4\) We have studied in detail the synthesis and properties of achiral compounds \( 1 \), in which the extended core is based on a concerted conformational preference owing to intramolecular H-bonding in the three acylated 3,3'-diamino-2,2-bipyridine moieties.\(^5\) Chiral analogue \( 1a \) is synthesized starting from (S)-citronellol, which was successively hydrogenated, brominated, coupled to methyl 3,4,5-trihydroxybenzoate and transformed by established procedures\(^5\) into the desired disc-shaped compound \( 1a \). Both \( 1a \) and \( 1b \) show a thermotropic liquid crystalline \( D_{3h} \) phase, and X-ray diffraction suggests the presence of a helical superstructure. In concentrations greater than or equal to 7% w/w in apolar solvents like hexane, dodecane, and cyclohexane, molecules \( 1b \) are organized in a columnar phase in which the 3.5 Å disc–disc distance within the columns is preserved.\(^6\)

UV spectra of \( 1a,b \) in different solvents show distinct differences in the \( \pi-\pi^* \) transition of the bipyridine moiety (Figure 1). In CHCl\(_3\), \( \lambda_{\text{max}} \) amounts to 351 nm \((\varepsilon = 5.3 \times 10^4 \text{ Lmol}^{-1} \text{cm}^{-1})\), whereas in dodecane a significant red shift of 13 nm is observed for \( \lambda_{\text{max}} \) to 364 nm \((\varepsilon = 3.2 \times 10^4 \text{ Lmol}^{-1} \text{cm}^{-1})\), and a shoulder in the spectrum in CHCl\(_3\) has developed into a peak at 384 nm \((\varepsilon = 2.3 \times 10^4 \text{ Lmol}^{-1} \text{cm}^{-1})\) in dodecane. The spectrum in dodecane resembles the UV spectrum of a sheared film of pure \( 1a \), which is in a \( D_{3h} \) phase at room temperature. Heating the dodecane solution to 100°C leads to a blue shift of the \( \lambda_{\text{max}} \) to 357 nm and the disappearance of the fine structure. These results imply that \( 1a \) is dissolved in CHCl\(_3\) as individual molecules (and in dodecane at 100°C), while aggregation occurs in dodecane (and related alkane solvents) at room temperature in which the packing of the molecules in columns is similar to that in neat \( 1a \).

In CHCl\(_3\), compounds \( 1a,b \) do not exhibit Cotton effects in the UV/Vis range of the circular dichroism (CD) spectrum. In dodecane, however, \( 1a \) shows a very strong, negative Cotton effect associated with the \( \pi-\pi^* \) absorption band of the bipyridine moiety at \( \lambda = 387 \) \((\Delta \varepsilon = -35.6 \text{ Lmol}^{-1} \text{cm}^{-1})\) and 369 nm \((\Delta \varepsilon = -23.6 \text{ Lmol}^{-1} \text{cm}^{-1})\) with chiral anisotropy factors\(^7\) \( g \) of \(-1.5 \times 10^{-3}\) and \(-7.4 \times 10^{-4}\), respectively. Heating the sample leads to a gradual decrease of the Cotton effects and a complete loss at 100°C. Subsequent cooling to room temperature restores the original Cotton effects. Most remarkably, the UV and CD spectra of the achiral compound \( 1b \) in optically active \((R)-(-)-2,6$\)$-dimethylcyclohexane 8 as solvent are almost identical to the spectra of chiral compound \( 1a \) in dodecane in the \( \pi-\pi^* \) absorption band of the bipyridine moiety (Figure 2). The anisotropy factors \( g \), however, are slightly lower \((8.5 \times 10^{-4}\) at \( \lambda = 386 \text{ nm} \) and \(5.3 \times 10^{-4}\) at \( \lambda = 367 \text{ nm}\)). Again, heating of this sample leads to a decrease of the Cotton effects, showing the dynamics in chiral solvation.\(^8\)

These results on chiral solvation indicate strong cooperative effects, suggesting a tendency of the stacks to take on a helical arrangement. We therefore attempted to apply the sergeants-and-soldiers principle to mixtures of \( 1a \) and \( 1b \) in hexane. As expected \( 1b \) does not show any Cotton effect in hexane. However, addition of only 2.5% of chiral \( 1a \) to achiral \( 1b \) in hexane generates a strong Cotton effect, especially in the bipyridine transition band, which was similar in magnitude as for pure \( 1a \) in hexane. The remarkable observation that the
The results given above are in full agreement with the strong cooperative effect of the sergeants-and-soldiers principle, but now in a dynamic system. To quantify the experimental results presented in Figure 3, we developed a theoretical model to fit these data. In this model the association constant $K$ and the cooperative length $L_0$, which is the length of that part of the stack with only one helical sense between the helix reversals—can be varied. We assume that the contributions to the Cotton effect in the bipyridine band of a stack is proportional to the number of monomeric units in the stack, and remaining nonassociated species do not contribute to the Cotton effect. Furthermore, the association constants $K$ of chiral and achiral monomers are equal, and if a stack contains a chiral monomer, the latter will induce chirality in other molecules in the stack not further away than $s$ units. For mixed stacks in equilibrium we can then deduce an equation to fit the experimental data points with $K$ and $s$ as variables.\[10]

A fit of this model to the experimental data leads to $K = (1 \pm 0.5) \times 10^3$ L mol$^{-1}$ and $s = (40 \pm 2)$ which yields $L_0 = 2.5 \pm 1 \approx 80$. We propose the following hypothesis to explain the cooperative response of compound 1 on external chiral information. The $C_2$ symmetrical molecules of type 1 adopt a propellerlike conformation in which the bipyridine wedges are tilted with respect to the central trimesic core.\[11] In hexane molecules 1 are aggregated in columnar stacks, and the packing between subsequent molecules will be optimal when all bipyridine wedges are tilted in the same direction, which results in a preferred stable chiral conformation of each disc-shaped molecule.\[12] This can be compared with propellers piled on top of each other. Rotating the first with respect to the second will improve the packing but will also give rise to a helix. Equal amounts of $P$ and $M$ helices are present within the stacks of achiral 1b. The stack length is concentration-dependent and corresponds with $K = 3 \times 10^3$ L mol$^{-1}$, while the cooperative length $L_0$ of one helical sense between helical reversals is not concentration-dependent and has the value $L_0 \approx 80$. On the other hand, the stacks of 1a are assumed to have only one helical sense $P$ or $M$. The instantaneous Cotton effect in the bipyridine band upon addition of chiral 1a to a solution of achiral 1b points to dynamic processes and an exchange of the molecules between different columns. By introducing on average one molecule of chiral 1a per 80 molecules of 1b into the stacks of 1b, the chiral component (the sergeants) will dictate the helical sense of the total stack (of soldiers) for steric reasons. That a chiral alkane solvent can also dictate the sense of helicity of a stack of achiral molecules presumably means that the first layer of solvent organizes itself along the peripheral alkoxy chains of the molecules with precision. Again, steric factors will dictate which helical sense will lead to the most favorable interactions between subsequent molecules.

In conclusion, it is shown that the sergeants-and-soldiers principle and chiral solvation are operative in dynamic, columnar stacks of molecules 1 in alkane solvents.

Keywords: chirality · circular dichroism · helical structures · stacking interactions · supramolecular
BaNdSi11N23—A Zeolite-Analogous Si—N Structure**

Hubert Huppertz and Wolfgang Schnick*

In the past few decades zeolites and aluminosilicates have found important technological applications as microporous solids. For the specific modification of their catalytic properties the tetrahedral centers aluminum and silicon were substituted by a large number of electropositive solids. Recently, the replacement of the bridging atoms O by different atoms or building units in the network structures was successful. For example, Zn6[P12N24]Cl2 with a sodalite-analogue microporous network structures from SiN4 tetrahedra can be realized. In contrast to conventional tetrahedra, the bond distances Si—N network structure is 1 O : 1. Thus Ba2Nd7Si1lN2, shows a three-dimensional network structure of corner-sharing SIN, tetrahedra according to Si—N network (Ba2⁺—N: 273(1)—316(2) pm; Nd3⁺—N: 175.4(12) pm) correspond to the values of terminal N atoms of (T= Al, Si; X= O). This ratio should also hold for zeolite-analogous nitridosilicates. All nitridosilicates obtained so far by high-temperature synthesis possess Si—N substructures in the range 0.5 ≤ T/X ≤ 0.75 having no open channels or large cavities.

The synthesis of BaNd6Si11N23 produced the first nitrido-silicate with a zeolite-analogous Si—N network structure. The new nitridosilicate was synthesized in a high-frequency furnace by reaction of stoichiometric amounts of barium and neodymium with silicon diimide under nitrogen atmosphere [Eq. (a)]. By this procedure BaNd6Si11N23 is formed as a coarse crystalline, dark blue solid. Like all other nitridosilicates synthesized in our group, BaNd6Si11N23 is stable up to 1600°C and insensitive to hydrolysis. The X-ray structure analysis [Eq. (a)] on single crystals of BaNd6Si11N23 shows a three-dimensional network structure of corner-sharing SIN, tetrahedra according to Si—N network (Ba2⁺—N: 273(1)—316(2) pm; Nd3⁺—N: 175.4(12) pm) correspond to the values of terminal N atoms of (T= Al, Si; X= O). This ratio should also hold for zeolite-analogous nitridosilicates. All nitridosilicates obtained so far by high-temperature synthesis possess Si—N substructures in the range 0.5 ≤ T/X ≤ 0.75 having no open channels or large cavities.

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\[
2 \text{Ba} + 7 \text{Nd} + 11 \text{Si} \left(\text{NH}_3\right)_{12} + 1/2 \text{N}_2 \xrightarrow{\text{900–1650°C, 40 h}} \text{BaNd}_6\text{Si}_{11}\text{N}_{23} + 11 \text{H}_2
\]

The X-ray structure analysis [Eq. (a)] on single crystals of BaNd6Si11N23 shows a three-dimensional network structure of corner-sharing SIN, tetrahedra according to Si—N network (Ba2⁺—N: 273(1)—316(2) pm; Nd3⁺—N: 175.4(12) pm) correspond to the values of terminal N atoms of (T= Al, Si; X= O). This ratio should also hold for zeolite-analogous nitridosilicates. All nitridosilicates obtained so far by high-temperature synthesis possess Si—N substructures in the range 0.5 ≤ T/X ≤ 0.75 having no open channels or large cavities.

The bond distances Si—N [Eq. (b)] in the network structure (167(1)—175.5(5) pm) are typical for simple bridging N atoms in nitridosilicates. The distances Si—N [Eq. (b)] (175.4(12) pm) correspond to the values of terminal N atoms in BaNd6Si11N23 (174–176 pm).

A measure for the microporosity of a zeolite-analogous structure is the framework density (FD), which indicates the number of molecules for a mixture of x zeolite analogues and y nitridosilicates. All nitridosilicates obtained so far by high-temperature synthesis possess Si—N substructures in the range 0.5 ≤ T/X ≤ 0.75 having no open channels or large cavities.

The successful synthesis of BaNd6Si11N23 is the first proof that not only highly condensed Si—N network structures but also open, zeolite-like networks of corner-sharing SIN tetrahedra can be realized. In contrast to conventional zeolites, which are synthesized by solvothermal procedures using templates, the nitridosilicates are only accessible by high-temperature synthesis. The next aim of our efforts will be the exchange of the bulky metal ions for hydrogen atoms.