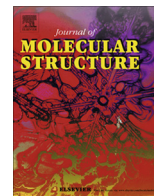




Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: [www.elsevier.com/locate/molstruc](http://www.elsevier.com/locate/molstruc)

# Orientalional disorder: A key to understand polarity of molecular crystals

J. Hulliger\*, K. Brahimi, M. Burgener, G. Dulcevscia

Department of Chemistry and Biochemistry, University of Berne Freiestr. 3, CH-3012 Berne, Switzerland

## HIGHLIGHTS

- Monte Carlo simulations and crystallization experiments demonstrate a reversal of the bi-polar state of a molecular crystal forming solid solutions.
- 4-iodo-4'-nitrobiphenyl, a polar crystal undergoes growth into a bi-polar state.
- Bi-polar state, concerning the average orientation of molecules can be reverted by adding an appropriate symmetrical molecule.

## ARTICLE INFO

Article history:  
Available online xxx

Keywords:  
Crystals  
Orientalional disorder  
Solid solutions  
Bi-polar state  
Polarity reversal  
Pyroelectric microscopy

## ABSTRACT

Polarity of molecular crystals is understood here as a result of 180° *orientational disorder* of asymmetrical building blocks. Symmetry arguments based on (i) a single rotational degree of freedom, (ii) the finite size of crystals and (iii) interactions in between asymmetrical molecules lead to the conclusion that such crystals should express a bi-polar ( $\infty/\infty m$ ) average state of zero polarity. This basic property of molecular crystals is exemplified by forming solid solutions of 4-iodo-4'-nitro-biphenyl (INBP) and symmetrical bi-phenyls (BP: A- $\pi$ -A, D- $\pi$ -D; A: acceptor; D: donor). Monte Carlo simulations based on a layer-by-layer growth model predict a reversal of the bi-polar state of pure INBP by forming a solid solution of (INBP)<sub>1-x</sub>(D- $\pi$ -D)<sub>x</sub>. In the case of the addition of A- $\pi$ -A reversal as found for pure INBP is promoted, i.e. needs less growth steps (layers) to be accomplished. Real crystals representing solid solutions were grown from 2-butanon solutions using symmetrical BPs. Scanning pyroelectric microscopy confirmed the qualitative behavior seen in Monte Carlo simulations. These findings represent an *experimentum crucis* supporting the general validity of the theory of stochastic polarity formation applied to single component or solid solution molecular crystals.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Crystals built of unsymmetrical but not necessarily chiral molecules are interesting systems to study their *polar real structure*, i.e. their non-uniform distribution of the electrical polarization P. For a discussion of polar symmetries and a graphical representation thereof the reduction of a molecular building block to a *polar vector* is convenient. However, for describing polar physical properties of molecules and crystals, higher order tensors of an uneven rank are required [1].

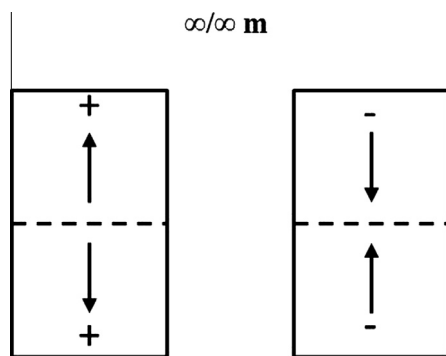
Here, we report on *orientational disorder* of polar vectors represented by molecules undergoing (i) crystal seed formation, (ii) growth of (hkl) faces or (iii) thermal equilibration in the as grown state. For a recent review on basic principles of stochastic polarity formation and experimentally investigated systems, see Ref. [2].

It was demonstrated by Monte Carlo (MC) simulations [3] that 180° *orientational disorder* can be a leading mechanism to produce growth sectors featuring a pyroelectric effect [4]. In case dipolar molecules involved in processes (i) to (iii) can attain a thermal equilibrium state with respect to orientational disorder (up vs down), *no net polarization* P for an entire crystal object may be favoured for reasons of symmetry [5]. This means, the real structure of molecular crystals providing locally a pyroelectric effect can be built up of symmetry related growth sectors featuring *opposite signs* of polarization. In particular cases simply a *bi-polar* structure [5] is obtained (see Fig. 1).

Well known examples showing a non-uniform distribution of polarization are *ferroelectric* molecular crystals composed of domains [6]. However, an essential difference as compared to crystals we address here, is, that ferroelectrics undergo a transformation into a state of uniform polarization by application of an *external* electrical field E.

\* Corresponding author. Tel.: +41 316314241.

E-mail address: [juerg.hulliger@iac.unibe.ch](mailto:juerg.hulliger@iac.unibe.ch) (J. Hulliger).



**Fig. 1.** Schematic representation of bi-polar states [9]. A real object will be composed of two adjacent domains featuring a different orientation of the polarization ( $P$ ).

The paper is arranged as such to provide at first a discussion on symmetry leading to a *bi-polar state* (Chap. 2), followed by a Monte Carlo MC analysis on the non-uniform polarization distribution in solid solutions made of polar and corresponding non-polar molecules (Chap. 3). Basic features predicted by MC are then demonstrated by real solid solutions made of 4-iodo-4'-nitro-biphenyl (INBP) and non-polar molecules (4,4'-diiodobiphenyl (DIBP) and 4,4'-dinitrobiphenyl (DNBP)). The inhomogeneous spatial distribution of polarity was investigated by scanning pyroelectric microscopy (SPEM) [7] (Chap. 4).

## 2. Symmetry and net polarization of condensed molecular matter

An essential base to understand equilibrium properties of systems is provided by the hypothesis of *ergodicity* [8]. Following Boltzmann, ergodicity implies that equilibrium properties of systems can be calculated from micro-canonical averages, so called thermal averages, e.g. ( $P$ ) for the polarization.

In gases and liquids molecules can access all orientational and translational degrees of freedom, realizing a maximum state of configurational entropy. However, crystals represent systems of *broken symmetries* [8], because molecules therein are confined to limited amplitudes of libration (rotation) and vibration (translation).

In cases where  $180^\circ$  orientational disorder is made possible by a low activation barrier, configurational entropy can be gained and ergodicity gets partially restored. This may take place during (i) the process of nucleation, (ii) at growing crystal-nutrient interfaces, and (iii) for as grown crystals exposed to high temperature below melting.

For geometrical reasons, averaging  $P$  to zero needs only *one* degree of rotational freedom. To define and the measure ( $P$ ) an axis is to be introduced onto which components ( $P_i$ ) of all molecules  $i$  within a system are projected. The infinite axis itself, i.e. a *straight line* represents  $\infty/m$  symmetry. Averaging a single degree of freedom as mentioned above, will obviously lead to ( $P$ ) =  $\sum_i \langle P_i \rangle = 0$ . However, crystals have a *finite size*, featuring boundaries (hkl faces). This implies that we have to reduce the straight line to a *line segment* compatible with symmetry  $\infty/\infty m$ . Consequently, the description of our system decomposes into two domains related by a mirror plan  $m$  located in the middle (Fig. 1). So, whatever effect may produce ( $P_{\text{domain}+}$ ), ( $P_{\text{domain}-}$ ) different from zero, the entire state of polarization will be bi-polar showing a total average polarization being zero. To describe such a state Shubnikov et al. had introduced [9] the symbol  $\infty/\infty m$  (symmetries found in textures, see Fig. 1).

What could be a reason to have ( $P_{\text{domain}}$ ) different from zero? Again we have to take into account the effect of the finite size,

i.e. the crystal faces (hkl). Considering the three different systems (i)–(iii) as mentioned above, we shall start our discussion by (i) the seed.

(i) In view of thermalizing *one* orientational degree of freedom we set up a seed composed of  $n \times n \times L$  molecules ( $n$ : lateral;  $L$ : longitudinal) interacting along chains and in between chains [5]. The MC result clearly represents  $\infty/\infty m$  symmetry, however, featuring non-zero but opposite polarity for each domain (Fig. 2). An Ising type Hamiltonian  $H_{\text{seed}}$  reveals the origin of the net polarity in the domains [10]:

$$H_{\text{seed}} = \varepsilon + 1/4\{S_o\Delta E_f - S_L\Delta E_f + \text{bilinear terms}\} + \text{lateral terms} \quad (1)$$

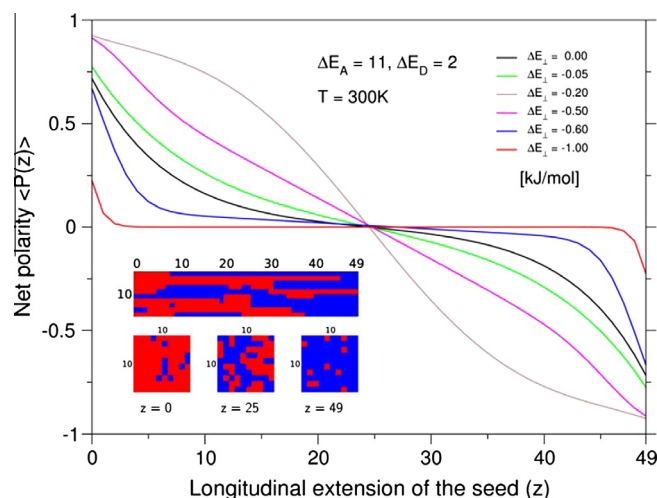
$\varepsilon$  is the constant;  $S_o$  is the effective particle operator for the *outermost* molecule at the left border of Fig. 2;  $S_L$  is the correspondingly for the right border of Fig. 2;  $\Delta E_f$  is the fundamental energy parameter accounting for the asymmetrical *longitudinal* interaction of molecules within a chain [5].

Apart from bilinear terms in Eq. (1) (accounting for longitudinal and lateral interactions), there are *linear* terms for the effective particle operators  $S$ , multiplied by the energy parameter  $\Delta E_f$ . These contributions in  $H_{\text{seed}}$  feature  $\infty m$  symmetry, i.e. they correspond to electrical field terms  $E$ , although there is no applied external electrical field. The action of  $E$  ( $\infty m$ ) on the degree of freedom ( $\infty/m$ ) implies that in each domain a non-zero polarization can exist [5]:

$$\infty m \cap \infty/m = \infty(\text{axial, polar}). \quad (2)$$

What type of intermolecular interactions are necessary to ensure  $\Delta E_f$  being non zero? Provided unsymmetrical molecules make up the seed, longitudinal interactions of the type “tip-to-tip” and “back-to-back” ( $-A \infty A$  vs  $-D \infty D$ ) are different giving thus rise to  $\Delta E_f = E_{AA} - E_{DD}$  different from zero (see also Chap. 3).

Interesting to notice that in case we allow only for dipole-dipole type coupling, no domain wise polarity formation will occur. Also magnetic systems do not show such an effect. To ensure  $\Delta E_f$  different from zero we need the full account of intermolecular



**Fig. 2.** Monte Carlo simulations for a nano-sized seed crystal ( $10 \times 10 \times 50$  A- $\pi$ -D entities,  $z = 0, \dots, 49$ ). ( $P(z)$ ): Average polarization projected on the axis  $z$ . Starting from a random distribution of dipolar orientations thermalization is leading to a bi-polar state. This means, the polarizations in the *left* and the *right* part of the figure are numerically equal but opposite in the signs. Longitudinal interactions parameters  $\Delta E_A, \Delta E_D$  correspond to realistic values for intra chain-type interaction of A- $\pi$ -D molecules. Different curves represent states for various lateral strengths of coupling preferring a parallel alignment of polar vectors. Inserts: snap shots of the state of alignment along the axis  $z$  (above) and perpendicular to it (below). Blue and red colors symbolize orientations “up” or “down” [2,5].

Download English Version:

<https://daneshyari.com/en/article/7809868>

Download Persian Version:

<https://daneshyari.com/article/7809868>

[Daneshyari.com](https://daneshyari.com)