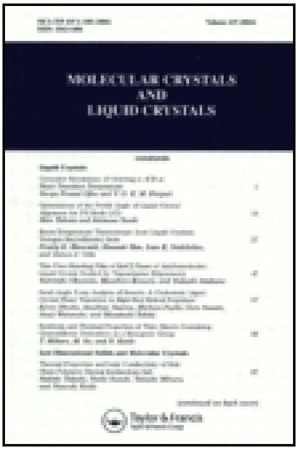

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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EXPERIMENTAL AND THEORETICAL MORPHOLOGY OF p-Nitro p'-Methyl Benzilidine Aniline, A NON-LINEAR OPTIC MATERIAL

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Abstract The theoretical habit of the non-linear optic material p-Nitro p'-Methyl Benzilidine Aniline, is calculated using an atom-atom potential method. This habit is compared with the habit predicted by the method of Donnay and Harker, and with the experimental habit. Differences in the three habits are explained in terms of the molecular structure at the growing crystal surfaces.

INTRODUCTION

p-Nitro p'-Methyl Benzilidine Aniline (NMBA) is an organic non-linear optic material. One route to making practical optical devices from this material is to grow large, high quality single crystals. This requires an understanding of both the internal factors (crystal structure and symmetry) and the external factors (solvent, supersaturation, temperature and purity) which control crystal growth. With the advent of reliable molecular mechanics calculations[1] and theoretical advances in crystal growth[2], it is now possible to predict the morphologies of molecular crystals from their crystal structures with some confidence[3,4]. Differences between such theoretical habits and the habits observed experimentally give insight into the role played by external factors such as solvent and impurities.

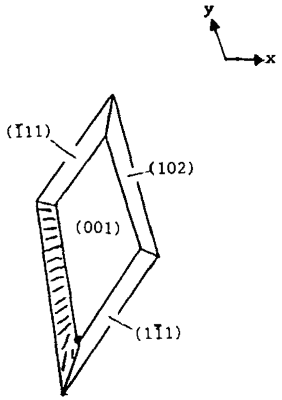
EXPERIMENTAL MORPHOLOGY OF NMBA

Large (>5mm) platelike single crystals were grown by solvent evaporation from saturated toluene solution at 40°C (Fig. 1). NMBA is monoclinic, space group Pb[5]. The corresponding point group, m, contains only one symmetry element, a mirror plane. This mirror plane lies in the plane of the photograph in Fig. 1, parallel to the large faces. Thus the morphology consists of two large parallel faces and eight smaller side faces. Six of these side faces were indexed on the unit cell previously reported[5], as shown in Fig. 1. The remaining two faces were too rough to be indexed unambiguously.

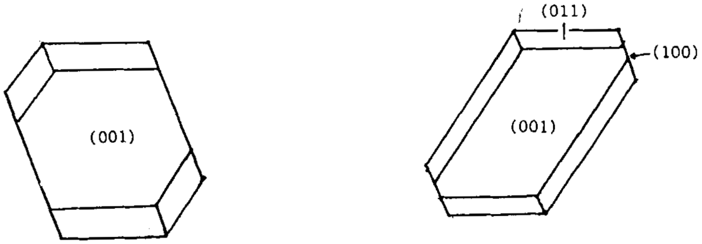
PREDICTED MORPHOLOGIES

Donnay-Harker

The empirical assumption of this method is that the growth rate of a crystal face is inversely proportional to its d-spacing[6]. The planes with largest d-spacing are thus the most likely to occur. Table I (below) gives the seven planes with largest d-spacing (after allowing for systematic absences). All seven planes were used as input to the computer programme SHAPE[7]; only four of these are present in the resulting morphology (Fig. 1).



Experimental



Predicted
Donnay-Harker

Predicted
Molecular Mechanics

Fig. 1: Comparison of theoretical and predicted morphologies

TABLE I Predicted Growth Rates

Face	Donnay-Harker (1/d)	Molecular Mechanics (E_{att})
(001)	0.857	4.693
$(1\bar{1}1)$	1.808	9.253
(011)	1.607	12.728
$(\bar{1}20)$	>2.3	14.025
$(1\bar{1}2)$	>2.3	14.669
(012)	2.189	17.581
(100)	1.499	18.378
$(2\bar{2}0)$	>2.3	18.479
(101)	1.671	19.445
(102)	2.235	20.687

Molecular Mechanics

The program used to predict the morphology, PCLEMC, has been described elsewhere[4]. Atomic coordinates and lattice parameters were taken from ref 5, the charge distribution on one molecule in a vacuum was calculated using MNDO, and standard A and B parameters were taken from Hopfinger[1]. Lattice energy calculations were performed with a gradually increasing limiting radius from 10Å to 40Å. The value converged at 25Å and above to -40.3kcal/mol. All subsequent calculations were carried out with a limiting radius of 25Å, and averaging the E_{att} values over both molecular sites. Calculations of the attachment energy, E_{att}, were performed for each of the eleven planes with the highest d-spacing. The results are presented in Table

I. Given that E_{att} is directly proportional to growth rate[2], these values can be used by SHAPE to produce plots of the predicted morphology. Fig. 1 shows such a plot obtained using E_{att} values for the first seven faces. Including additional faces did not alter the plot.

DISCUSSION

Comparison of Theory and Experiment

Fig. 1 shows that both predicted morphologies are reasonably close, with the molecular mechanics morphology slightly better. All the morphologies display the point symmetry m, consistent with the space group Pb. Each of the three forms observed experimentally is now discussed separately.

{001}: Theory and experiment agree that this is by far the most important form. The two parallel faces, (001) and $(00\bar{1})$, in this form are responsible for the plate-like appearance of the NMBA crystals.

$\{1\bar{1}1\}$ and $\{\bar{1}11\}$: In the theoretical and experimental morphologies, the importance of the $\{1\bar{1}1\}$ planes is the same as the $\{\bar{1}11\}$ planes, although they are not related by symmetry. The calculated importance of these faces agrees with the experimental morphology, but not with the predictions of the Donnay-Harker method. This is consistent with the molecular orientation in the crystal, which is almost parallel to these planes, resulting in a small E_{att}.

{102} and $\{\bar{1}02\}$: Neither theoretical method predicts that these forms will appear. Experimentally, only one of these forms appears; (it is impossible to say which from the goniometric measurements). Neither theoretical method is capable of predicting such behaviour because both methods effectively assume a centre of symmetry. A possible explanation would be that some other material selectively absorbs on the faces of one of these forms, slowing down their growth rate and causing the two faces to appear in the final morphology.

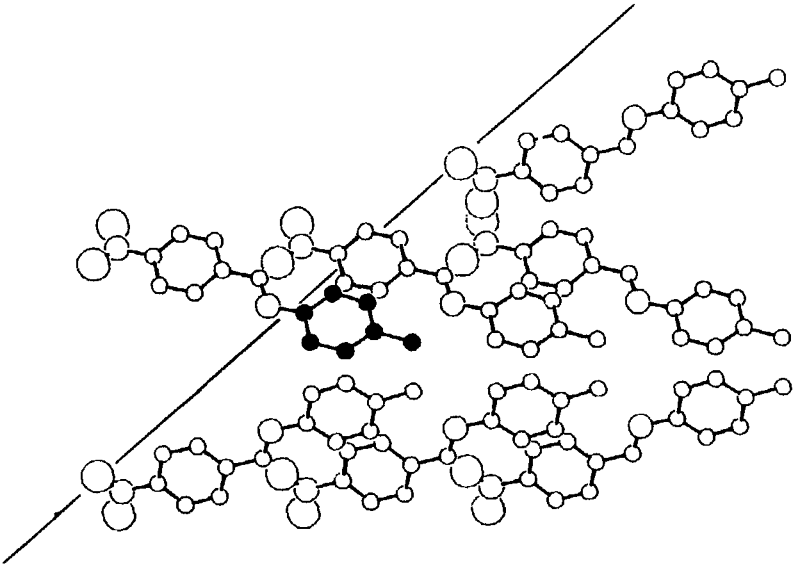


Fig. 2: End-on view of (102) slice, hydrogens omitted

The Role of the Solvent

This may be considered with reference to Fig. 2, which shows an 'end on' view of a growing (102) crystal surface. The incoming molecule presents the toluene-like end (coloured black) to the crystal surface. The remainder of the molecule projects outwards. Therefore an incoming toluene molecule could be absorbed on this site, decreasing its growth rate rate and increasing its importance. Toluene molecules could not absorb on the $\{\bar{1}02\}$ faces, though it follows that nitrobenzene would. This observation identifies the observed form as $\{102\}$, and is an example of the determination of the orientation of a polar axis by stereoselective adsorption of a 'tailor-made' solvent[8].

CONCLUSIONS

The Donnay-Harker method provides a crude, approximate way of predicting the morphology of NMBA. It is of limited usefulness because discrepancies between observed and predicted morphologies can be ascribed to either internal, structural effects or to external effects. The molecular mechanics approach enables the structural features of NMBA to be accounted for explicitly. The resulting predicted morphology is a better match with that observed. The remaining inconsistency can be explained qualitatively by considering the effect of solvent. There is a need for quantitative computational methods to deal with such solvent effects, especially for polar structures.

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