On intrinsic and extrinsic defect-forming mechanisms determining the disordered structure of 4-iodo-4′-nitrobiphenyl crystals

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Following up two recent *Chemical Communications* on the structure of the title compound, a theoretical study confirms that the presence of 4,4′-dinitrobiphenyl as an impurity can give rise to disordered crystals, resulting from a chain inversion mechanism.

Recent issues of this journal have contained communications[1,2] on the disordered crystal structure of 4-iodo-4′-nitrobiphenyl (INB), in which the INB molecules pack as parallel and polar ribbons (mm2). From the original viewpoint of designing efficient nonlinear optical (NLO) materials,[1] this type of packing of dipolar entities represents an interesting and relatively seldom case[3] of a material in which all the β_{zzz} axes of the molecular hyperpolarisability β are aligned co-parallel.

The difficulties encountered initially by Sarma *et al*.[1] in obtaining a reliable structural model from X-ray data were resolved more recently by Masciocchi *et al*.[2] and Langley *et al*.[4] through careful sample purification. In interpreting the data of Sarma *et al*., the Milan group[2] identified two possible causes of defect formation in INB: (i) polarity inversion of single ribbons (chains) of INB in the presence of 4,4′-dinitrobiphenyl (DNB) impurity molecules (in analogy to 180° opposed polar macro-domain formation in perhydrotriphenylene inclusion compounds[5]); (ii) two dimensional polytypes, *i.e.* a defect para-crystal composed of many fine grains. The effect of impurity molecules on the NLO characteristics of a host crystal has been demonstrated earlier by Weissbuch *et al*.[6,7] Whilst the mechanisms which permit the favourable creation of such defects at growing crystal faces are mainly well understood,[6,7] the subsequent fates of these faults, and their distribution throughout the structures of the resulting bulk crystals, often remain elusive.

Here we discuss further using energetic arguments the relative likelihood of *intrinsic* (180° orientational disorder) and *extrinsic* [due to DNB and/or 4,4′-diiodobiphenyl (DIB) impurities] defect formation in INB, and the likely true structure of INB which results. Attachment processes during the assembly of INB crystals are driven by the alignment of INB into parallel chains, as well as collinear functional group interactions (NO_2···I, I···I) between molecules already attached at the {001} surfaces and incoming INB, DNB or DIB molecules (Fig. 1). The total attachment energy E_{att} per molecule in the $+c$ or $-c$ direction contains contributions from lateral and long-range interactions between chains, as well as short-range collinear interactions between the terminal moieties. With respect to the former, we can make a distinction between E_p (parallel) and E_{ap} (antiparallel), that is, the energies corresponding to preferred and defect modes of lateral attachment, respectively (Fig. 1). Values E_{AD}, E_{DD} for the terminal intermolecular interaction energies of isolated, collinear NO_2···I (A···D) and I···I (D···D) synthons have been calculated to be -5.7 (3.4 Å) and -2.8 (4.0 Å) kJ mol^{-1}, respectively.[8] The NO_2···O_2N (A···A) intermolecular interaction is considered a defect configuration of low occurrence[6,8–9] because a positive interaction energy E_{AA} of ~ 10 kJ mol^{-1} was estimated for a van der Waals contact of 3.4 Å.[8]

Intrinsic defects, *i.e.* those resulting from 180° orientational disorder during the assembly of a pure INB system, can occur at the growing faces (Fig. 2). For growth along the $+c$ and $-c$ directions, there are two non-degenerate configurations for defect attachments, represented by the energies ΔE_{defect} ($+c$ or $-c$). As a result of a Schottky-type calculation[9] accounting for the molar fraction x of orientational defects, we find that: (i) the temperature of crystal growth can significantly affect the concentration of defects; and (ii) a perfect seed crystal will during growth segregate into two adjacent volumes containing a different number of defects. The ratio of the orientational defects within these two domains can be estimated using the intermolecular interaction energies given above: $x(+c)/x(-c) \cong \exp[(E_{AA} - E_{DD})/RT]$. Since the intermolecular interaction NO_2···O_2N is strongly endothermic, $x(+c)/x(-c)$ is expected to vary between *ca*. 170 and 20 (300–510 K). Continuation of growth along both c-directions after defect formation gives rise to one of two different phenomena: *healing* (correction) of the defect or *chain inversion* (Fig. 3). With each phenomenon there are again associated two different energies, corresponding to the two different growth directions $+c$ and $-c$ [see eqn. (1) below].
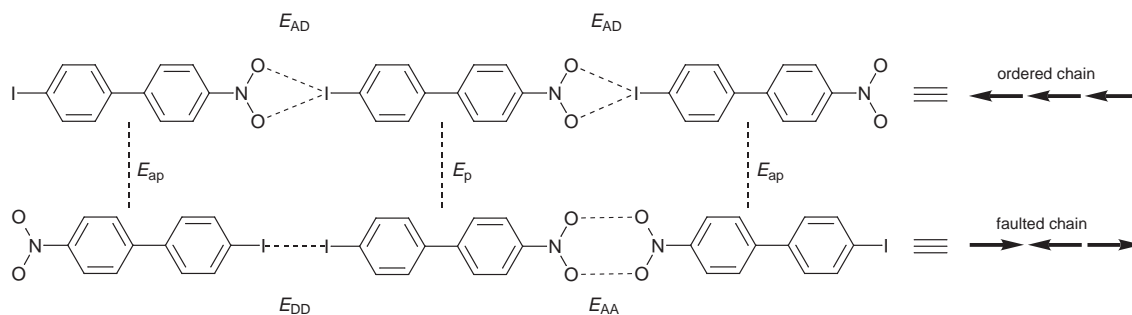
Fig. 1 Model representation of ordered and intrinsically disordered molecular chains of INB. This figure is used to illustrate the interaction energies (positive or negative; represented by dashed lines) under consideration during packing. Definition of interaction energies: $E_p \equiv$ lateral and long-range interactions between molecules (excluding collinear short-range contributions of terminal functional groups) whose dipoles are oriented co-parallel; $E_{ap} \equiv$ same as E_p but between dipoles oriented antiparallel; E_{AD}, E_{DD}, $E_{AA} \equiv$ collinear intermolecular terminal functional group interactions A···D, D···D, A···A, respectively. A and D are defined in the main text. Subsequent figures employ the symbol $\rightarrow$ as a simplified representation of INB, corresponding to the intramolecular dipole orientation $O_2N \rightarrow I$.

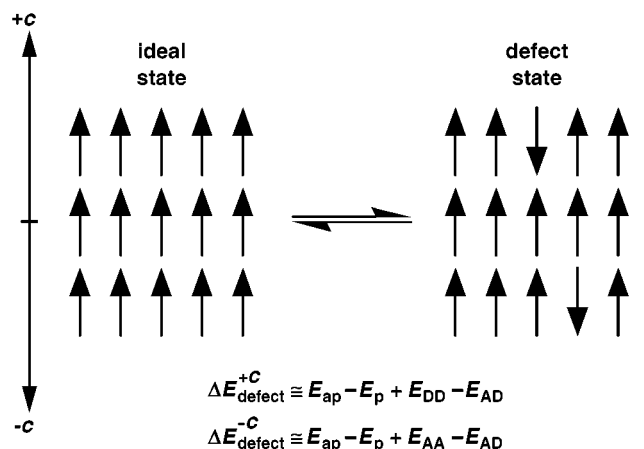$$\Delta E_{\text{defect}}^{+c} \cong E_{\text{ap}} - E_{\text{p}} + E_{\text{DD}} - E_{\text{AD}}$$

$$\Delta E_{\text{defect}}^{-c} \cong E_{\text{ap}} - E_{\text{p}} + E_{\text{AA}} - E_{\text{AD}}$$

Fig. 2 Intrinsic orientational defect equilibrium at growing faces ($+c$, $-c$) of a polar crystal such as INB.

$$E_{\text{healing}}^{+c} = E_{\text{p}} + E_{\text{AA}}$$
$$E_{\text{healing}}^{-c} = E_{\text{p}} + E_{\text{DD}}$$

versus

$$E_{\text{inversion}}^{+c} = E_{\text{ap}} + E_{\text{AD}}$$
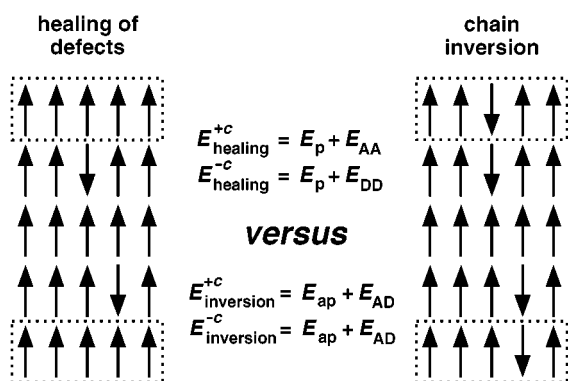$$E_{\text{inversion}}^{-c} = E_{\text{ap}} + E_{\text{AD}}$$

Fig. 3 Healing of defects *versus* chain inversion within the next growth layer after occurrence of primary (intrinsic) defects.

Extrinsic defects can arise due to solid solution formation of INB with DNB or DIB (Fig. 4). In the case of these symmetrically disubstituted components, the preferred mode of incorporation is driven only by the relative strengths of the terminal functional group intermolecular interactions. At an impurity level (in solution) of *ca.* 0.1, both DNB and DIB are incorporated into the growing crystal structure with different degrees of probability with respect to the $+c$ and $-c$ directions. From simplistic energy considerations it can be shown that when healing intrinsic defects, DNB attaches preferentially to defect sites along $-c$ whilst DIB attaches along $+c$. Conversely, when DNB and DIB are the defects themselves, preferred incorporations are along $+c$ and $-c$, respectively (Fig. 4).
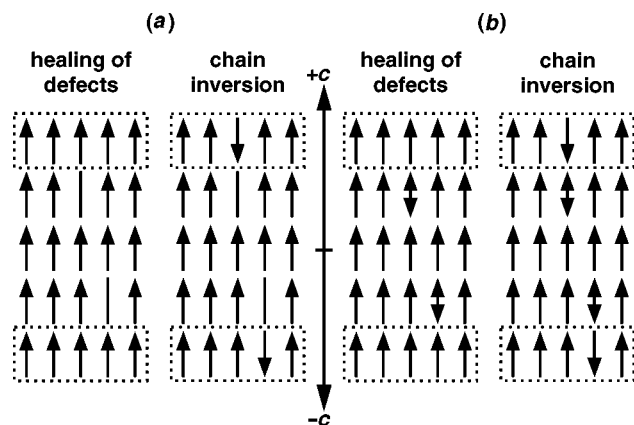

Fig. 4 Influence of DNB (——) or DIB (↔) impurities on subsequent growth layers: (*a*) healing *versus* chain inversion after preferred incorporation of DNB in the $+c$ direction; (*b*) similar scheme for DIB, where in the $-c$ direction favourable induction of a chain inversion may occur.

Which of healing or chain inversion by INB molecules in the next growth layer is the more probable is still, of course, a function of both defect (DNB or DIB) and growth direction ($\pm c$). At $x_1(\text{DNB}) \approx x_1(\text{DIB})$, DIB can serve to heal the defects created by DNB and *vice versa*.

In the realistic case reported by Masciocchi *et al.*[2] a more complicated situation arises: preferred attachments of DNB present in the growth medium will occur along $+c$ but healing by INB in the next layer would involve unfavourable $NO_2 \cdots O_2N$ intermolecular interactions. If at this point we allow for an inversion of single chains, the energy $E_{\text{inversion}}$ would at each layer have to be lower than the energy of a configuration providing healing by antiparallel attachments (Fig. 4). The corresponding energy difference between is then given by eqn (1).

$$\Delta E(+c, \text{DNB}) \equiv E_{\text{inversion}} - E_{\text{healing}} \cong$$
$$- RT\ln x(+c) + 2E_{\text{AD}} - E_{\text{AA}} - E_{\text{DD}} \qquad (1)$$

The logarithmic term refers to the concentration of intrinsic defects in pure INB crystals from which an estimate of the unknown difference $E_{\text{ap}} - E_{\text{p}}$ has been derived. Using the calculated energy values given above it follows that chain inversion is more stable [$\Delta E(+c) < 0$] as long as the concentration of intrinsic defects in pure INB crystals (300 K) is larger than about 6×10^{-4}. A $wR2$ value of 0.032 (crystal 1 in ref. 2; see also ref. 4) sets an upper limit for $x(+c)$ to a range of a few percent. Although a lower limit cannot be extracted from the present X-ray data, we consider it a reasonable estimate that $x(+c)$ is larger than $\sim 6 \times 10^{-4}$ ($\Delta E_{\text{defect}} \leqslant 18.6$ kJ mol^{-1}).

In view of our calculations, we conclude that chain inversion provides a mechanism to continue attachments at sites where preferred intrinsic defects or substitutions by DNB have been formed. Conversely, continuation of attachments at non-preferred sites by DNB is more favoured by healing. Both primary and secondary defect formation contribute to the disordered structure of INB and possibly other structurally similar materials (*i.e.* A,D-disubstituted rod-like molecules). The main conclusion of this work is in agreement with the experimental results and mechanistic proposition given by Masciocchi *et al.*[2] However, the true structure is such that about one half ($+c$) of the crystal volume should show a significant concentration of DNB defects continued by chain inversion, whereas the other half ($-c$) should exhibit diffraction phenomena similar to a well-ordered, monodomain crystal.

Notes and references

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4 Atomic co-ordinates and geometric parameters *etc.* have been deposited at the Cambridge Structural Database (P. J. Langley, D. Abeln, O. König, J. Hulliger and H.-B. Bürgi, in preparation).
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8 Collinear intermolecular interaction energies were calculated by applying the DREIDING 2.2.1 force field. Atomic charges for calculation of the Coulombic interactions were obtained from MOPAC, using the MNDO approximation. Both sets of calculations were performed using Cerius 2 software (Molecular Simulations Ltd., Cambridge, UK).
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