Shear-Slip Transitions in Polytypes: Aspirin as a Case Study
Luc M. LeBlanc\textsuperscript{1}, Alberto Otero-de-la-Roza\textsuperscript{2} and Erin R. Johnson\textsuperscript{1,*}
\textsuperscript{1}Department of Chemistry, Dalhousie University, Halifax, NS, Canada
\textsuperscript{2}Department of Chemistry, University of British Columbia, Okanagan, Kelowna, BC, Canada

Introduction

Two-crystalline forms of aspirin (\(\text{C}_{9}\text{H}_{8}\text{O}_2\text{N})\) are presently known. The prediction of the second form, aspirin-II, was made just over a decade ago. Since then, many efforts have been directed towards crystallizing pure crystals of aspirin-II only to find that it is metastable and converts to aspirin-I under ambient and shear-stress conditions.\textsuperscript{2,3} Interconversion between these two forms, however, does not occur under application of high pressures of up to 10 GPa.\textsuperscript{4,5}

The two forms are related by polytypism, i.e., they differ only in the stacking sequence along one of the unit-cell dimensions (Figure 1). Thus, in principle, they can interconvert through a shear-slip mechanism.\textsuperscript{5}

Figure 1: Forms-I and -II of aspirin viewed along the \(ac\)-plane. Red and blue lines highlight the different molecular orientations with respect to this plane. Stacking differs along the \(a\)-axis, in which adjacent pairs of aspirin dimers are aligned the same way in form-I, and in opposite orientations in form-II.

Computational Methods

Computations were performed using the D80-PBE functional with the exchange-hole dipole moment (XDM) dispersion correction,\textsuperscript{6,7} as implemented in Quantum Espresso version 5.1 with the projector-augmented wave method and pseudopotentials approach (60 and 80 Ry cutoffs for the energy and density, respectively, 2\(\times\)2\(\times\)2 MP-scheme \(k\)-point sampling). The values of the two parameters in the XDM damping function were set to \(a_{\delta} = 0.6542\) and \(a_{\gamma} = 1.6543\) Å.

Crystal structures of aspirin-I and aspirin-II were retrieved from the Cambridge Structural Database and fully optimized, allowing for cell-relaxation. A unit-cell of aspirin-I/II was then doubled along the \(\langle 100\rangle\) direction in order to investigate the slip system of interest, i.e., \(\{100\}\) \(-\text{c}\).

One layer of aspirin dimers (cf. Figure 1) was translated relative to the other in increments \(\Delta_{\text{c}}\) along the \(\langle 001\rangle\) direction, allowing for the interconversion between the two forms. Each intermediate structure along the phase transition was then relaxed, freezing only the coordinate along the slip direction. Similar results were obtained when using the Nudged-Elastic Band method as implemented in Quantum Espresso (not shown).

Results

Figure 2: \{100\}-\text{c}\)-slip mechanism between aspirin-I (\(\delta_{c} = 0\)) and aspirin-II (\(\delta_{c} = 0.5\)) under ambient conditions. PES scan (bottom left) and key intermolecular interactions (top and bottom right) for the phase transition. Energies are given in kJ/mol per molecule.

The barrier for the interconversion of aspirin-II to aspirin-I is calculated to be 30 kJ/mol per molecule. This is reasonable in light of the fact that two C-H - O pseudohydrogen bonds are broken en route to the transition state (Figure 2). This barrier is also found to be reasonable considering that the binding energy of a formaldehyde dimer (bound by two analogous C-H - O interactions) is 14.3 kJ/mol.

Aspirin-II crystals have been found to transform to aspirin-I crystals over a period of several months under ambient conditions.\textsuperscript{8} Making use of the calculated barrier for the interconversion of the two forms of aspirin, along with a simple kinetics model,\textsuperscript{9} one can estimate the conversion time for an ideal crystal (Figure 3). Estimating the free-energy barrier by including phonon contributions to the electronic energy barrier reduces it to 9.5 kJ/mol per molecule. Under applied pressures up to 12 GPa, the barrier for slip increases to a maximum of 18 kJ/mol per molecule (Figure 4). This is not unexpected, but clearly suggests that applying pressure to induce phase transition between these polytypes is not well founded. Overall, this is consistent with experimental findings that the two forms of aspirin do not interconvert at higher pressures.\textsuperscript{4,5}

Conclusions

Through the use of periodic-boundary density-functional theory (B86-PBE-XDM), the barrier for the shear-slip mechanism between aspirin-I and aspirin-II has been computed and related to the observed conversion by a simple kinetics model.

Consideration and evaluation of the slip systems could prove to be helpful in understanding the relative stability and potential interconversion of polytypes in the presence of shear stress, high pressures, or even under ambient conditions.

References


Acknowledgements