Electronic Supplementary Material for CrystEngComm

Electronic Supplementary Information

Small Energy Differences in Molecular Crystals: A First Principles Study of Tautomerism and Dynamics in Benzoic Acid Derivatives

Derek S. Middlemiss, Mark Facchini, Carole A. Morrison and Chick C. Wilson

Computational Method

(i) Gas Phase Calculations

The simulation of monomer and dimers of benzoic acid and derivatives in the gas phase is a necessary part of our study, if the effect of the extended crystalline environment upon structure is to be isolated and analysed. To this end, hybrid, spin restricted B3PW91 (RB3PW91) calculations were performed for candidate monomer and dimer structures with the Gaussian03 package. Initial geometries were obtained from Berny algorithm optimisations within the spin restricted Hartree- Fock (RHF) Hamiltonian using standard Pople 3-21G* basis sets. Assurance of conformational stability and starting force constants for subsequent DFT optimisations were obtained from vibrational frequency analysis of the final molecular geometry. The subsequent RB3PW91 6-311G* calculations proceeded from the converged RHF structures. The SCF convergence threshold for all runs was set at a total energy change of 1×10-6 a.u, while geometry optimisation convergence criteria were 0.45×10-3, 0.3×10-3, 1.8×10-3 and 1.2×10-3 a.u. for maximum force, RMS force, maximum displacement and RMS displacement respectively.

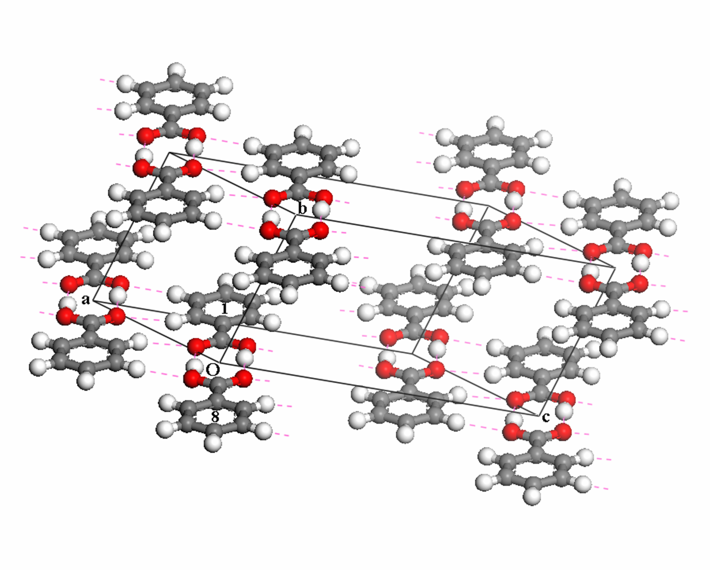
(ii) Solid State Calculations

The plane wave pseudopotential method, as embodied in the CASTEP code was applied to lattices of interest. All interactions of valence electrons with ion cores were approximated by use of highly transferable ultrasoft pseudopotentials of the type proposed by Vanderbilt, while electron exchange and correlation were approximated by use of the Perdew-Burke-Ernzerhof GGA-type functional. Convergence tests were conducted by examination of the variation in the relative stability of the two tautomeric forms of 4-chloroBA with increase in basis kinetic energy cutoff and reciprocal space sampling density. It was found that an increase in cutoff from 450 to 500eV, accompanied by an increase in the number of **k-**points in the irreducible part of the first Brillouin zone from 28 to 54 resulted in a change in this relative stability from 22.9 to 22.2 meV per dimer respectively. Thus, a cutoff of 450eV and a Monkhorst-Pack **k-**space mesh of a line density as close as possible to 0.04Å were used in all subsequent runs.

Save where otherwise noted, full use was made of space group symmetry. SCF and optimisation convergence tolerances were set at 2×10-6 eV/atom, 1×10-6 eV, 5×10-6 eV/atom, 1×10-2 eVÅ-1 and 5×10-4 Å for the change in total energy in SCF, change in eigenvalue, change in total energy in optimisation, maximum absolute atomic force and maximum absolute atomic displacement respectively. In order to avoid aliasing and symmetrisation errors a fast Fourier transform grid with a sphere of 2.3 times the diameter of the basis sphere was used. The NVT-ensemble dynamics calculations sampled trajectories of 2ps total length, using a timestep of 0.4fs, first order wavefunction extrapolation and chains of five Nosé-Hoover thermostats. Given the averaging of errors typical of MD runs, it was possible to use a lower cutoff of 300eV, and Γ-point reciprocal space sampling. The first 0.4ps of each trajectory were discarded to allow for equilibration.

Supercells with Edge-On Dimer Interactions Only

The figure below shows the edge-on C-H···O linked dimer configuration obtained in benzoic acid by removal of molecules 2–7 from the supercell shown in Figure 3 of the main paper. Although difficult to visualise, the structure comprises ribbons of edge-linked dimers that are isolated from each other in the direction perpendicular to the dimer plane.



Supercells for Terephthalic Acid Cohesive Energy Calculations

The isolated TA chain was represented within a monomolecular supercell defined by (a,b,c,α,β,γ) = 9.54, 12, 12Å, 86.95, 134.65, 104.9º. The periodic array of isolated chains formed point along the a-axis. The isolated TA monomer was represented within a cuboidal supercell with cell lengths (a,b,c) = 9, 9, 16Å, where the long axis of the monomer was oriented along the c-axis of the supercell.