Electronic Supplementary Material (ESI) for CrystEngComm.

SUPPLEMENTARY MATERIAL

Competition between Hydrogen Bonding and Dispersion Interactions in the Crystal Structures of the Primary Amines

Andrew G. P. Maloney,[1] Peter A. Wood[2] and Simon Parsons[1]*

[1] *EaStCHEM School of Chemistry and Centre for Science at Extreme Conditions, The University of Edinburgh, King's Buildings, West Mains Road, Edinburgh, Scotland. EH9 3JJ*
[2] *Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England. CB2 1EZ.*

S1: Principal Intermolecular Contact Energies

All energies ($kJmol^{-1}$) in the tables below were determined with the PIXEL method.

Ethylamine Phase 1

Symmetry	E_{Coul}	E_{Disp}	E_{Rep}	E_{Pol}	E_{Tot}	Interaction
x, 1.5-y, ½+z	-22.1	-13.2	25.0	-8.1	-18.4	H-bond
1-x, 1-y, 1-z	-7.7	-7.6	4.3	-1.6	-12.7	Dipole-dipole
1-x, y-½, 1.5-z	-4.3	-5.4	2.8	-1.4	-8.3	H-bond
1-x, 1-y, 2-z	1.3	-10.6	4.4	-1.0	-5.9	Dispersion
-x, 1-y, 1-z	-1.0	-6.7	3.7	-0.3	-4.4	Dispersion
x, ½-y, ½+z	-0.7	-6.3	4.2	-0.4	-3.3	Dispersion

Ethylamine Phase 2

Symmetry	E_{Coul}	E_{Disp}	E_{Rep}	E_{Pol}	E_{Tot}	Interaction
1-x, ½+y, 1.5-z	-23.1	-10.6	25.2	-8.5	-17.0	H-bond
x, ½-y, ½+z	-7.2	-12.4	11.0	-2.8	-11.4	H-bond
x, 1+y, z	-2.9	-5.2	3.6	-0.9	-5.4	Dispersion
1-x, -y, 2-z	-3.7	-1.5	0.2	-0.2	-5.3	Dipole-dipole
1-x, 1-y, 2-z	1.6	-9.6	3.6	-0.7	-5.2	Dispersion

-x, 1-y, 1-z	-1.9	-8.3	6.7	-0.7	-4.2	Dispersion

Propylamine

Symmetry	E_{Coul}	E_{Disp}	E_{Rep}	E_{Pol}	E_{Tot}	Interaction
1.5-x, 1.5-y, ½ + z	-19.5	-10.1	19.7	-6.5	-16.4	H-bond
1.5-x, ½+y, z	-13.2	-9.6	14.1	-4.5	-13.2	H-bond
x, 1-y, ½+z	-1.4	-14.5	9.7	-1.6	-7.8	Dispersion
x, 2-y, ½+z	-0.5	-11.6	6.0	-0.8	-6.9	Dispersion
x, y, z+1	-0.1	-1.5	0.1	-0.0	-1.6	Dispersion

Butylamine

Symmetry	E_{Coul}	E_{Disp}	E_{Rep}	E_{Pol}	E_{Tot}	Interaction
1.5-x, ½-y, ½+z	-25.2	-11	28.6	-9.6	-17.3	H-bond
x, 1-y ½+z	-2.6	-18.7	10.8	-1.7	-12.1	Dispersion
1.5-x, ½+y, z	-5.3	-7.1	4.7	-1.8	-9.5	H-bond
x, -y, ½+z	-1.5	-14.6	9.2	-1.1	-8.0	Dispersion
x, y, 1+z	-1.0	-4.6	1.5	-0.3	-4.4	Dispersion

Pentylamine

Symmetry	E_{Coul}	E_{Disp}	E_{Rep}	E_{Pol}	E_{Tot}	Interaction
1.5-x, ½-y, ½+z	-24.8	-11.2	29.8	-9.3	-15.6	H-bond
x, 1-y ½+z	-3.7	-22.7	14.8	-2.0	-13.7	Dispersion
x, -y, ½+z	-2.2	-19.9	11.6	-1.4	-11.8	Dispersion
1.5-x, ½+y, z	-7.9	-8.4	9.0	-3.0	-10.3	H-bond
x, y, 1+z	-0.7	-.38	0.4	-0.1	-4.1	Dispersion

Hexylamine

Symmetry	E_{Coul}	E_{Disp}	E_{Rep}	E_{Pol}	E_{Tot}	Interaction
1.5-x, y, ½+z	-4.9	-27.6	17.1	-2.3	-17.7	Dispersion
1-x, -y, ½+z	-24.9	-11.5	29.7	-9.8	-16.5	H-bond
½-x, y, ½+z	-2.9	-22.9	13.8	-1.6	-13.6	Dispersion
½+x, -y, 1+z	-3.7	-6.4	3.2	-1.3	-8.2	H-bond
x, y, 1+z	-1.9	-9.6	4.2	-0.6	-7.9	Dispersion

Heptylamine

Symmetry	E_{Coul}	E_{Disp}	E_{Rep}	E_{Pol}	E_{Tot}	Interaction
x, y, z	-5.8	-31.3	20.4	-2.6	-19.3	Dispersion
1+x, y, z	-3.4	-27.6	16.4	-1.8	-16.4	Dispersion
-1+x, ½-y, 1.5+z	-21.5	-10.9	27.7	-8.9	-13.7	H-bond
-1+x, y, 1+z	-2.1	-11.7	5.7	-0.9	-8.9	Dispersion
x, ½-y, ½+z	-4.6	-6.0	3.2	-1.4	-8.8	H-bond

Octylamine

Symmetry	E_{Coul}	E_{Disp}	E_{Rep}	E_{Pol}	E_{Tot}	Interaction
1.5-x, y, ½+z	-6.5	-36.4	23.2	-3.0	-22.8	Dispersion
½-x, y, ½ +z	-4.3	-31.5	19.5	-2.2	-18.5	Dispersion
1-x, -y, ½+z	-24.9	-11.5	30.5	-9.8	-15.7	H-bond
x, y, 1+z	-2.8	-14.7	7.5	-1.1	-11.0	Dispersion
½+x, -y, z	-3.7	-6.1	2.9	-1.2	-8.1	H-bond

Nonylamine

Symmetry	E_{Coul}	E_{Disp}	E_{Rep}	E_{Pol}	E_{Tot}	Interaction
x, 1.5-y, ½+z	-7.4	-39.7	25.1	-2.9	-25.0	Dispersion
x, 1.5-y, ½+z	-4.7	-35.1	20.4	-2.2	-21.7	Dispersion
x', y', z'	-25.1	-11.3	30.6	-10.2	-15.9	H-bond
-1+x, y, z	-3.3	-16.9	9.2	-1.3	-12.4	Dispersion
x, 1.5-y, ½ + z	-3.5	-5.7	2.6	-1.1	-7.7	H-bond

Decylamine

Symmetry	E_{Coul}	E_{Disp}	E_{Rep}	E_{Pol}	E_{Tot}	Interaction
1.5-x, y, ½+z	-8.1	-44.5	28.0	-3.4	-27.9	Dispersion
½-x, y, ½+z	-5.6	-40.1	24.7	-2.7	-23.7	Dispersion
1-x, 1-y, ½+z	-25.6	-11.8	30.9	-10.2	-16.7	H-bond
x, y, 1+z	-3.8	-19.6	10.6	-1.6	-14.3	Dispersion
½+x, 1-y, z	-2.9	-6.1	2.7	-1.1	-7.5	H-bond

S2 Procedure for Carrying-out the "Crystal Packing Feature" Search for Methyl-Methyl Interactions

The .cif files which were to be compared were loaded into Mercury CSD. Using the "Reveal symmetry-generated molecules at click positions" button, a cluster of 24 molecules was built to display the methyl-methyl interactions between slabs of molecules. See Figure S1 for an example using hexylamine. In this case, the hexylamine molecules had to be inverted to allow the underlying coordinates to correspond to those of the other molecules being investigated.

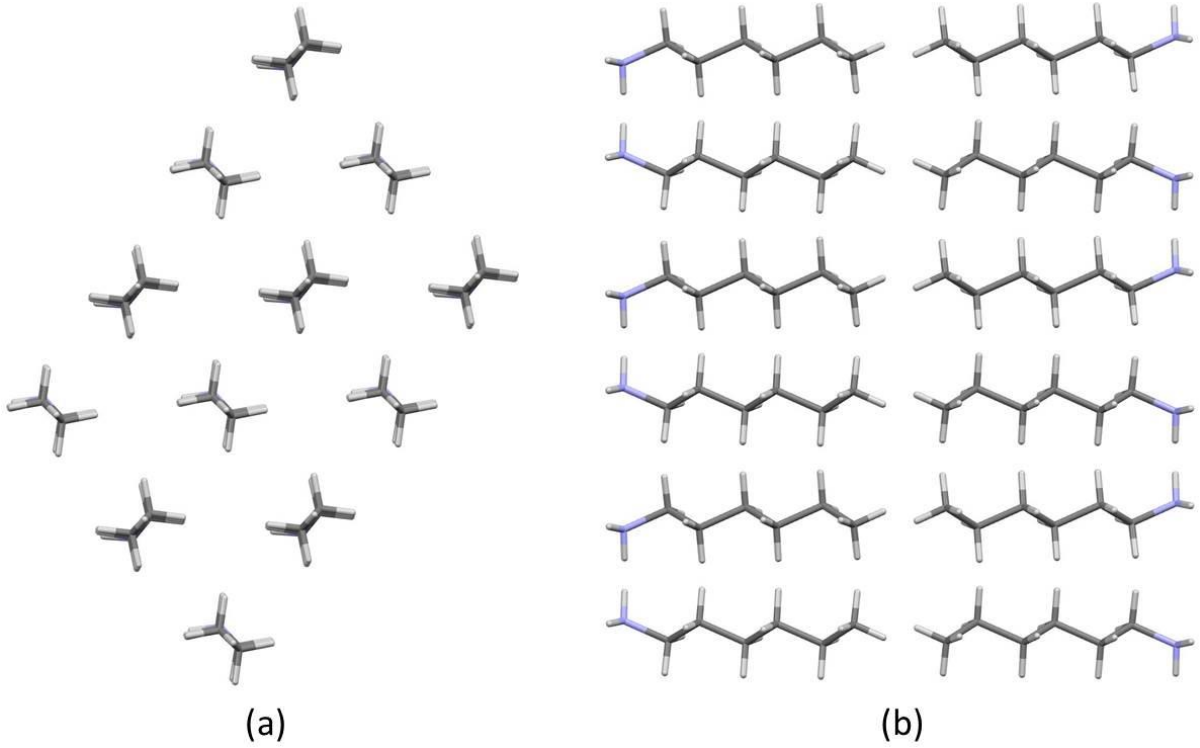

Figure S1: The cluster of hexylamine molecules used for analysis. An end-on view of 12 molecules (a) and a side on view of 12 molecules (b) are shown for clarity.

The lasso tool was then used to select all of the carbon and hydrogen atoms of the chains. Care was taken not to select any atoms from the amine groups of any of the molecules. The "Crystal Packing Feature…" option was then selected from the "Solid Form" menu of Mercury. The graphical interface confirmed that, in the case of hexylamine, 456 atoms from 24 molecules had been selected.

Continuing through the Packing Feature Search, no constraints were added to the number of hydrogens, the number of bonds, the charge or the cyclicity of the molecules, and no atoms or bonds were modified. A medium level of geometric similarity was requested. No distance, angle or torsion parameters were specified.

The hexylamine model was compared to heptyl-, octyl-, nonyl and decylamine for the purpose of this search. The search was then started, and after some time yielded the results as shown in the main body of this paper. This process was then repeated for other structures of interest.