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ELECTRONIC SUPPLEMENTARY INFORMATION

Energy frameworks: Insights into interaction anisotropy and the mechanical properties of molecular crystals

*Michael J. Turner, Sajesh P. Thomas, Ming W. Shi, Dylan Jayatilaka and Mark A. Spackman**

School of Chemistry & Biochemistry, University of Western Australia, Crawley WA 6009, Australia

COMPUTATIONAL DETAILS

Monomer electron distributions were obtained with *Gaussian09*[1] at the B3LYP/6-31G(d,p) level, using experimental crystal geometries with bond lengths to H atoms normalised to standard neutron diffraction values. The calculation of intermolecular energies, implemented in *CrystalExplorer*,[2] is automated for all unique molecular pairs in the first coordination sphere of a molecule. The terms in the interaction energy are defined as follows:

E_{ele} Classical electrostatic energy of interaction between unperturbed charge distributions of the monomers;

E_{pol} Polarization energy as a sum over nuclei with terms of the kind $-\frac{1}{2}\alpha_{mean}|F|^2$, where the electric field at each nucleus is computed from the charge distribution of the other monomer, and α_{mean} are recommended isotropic atomic polarizabilities from Thakkar & Lupinetti;[3]

E_{dis} Grimme's D2[4] or D3(BJ)[5] dispersion correction, summed over all intermolecular atom pairs;

E_{rep} Exchange-repulsion energy, calculated between unperturbed charge distributions of the monomers.

Complete details are provided elsewhere,[6] and the basic expression for the interaction energy includes four scale factors obtained by fitting to a training set of intermolecular energies derived from dispersion- and counterpoise-corrected energies obtained at the B3LYP/6-31G(d,p) level:

$$E_{tot} = 1.063E_{ele} + 0.756E_{pol} + 0.843E_{dis} + 0.595E_{rep} \qquad (1)$$

The computation of energies and the energy frameworks is summarized by the following steps:

(i) B3LYP/6-31G(d,p) molecular wavefunctions are calculated using the crystal geometry, with X–H bond lengths normalized to standard neutron diffraction values;

(ii) For each molecule in the asymmetric unit, crystallographic symmetry operations are applied to their density matrix to generate those of the neighbouring molecules;

(iii) Intermolecular electrostatic, polarization, dispersion and exchange-repulsion energy terms are calculated as above, and summed to obtain interaction energies for all unique molecular pairs for which any atom is within 3.8 Å of a central molecule (This corresponds to the energy model labelled CE-B3LYP(Fit=D2) in reference 6);

(iv) Energies between molecular pairs are represented as cylinders joining the centres of mass of the molecules, with the cylinder radius proportional to the magnitude of the interaction energy;

In the following tables of energies, the columns 'Coul.', 'Polariz.', 'Disp.' and 'Repul.' refer to *unscaled* components E_{ele}, E_{pol}, etc., while 'Total' represents the total energy, E_{tot}. 'Dist.' is the distance between centres of mass of pairs of molecules (Å), and 'Symop' gives the symmetry operation relationship between the two molecules. For orthoboric acid, with two molecules in the asymmetric unit, no symmetry relationship is given for interactions between pairs of unrelated molecules.

Energy frameworks are obtained via a menu option in *CrystalExplorer*. Separate frameworks can be produced (in different colours) for scaled electrostatic (red), scaled dispersion (green) and total interaction (blue) energies, as in (1). All frameworks for a

particular crystal structure use the same overall – and arbitrary - scale factor (i.e. relative size of interaction tubes); as used in the present paper a scale factor of 10 results in a tube thickness of 2 Å for an energy of 100 kJ mol^{-1}. Interaction energies with magnitude less than a specified threshold can be ignored when constructing the energy frameworks.

Model energies and energy frameworks have been incorporated in *CrystalExplorer* version 3.2, which is expected to be available at www.hirshfeldsurface.net in early 2015.

CRYSTAL STRUCTURES AND UNIQUE INTERACTION ENERGIES (kJ mol^{-1})

61365-ICSD Orthoboric acid[7] ($P\bar{1}$, Z' = 2.0)

Symop	Dist.	Coul.	Polariz.	Disp.	Repul.	Total
-x, -y, -z	4.46	1.5	-0.3	-5.2	1.2	-2.3
-	4.06	-94.8	-19.7	-13.2	115.5	-58.1
-x, -y, -z	5.90	-0.2	-0.1	-1.1	0.0	-1.2
-	3.59	-1.5	-0.4	-10.4	6.0	-7.2
-x, -y, -z	4.89	1.7	-0.3	-2.8	0.3	-0.6
-	4.07	-92.4	-18.9	-13.2	112.9	-56.5
-	3.58	-1.8	-0.3	-10.9	6.0	-7.9
-x, -y, -z	4.08	0.8	-0.3	-6.3	1.8	-3.6
-	4.06	-94.5	-19.4	-13.1	116.1	-57.0
-x, -y, -z	5.91	-0.4	-0.1	-1.1	0.0	-1.4
-x, -y, -z	4.07	0.9	-0.2	-6.0	1.5	-3.4
-x, -y, -z	4.45	1.4	-0.3	-5.7	1.4	-2.6
-x, -y, -z	4.88	1.8	-0.2	-2.8	0.3	-0.5

GEJVEW adamantane-1,3,5,7-tetracarboxylic acid[8] ($I4_1/a$, Z'=0.25)

Symop	Dist.	Coul.	Polariz.	Disp.	Repul.	Total
-x, -y, -z	6.71	-16.9	-6.0	-39.2	23.5	-41.6
-x, -y, -z	10.07	-89.5	-20.2	-13.1	91.8	-66.9
x, y, z	7.51	3.2	-1.2	-26.1	17.1	-9.3
x, y, z	10.62	5.0	-0.7	-3.2	0.3	2.2

HCLBNZ11 hexachlorobenzene[9] ($P2_1/n$, Z'=0.5)

Symop	Dist.	Coul.	Polariz.	Disp.	Repul.	Total
x, y, z	3.84	-7.8	-0.8	-55.4	37.6	-33.2
x, y, z	8.92	-2.0	-0.1	-7.8	6.1	-5.1
-x+1/2, y+1/2, -z+1/2	8.52	-2.1	-0.1	-7.3	6.6	-4.6

-x+1/2, y+1/2, -z+1/2	8.78	-2.0	-0.1	-7.2	7.1	-4.0
x, y, z	8.05	-1.0	-0.0	-8.7	6.8	-4.4

TCHLBZ 1,3,5-trichlorobenzene[10] ($P2_12_12_1$, *Z*'=1.0)

Symop	Dist.	Coul.	Polariz.	Disp.	Repul.	Total
x, y, z	3.91	-4.5	-0.1	-34.5	22.0	-20.8
-x, y+1/2, -z+1/2	6.91	-3.8	-0.4	-11.3	10.0	-8.0
-x+1/2, -y, z+1/2	8.57	-1.1	-0.0	-3.8	3.9	-2.1
x+1/2, -y+1/2, -z	8.50	-0.9	-0.0	-3.7	3.7	-2.0
-x, y+1/2, -z+1/2	7.06	-3.0	-0.2	-8.8	5.9	-7.2
-x+1/2, -y, z+1/2	6.33	-3.6	-0.3	-13.5	10.8	-9.0

NAPHTA22 naphthalene[11] ($P2_1/a$, Z'=0.5)

Symop	Dist.	Coul.	Polariz.	Disp.	Repul.	Total
-x+1/2, y+1/2, -z	4.79	-10.9	-1.5	-34.6	38.5	-18.9
-x+1/2, y+1/2, -z	7.54	-4.8	-0.5	-14.4	17.0	-7.5
x, y, z	8.40	-3.1	-0.3	-11.5	11.5	-6.3
x, y, z	5.72	-8.9	-0.8	-23.5	24.4	-15.5
x, y, z	10.16	0.4	-0.0	-1.3	0.1	-0.7

ZEXQAU 1,3,5-tricyanobenzene[12] ($P2_1$, Z'=1.0)

Symop	Dist.	Coul.	Polariz.	Disp.	Repul.	Total
-x, y+1/2, -z	8.57	-15.3	-2.4	-6.2	10.5	-17.0
-x, y+1/2, -z	7.80	-5.6	-1.5	-7.0	4.7	-10.2
x, y, z	3.88	11.1	-4.4	-36.4	19.0	-11.0
-x, y+1/2, -z	7.96	-8.6	-1.6	-6.7	5.5	-12.7
x, y, z	8.64	-16.1	-2.5	-5.5	12.0	-16.5
-x, y+1/2, -z	8.40	-15.3	-2.4	-5.7	12.3	-15.6
x, y, z	7.73	-7.8	-1.6	-7.8	5.9	-12.5

MIRQOV02 4-bromo-3-chlorophenol[13] ($I4_1/a$, Z'=1.0)

Symop	Dist.	Coul.	Polariz.	Disp.	Repul.	Total
x, y, z	3.97	-0.4	-1.2	-34.2	18.0	-19.4
-y+3/4, x+3/4, -z+3/4	6.58	-4.7	-0.3	-8.0	8.8	-6.8
y+3/4, -x+3/4, z+3/4	7.68	-38.3	-9.1	-14.7	50.1	-30.2
y+3/4, -x+3/4, z+3/4	8.17	-1.7	-0.6	-7.4	3.3	-6.5
-y+3/4, x+3/4, -z+3/4	6.10	-3.4	-0.6	-10.7	6.5	-9.1
-x+1/2, -y, z+1/2	10.95	-2.2	-0.3	-1.4	0.0	-3.6
-x, -y, -z	7.83	-2.1	-0.0	-3.8	8.5	-0.4

DCLPHM03 3,4-dichlorophenol[13] ($I4_1/a$, Z'=1.0)

Symop	Dist.	Coul.	Polariz.	Disp.	Repul.	Total
x, y, z	3.85	0.0	-1.0	-33.6	20.7	-16.7
y+1/4, -x+1/4, z+1/4	7.45	-2.6	-0.7	-7.8	3.8	-7.6
y+1/4, -x+3/4, -z+3/4	7.05	-3.3	-0.3	-6.8	7.7	-4.9
-y+1/4, x+3/4, z+3/4	6.94	-40.4	-9.5	-14.1	53.1	-30.4
-x+1/2, -y, z+1/2	9.91	-2.7	-0.3	-1.4	0.0	-4.2
y+1/4, -x+3/4, -z+3/4	6.58	-3.1	-0.6	-9.3	6.8	-7.6
-x, -y, -z	7.74	-3.5	-0.0	-3.7	10.1	-0.9

PFBZCY 4-fluorobenzonitrile[14] ($P\bar{1}$, Z' = 1.0)

Symop	Dist.	Coul.	Polariz.	Disp.	Repul.	Total
-x, -y, -z	6.92	-0.5	-0.2	-6.0	1.0	-5.1
-x, -y, -z	7.49	-4.1	-0.4	-6.7	4.7	-7.5
-x, -y, -z	7.24	-10.8	-2.8	-9.1	6.4	-17.5
x, y, z	3.87	4.4	-0.7	-25.0	11.8	-9.8
x, y, z	6.56	4.6	-0.8	-5.5	1.7	0.6
-x, -y, -z	7.10	-17.4	-3.1	-9.2	11.9	-21.6
-x, -y, -z	7.17	-3.1	-0.6	-7.6	4.9	-7.3
-x, -y, -z	7.29	-1.3	-0.2	-5.7	1.3	-5.5

-x, -y, -z	7.42	-21.2	-4.2	-9.6	15.3	-24.6
-x, -y, -z	6.83	-8.4	-2.4	-9.7	5.5	-15.7

HXACAN12 paracetamol – form I[15] ($P2_1/n$, Z'=1.0)

Symop	Dist.	Coul.	Polariz.	Disp.	Repul.	Total
-x, -y, -z	3.35	-32.9	-7.0	-79.0	95.6	-50.0
x+1/2, -y+1/2, z+1/2	6.45	-49.1	-9.1	-26.6	86.2	-30.3
-x, -y, -z	5.62	-14.8	-2.9	-31.8	33.1	-25.0
-x+1/2, y+1/2, -z+1/2	7.61	-4.1	-1.0	-9.6	16.3	-3.5
x, y, z	6.62	-8.8	-1.2	-6.5	1.2	-15.1
-x, -y, -z	11.23	-0.8	-0.1	-1.4	0.1	-2.0
x+1/2, -y+1/2, z+1/2	7.39	-65.2	-16.3	-15.8	110.8	-29.1
-x+1/2, y+1/2, -z+1/2	6.89	-17.5	-2.6	-21.3	35.0	-17.8
-x, -y, -z	5.64	-9.4	-7.6	-20.0	27.3	-16.3
-x+1/2, y+1/2, -z+1/2	7.85	0.7	-1.2	-8.0	5.6	-3.7

HXACAN23 paracetamol – form II[16] (P*cab*, Z'=1.0)

Symop	Dist.	Coul.	Polariz.	Disp.	Repul.	Total
-x, -y, -z	6.84	-12.6	-2.0	-20.3	7.7	-27.5
x+1/2, -y, -z+1/2	5.13	-8.2	-2.0	-23.5	15.3	-21.0
x+1/2, -y+1/2, z	5.40	-0.0	-1.0	-16.0	9.6	-8.5
x+1/2, -y+1/2, z	8.73	1.8	-0.3	-1.5	0.1	0.4
x, y+1/2, -z+1/2	6.61	-25.9	-5.6	-16.7	32.6	-26.5
-x, -y, -z	7.25	-10.1	-1.9	-14.4	6.7	-20.3
-x+1/2, y, z+1/2	8.59	-51.2	-12.0	-13.4	57.0	-40.9
-x+1/2, y+1/2, -z	8.19	-9.2	-1.7	-9.8	6.8	-15.2

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