

Test suite for NEIGHCRYS_2.0.8 and DMACRYS_2.0.8

This suite provides a set of files for the new installations of NEIGHCRYS_2.0.8 and DMACRYS_2.0.8 and above. The comments, instructions and examples below are to supplement information given in the paper describing the DMACRYS programme¹ and the associated manual, to act as illustrations for users (but not necessarily of best practice, as designed for fast testing).

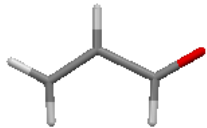
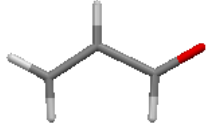
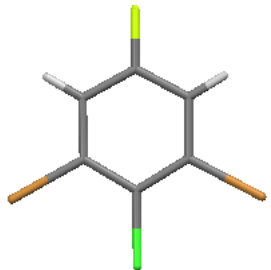
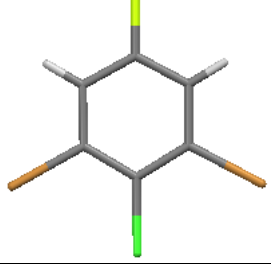
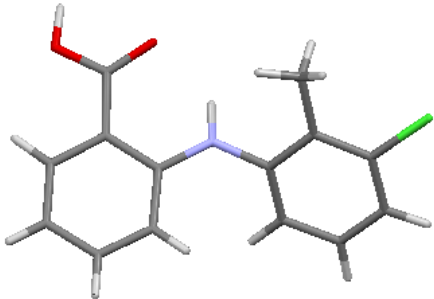
The directory

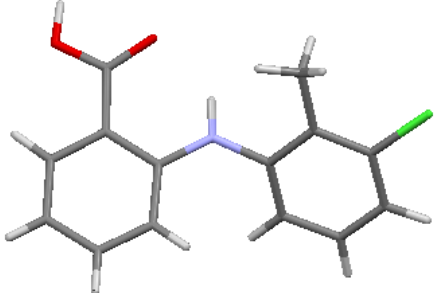
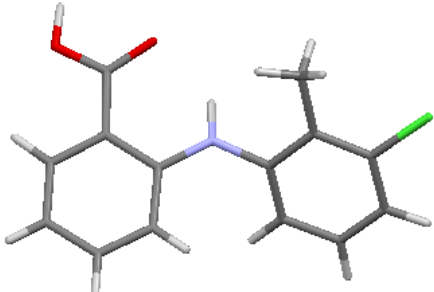
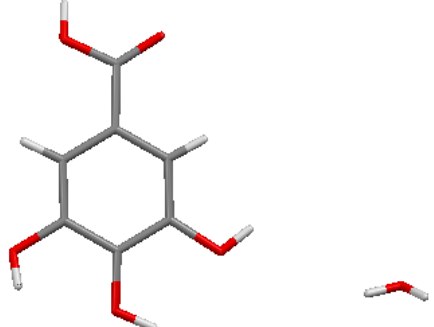
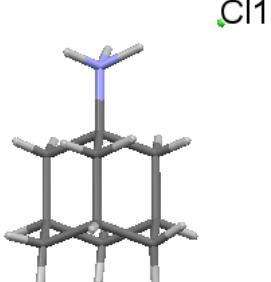
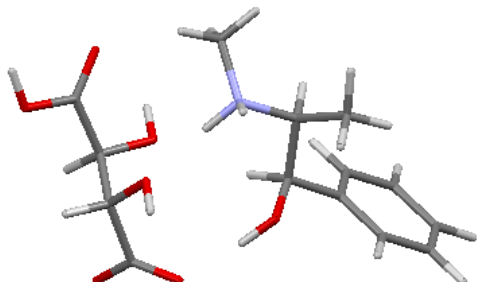
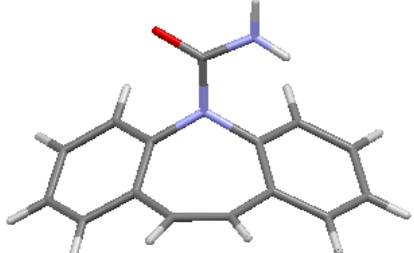
test#_testing_REFCODE contains a README and directories including NEIGHCRYS_input, which contains the input files:

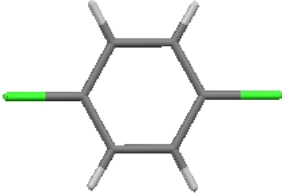
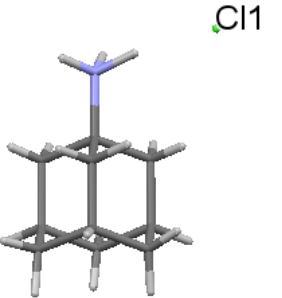
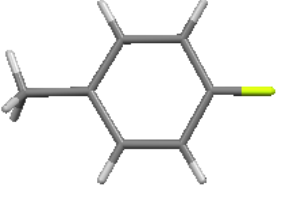
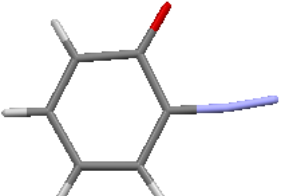
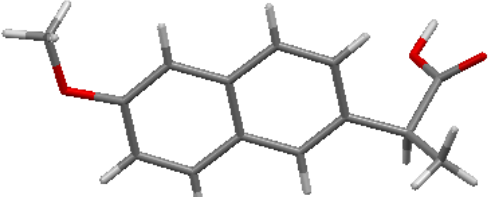
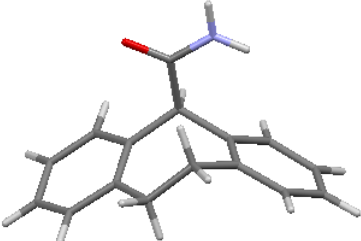
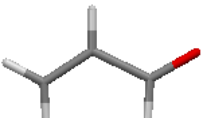
REFCODE.res (Crystal structure), bondlengths (define molecule bonds), dmacrys.dma (Distributed multipoles) dmacrys.mols (Molecular Axes) pote.dat/fit.pots/will101.pots (repulsion-dispersion model).

If you want to run NEIGHCRYS interactively, then the answers you need are in neighcris_answers.

All the test examples were created on Xenon using the above version of the code.

Test#_molecule#	Example of & crystal structure	Molecular diagram
01_I	Lattice energy minimization with FIT exp-6 potential and distributed multipoles. The example files are for a computational model corresponding to AXOSOW	
02_I	Lattice energy minimization with WILLIAMS potential, where interaction sites on H are shifted, as contrast to 01. The example files are for a computational model corresponding to AXOSOW.	
03_II	Lattice energy minimization with a custom potential . The example files are for a computational model corresponding to SOXLEX.	
04_II	Lattice energy minimization with a custom potential and without splines . The example files are for a computational model SOXLEX. The input files for NEIGHCRYS are identical to example 3, but the output file (.dmain) has been edited before running DMACRYS.	
05_III	Lattice energy minimization of a large Z'>1 unit cell with 15 Å cutoff. The example files are from the CSD entry KAXXAI02.	

06_III	<p>Lattice energy minimization of a large $Z' > 1$ unit cell with 15 Å and without splines. The example files are from the CSD entry KAXXAI02. The input files for NEIGHCRYS are identical to example 5, but the output file (.dmain) has been edited before running DMACRYS.</p>	
07_III	<p>Lattice energy minimization of a large $Z' > 1$ unit cell with 30 Å and without splines. The example files are from the CSD entry KAXXAI02. The input files for NEIGHCRYS are identical to example 5, but the output file (.dmain) has been edited before running DMACRYS.</p>	
08_IV	<p>Lattice energy minimization of a small 2 component system. The example files are for a computational model corresponding to KONTIQ01.</p>	
09_V	<p>Lattice energy minimization of a crystal structure containing a spherical ion. The example files are for a computational model corresponding to FINVAZ.</p>	
10_VI	<p>Lattice energy minimization of a complex salt. The example files are for a computational model corresponding to the experimentally observed form of ephedrinium tartrate (CSD code pending).</p>	
11_VII	<p>Properties calculation of a crystal structure. The example files are for a computational model corresponding to CBMZPN10. The NEIGHCRYS output file (.dmain) has been edited before running DMACRYS.</p>	

12_VIII	<p>Properties calculation of a crystal structure using an anisotropic repulsion custom potential. The example files are for a computational model corresponding to DCLBEN06. The NEIGHCRYST output file (.dmain) has been edited before running DMACRYST.</p>	
13_V	<p>Properties calculation of a crystal structure containing a spherical ion FINVAZ. This is also a large cell (C2/c Z=8), so takes longer to run.</p>	
14_IX	<p>Lattice energy minimization with pressure. The example files are for the experimentally observed form at high pressure (0.5 GPa) of 4-fluorotoluene (CSD code pending). The NEIGHCRYST output file (.dmain) has been edited before running DMACRYST to specify the pressure.</p>	
15_X	<p>Lattice energy minimization with induction. The example files are for a computational mode corresponding to OBEQUJ.</p>	
16_XI	<p>Symmetry reduction. The example files are for a computational model corresponding to PAPTUX, which corresponds to a transition state. The run which required this symmetry reduction is given for information in the directory reasons.</p>	
17_XII	<p>Pasting. The example files are for TEVSOD, with a molecule optimized using GAUSSIAN being substituted for the crystallographically determined molecular structure.</p>	
18_I	<p>Using default values. This is a run of NEIGHCRYST which uses the default values for filenames corresponding to AXOSOW.</p>	

I – AXOSOW 01.lem_fit_AXOSOW & 02.lem_will01_AXOSOW

This molecule was set as one of the challenges in the Fourth Blind Test of Crystal Structure Prediction.² The starting files are trial crystal structures generated by MOLPAK, with the distributed multipoles (dma) generated using GAUSSIAN³ and GDMA⁴, as in all these examples.

The examples are given to show the differences in the FIT and Williams exp-6 potentials, whose coefficients are given in pote.dat (generic file type) file called fit.pots or will01.pots respectively. The two potentials do not only differ in the coefficients in pote.dat, but critically in the Williams potential has the hydrogen atom interaction sites moved in along the bonds by 0.1 Å to reflect the position of the centre of electron density. Further details of these two potentials, which are widely used for modelling organic crystals are given in the SI of the DMACRYS paper.¹ The wider range of atomic types and need for NEIGHCRYST to set up the shift the hydrogen interaction site positions for the Williams potential, leads to specific questions in the NEIGHCRYST input. The first difference in the output is the atomic types as seen in the fort.21 (NEIGHCRYST output), which are used to describe the atoms in the dmacryst.mols, dmacryst.dma and potential (fit.pots or will01.pots in these examples).

I_1 – FIT potential					I_2 – Williams potential				
Inequivalent basis atoms					Inequivalent basis atoms				
atom invert index flag	atomic number	name	input name	molecule number	atom invert index flag	atomic number	name	input name	molecule number
F	1	C_F1_1____1____	C1	1	F	1	C_W3_1____1____	C1	1
F	2	C_F1_2____2____	C2	1	F	2	C_W3_2____2____	C2	1
F	3	C_F1_3____3____	C3	1	F	3	C_W3_3____3____	C3	1
F	4	O_F1_1____4____	O1	1	F	4	O_W1_1____4____	O1	1
F	5	H_F1_1____5____	H1	1	F	5	H_W1_1____5____	H1	1
F	6	H_F1_2____6____	H2	1	F	6	H_W1_2____6____	H2	1
F	7	H_F1_3____7____	H3	1	F	7	H_W1_3____7____	H3	1
F	8	H_F1_4____8____	H4	1	F	8	H_W1_4____8____	H4	1

The new hydrogen interactions sites required if Williams and foreshortening are requested in the NEIGHCRYST input are also given in fort.21

```

Hydrogen positions have been foreshortened.
Positions of all atoms (with hydrogens not foreshortened)
in the local axis system and centre of mass of the molecule
with foreshortened hydrogens for molecule 1
    
```

basis No.	Species	x	y	z (Angstroms)	Mass
1	C_W3_1____	-1.458172	-1.140127	0.000053	12.010700
9	C_W3_2____	-0.777841	0.015796	0.000053	12.010700
17	C_W3_3____	0.694194	0.015796	0.000053	12.010700
25	O_W1_1____	1.379974	1.032471	-0.000181	15.999400
33	H_W1_1____	-0.937040	-2.089399	0.001173	1.007940
41	H_W1_2____	-2.537638	-1.172483	0.000416	1.007940
49	H_W1_3____	-1.271744	0.978875	-0.001055	1.007940
57	H_W1_4____	1.158534	-0.988833	0.000507	1.007940

```

Foreshortened hydrogen atom positions in the same
local axis system
    
```

basis No.	Species	x	y	z (Angstroms)	Mass
33	H_W1_1____	-0.985163	-2.001740	0.001069	1.007940
41	H_W1_2____	-2.437683	-1.169487	0.000382	1.007940

etc

This data is used to calculate the distributed multipoles with the H nuclei in the foreshortened positions, using options in GDMA⁴, to analyse the ab initio wavefunction with the H nuclei in their true positions. Hence, the dma's in the two examples differ: not only in the H atom positions and multipoles, but also the non-hydrogen atoms will have the same positions (relative to the local axis system) but different multipoles because of the change in allocation of the electron density between the sites caused by the shift in H positions. However, as shown below, although the various contributions to the lattice energy change, the total electrostatic contribution to the initial lattice energy does not change by much compared with the difference in the repulsion-dispersion potential. Note that the change in potential does make a considerable difference to the structure at the lattice energy minimum.

FIT First evaluation of lattice energy	Williams First evaluation of lattice energy
Contributions to lattice energy [kJ/mol]) Z = 8 Ewald summed charge-charge energy.....= - 0.902441600784E+01[-0.108839591947E+03] Intra-molecular charge-charge energy....= - 0.782278003933E+01[-0.943471784361E+02] Inter-molecular charge-charge energy....= - 0.120163596852E+01[-0.144924135112E+02] Total charge-dipole energy= 0.204224492158E+00[0.246306357916E+01] Total dipole-dipole energy= 0.179726824703E+00[0.216760777048E+01] Total charge-dipole+dipole-dipole energy= 0.383951316861E+00[0.463067134964E+01] Higher multipole interaction energy.....= - 0.753265264345E+00[-0.908480769593E+01] Total isotropic repulsion-dispersion....= - 0.200738449184E+01[-0.242101991734E+02] Total anisotropic repulsion energy.....= 0.000000000000E+00[0.000000000000E+00] Intermolecular induction energy.....= 0.000000000000E+00[0.000000000000E+00] Total lattice energy.....= 0.357833440784E+01[-0.431567490309E+02]	Contributions to lattice energy (eV per unit cell [kJ/mol]) Z = 8 Ewald summed charge-charge energy.....= - 0.76909972E+01[-0.92757803E+02] Intra-molecular charge-charge energy....= - 0.67563847E+01[-0.81485844E+02] Inter-molecular charge-charge energy....= - 0.93461253E+00[-0.11271959E+02] Total charge-dipole energy= 0.39674038E-02[0.47849147E-01] Total dipole-dipole energy= 0.14317093E+00[0.17267229E+01] Total charge-dipole+dipole-dipole energy= 0.14713833E+00[0.17745720E+01] Higher multipole interaction energy.....= - 0.74209737E+00[-0.89501165E+01] Total isotropic repulsion-dispersion....= - 0.21696973E+01[-0.26167785E+02] Total anisotropic repulsion energy.....= 0.00000000E+00[0.00000000E+00] Intermolecular induction energy.....= 0.00000000E+00[0.00000000E+00] PV energy.. (P = 0.00E+00 Pa)..... 0.00000000E+00[0.00000000E+00] Total lattice energy.....= 0.36992689E+01[-0.44615288E+02]
Total Electrostatic contribution -18.94 kJ/mol	Total Electrostatic contribution -18.45 kJ/mol

II – SOXLEX 03.lem_custom_spli_SOXLEX & 04.lem_custom_nospli_SOXLEX

This example shows how the user makes their own definition of the atomic types, and uses an anisotropic atom-atom repulsion potential. This crystal structure was set as one of the challenges in the Fourth Blind Test of Crystal Structure Prediction.² The starting files are trial crystal structures generated by MOLPAK, with the dma generated using GAUSSIAN³ and GDMA.⁴ The repulsion dispersion potential was generated using SAPT(DFT).⁵

A custom potential has different atomic types from FIT or WILLIAMS. The labels file lists all atoms from the input crystal structure file and assigns them the potential types which are used in the dmacryst.mols, dmacryst.dma and potential (pote.dat) files.

The labels file, defining atomic types	
Br2	BR
Br1	BR
Cl	CL
F	FL
C1	CA
C3	CC
C4	CA
C5	CB
H1	HY
C6	CD
C2	CB
H2	HY

The anisotropic atom-atom repulsion potential requires the definition of a local axis system for each atom, and the anisotropic potential needs to be defined for every pair of atom types:

Starting excerpt from dma .mol.s file, showing definition of local axis on a Cl atom

```
MOLX 1
X LINE C_CC_2_____ C_CD_5_____ 3
Y PLANE C_CC_2_____ C_CD_5_____ 3 C_CA_1_____ 1
ANIS
ClCL 1
Z LINE C_CC_2_____ ClCL_1_____ 1
X PLANE C_CC_2_____ C_CA_1_____ 1 C_CB_6_____ 2
C CC 2
```

Excerpt from pote .dat file, showing the anisotropic repulsion potential for Br...Br

```
BUCK BrBR BrBR
2662.410975 0.330736 120.676039 0.0 70.0
ANIS BrBR BrBR
0 0 0 1 1 0.122057
0 0 1 0 1 0.122057
0 0 0 2 2 -0.237815
0 0 2 0 2 -0.237815
ENDS
```

The output has

```
Total isotropic repulsion-dispersion....= -5.9036[ -142.4005 ]
Total anisotropic repulsion energy.....= 2.7395[ 66.0805 ]
```

which is slightly misleading as when a custom (anisotropic) repulsion is used, all the repulsion, isotropic and anisotropic, comes to 66.0805 kJ/mol and the dispersion contribution is -142.4005 kJ/mol.

NEIGHCRYS automatically sets up the limits used in summing the contributions to the lattice energy. These are a compromise between timing and accuracy and may need changing for different studies. Splines have been introduced rather than abrupt cutoffs in the direct space summations, so to give continuous first derivatives. The effect of splines using the default cutoff (see next example III) is shown, with examples 3 and 4 respectively. The line to bring the splines into play is automatically written out into the .dmain file.

SPLI 2.0 4.0

This is manually removed from example 4, so that the repulsion-dispersion energy stops abruptly at 15 Å, which is only marginally longer than the c vector. The effect of the splines is expected to be much larger for this molecule than for III or other C/N/O/H molecules, because the dispersion coefficients for Br and Cl are much larger than for first row atoms, their repulsion is longer range, and they have significant atomic quadrupoles, so the inter atomic potentials at the cutoff can be much larger and not necessarily attractive.

II_3 – With splines	II_4 – Without splines
Initial Lattice Energy: -84.704124 kJ/mol	Initial Lattice Energy: -85.897522 kJ/mol
Final Lattice Energy: -85.195328 kJ/mol	Final Lattice Energy: -86.161606 kJ/mol
gamma a b c alpha beta	gamma a b c alpha beta
Initial => 3.805200 13.790700 14.531400	Initial => 3.805200 13.790700 14.531400
90.000000 93.780000 90.000000	90.000000 93.780000 90.000000
Final => 3.843485 14.005488 14.508371	Final => 3.828604 13.884086 14.640547
90.000000 92.586202 90.000000	90.000000 94.491295 90.000000
F = 8.520573	F = 2.759047
Total run time..... 22.320000	Total run time..... 4.970000

III – KAXXAI02 05.largecell_KAXXAI , 06.largecell_KAXXAI_nospli and 07.largecell_KAXXAI_30ang

This example illustrates the use of experimental X-ray structures as input, including when there are two symmetry independent molecules in the asymmetric unit cell. Test 5 uses summation defaults, which are contrasted with other treatments of the direct summation in tests 6 and 7. This molecule, tolfenamic acid, was studied as part of a series of fenamic acids.⁶ The starting file was the crystal structure determination from the CSD, but with the atoms renumbered (to conform to the numbering scheme used in the rest of the series).

Since this is an experimental X-ray structure, the positions of the hydrogen atoms suffer from the systematic foreshortening of bonds to hydrogen. NEIGHCRYS has the question

Do you want to standardise bond lengths to hydrogen?

and the response $y(es)$ will automatically change the hydrogen atomic positions by elongating the bond lengths to hydrogen to standard neutron values⁷. This can make a considerable difference to the results of the modelling. The hydrogen atom positions do not need correcting if the crystal structure has been determined by neutron diffraction, or the molecular structure obtained by ab initio optimisation, as the bond lengths to hydrogen should be similar or more accurate.

Although the two molecules in the asymmetric unit are the same, the axis system must be defined for each molecule, and the distributed multipoles calculated separately for each molecule to reflect the differences in conformation. Generating the dma for a two-component system requires generation of each dma separately (using GAUSSIAN³ and GDMA⁴) and the two combined using `gdmaneighcrys` (supplied with the DMACRYS/NEIGHCRYS release bundle).

Definition of axis system for two molecules

```
MOLX 2
X LINE C_F1_2_____ C_F1_5_____ 3
Y PLANE C_F1_2_____ C_F1_5_____ 3 N_F1_1_____ 2
X LINE C_F1_16_____ C_F1_19_____ 3
Y PLANE C_F1_16_____ C_F1_19_____ 3 N_F1_2_____ 2
ENDS
```

Note that corresponding atoms have been used to define the axis system. However, as the molecules differ in the central torsion angle and hence centre of mass, so there are differences in the coordinates of all atoms in the local axis system.

Contrasting the .dma entry for two equivalent atoms in the same molecule.

```
2 C_F1_2_____ -0.742683 5.289326
0.071526 Next 3 Limit 4
-0.059318
0.002371 -0.008579 -0.044884
-1.263432 -0.020244 -0.019694 0.061451 -
0.020968
-0.015451 -0.320041 -0.143841 0.004144 -
0.033650 -1.111576 0.161357
-1.713140 -0.048270 -0.074806 0.249255 -
0.226941 0.032375 -0.002643
-0.079820 -0.184937
```

```
32 C_F1_16_____ -0.518412 5.187897 -
0.826132 Next 33 Limit 4
-0.063162
0.007418 -0.007997 -0.047917
-1.276015 -0.042648 -0.007954 0.063306 -
0.011778
-0.016989 -0.312273 -0.146901 0.026483
0.015987 -1.112546 0.153051
-1.770809 -0.095468 0.051984 0.271955 -
0.220172 0.021388 -0.011882
-0.083770 -0.195849
```

The molecule itself is quite large, having a distance of 9.79 Å between the two most separated hydrogen atoms. The cutoff over which DMACRYS calculated intermolecular interactions is written in the .dmain file by NEIGHCRYS. By default, the limit of the repulsion-dispersion potential is 15 Å, and the higher multipole contributions are calculated for all atoms in molecules whose centre of mass are within 15 Å. The limit of the repulsion-dispersion in the potential file can be greater than this (it is 70 Å in the files provided with the distribution), but it is overridden by the .dmain. Ideally the summation limits should not be exactly an integer number of lattice vectors.

The three examples given for the lattice energy minimization of KAXXAI02 are (5) with NEIGHCRYS defaults of 15 Å cutoffs and splines, (6) with NEIGHCRYS default of 15 Å cutoffs, but no splines and (7) with a longer 30 Å cutoff and no splines. Note that since DMACRYS does not know that the two molecules in the asymmetric unit cell are the same molecule, all lattice energies need to be divided by 2 to be strictly in kJ/mol and comparable with the lattice energy of the Z'=1 polymorphs of tolfenamic acid.

III_5 – 15 Å cutoff and splines	III_6 – 15 Å cutoff without splines	III_7 – 30 Å cutoff without splines
CUTO 28.065000 0.534474 RDMA 0.534474 . . . SPLI 2.0 4.0	CUTO 28.065000 0.534474 RDMA 0.534474 . . .	CUTO 28.065000 1.068948 RDMA 1.068948 . . .
Initial Lattice Energy -268.529824 kJ/mol Final Lattice Energy: -276.429253	Initial Lattice Energy -267.352430 kJ/mol Final Lattice Energy: -275.316083	Initial Lattice Energy: 272.043168 kJ/mol Final Lattice Energy: -279.909713
alpha beta gamma c Initial => 7.635600 11.305000 28.065000 90.000000 93.030000 90.000000 Final => 7.742007	alpha beta gamma c Initial => 7.635600 11.305000 28.065000 90.000000 93.030000 90.000000 Final => 7.749326	alpha beta gamma c Initial => 7.635600 11.305000 28.065000 90.000000 93.030000 90.000000 Final => 7.745189

11.545649 27.864126 90.000000 91.269169 90.000000	11.562909 27.844601 90.000000 91.253097 90.000000	11.525954 27.890310 90.000000 91.246592 90.000000
F = 20.473941	F = 22.245230	F = 19.773173
Total run time... 81.489998	Total run time... 66.949997	Total run time 442.360016

When calculating the interatomic interactions over a larger number of molecules (example 7 with 30 Å limits to interaction calculation), the accuracy of the calculation is much greater as the longer range interactions are included, but the time taken is much longer. Increasing the cutoff or adding splines usually makes the lattice energy slightly lower because the attractive dispersion is the longest range contribution.

IV – KONTIQ01 **08.2comp_KONTIQ**

This illustrates using two different molecules in the asymmetric unit, with one being water. Gallic acid monohydrate was set as one of the challenges in the Fifth Blind Test of Crystal Structure Prediction,⁸ to predict the structures of two new polymorphs, with this structure and that of another polymorph were already published. It also had the complication of being a hydrate. Further screening resulted in characterising a further monohydrate, i.e. five polymorphs in all⁹.

The starting files in this example are from the end point of a CrystalOptimizer calculation, which optimizes the molecular conformation and crystal lattice together, including generating the .dma using GAUSSIAN³ and GDMA⁴ for sufficient conformations that a database can be used to speed these calculations over a large set of crystal structures.¹⁰ Note that `gdmaneighcrys` has to be used as part of the process to combine the gallic acid and water dmas.

DMACRYS automatically assigns hydrogen atoms in water molecules as a different atomic type – H_Wa. The *exp-6* potential used for the water hydrogens was the same as for other polar hydrogen atoms in this case, but a different potential could have been chosen for H_Wa without the need to use a custom potential and `labels` file. Since the `pote.dat exp-6` input is required for each pair of atomic types, the `crosspot` utility supplied with the DMACRYS/NEIGHCRYST release bundle is useful for generating the unlike interaction parameters using the combining rules for extensions to the *exp-6* potentials of the FIT or Williams type.

V – FINVAZ **09.salt_FINVAZ & 13.properties_FINVAZ**

Amantidine hydrochloride is an example of a lattice energy minimization, using the Williams potential, of a salt containing a spherical ion. In this case, the dma is generated for the molecular ion using GAUSSIAN³ and GDMA⁴ and the resulting `dmacrys.dma` file is manually edited to add the unit negative charge for the chloride ion. Rotations of the spherical chloride ion are meaningless; hence it does not require an axis system etc. It is also an example of a centred cell, C2/c (Z=8, Z'=1).

Salts such as FINVAZ have lattice energies that are orders of magnitude more stabilising than neutral systems, because of the high electrostatic interaction between the two species in the crystal. Nonetheless, as the properties calculation shows, such structures still have phonon modes of comparable frequencies to neutral organic molecules.

VI – Ephedrinium Tartrate **10.largesalt_EphTart**

Ephedrinium Tartrate is provided as an example of a lattice energy minimization of a salt with two large molecular components. It is a structure where the hydrogen atoms were positioned following a CSP study.¹¹ The same considerations as in previous examples should be made, namely it has large lattice energy, the dma needs to be calculated separately for the two species and combined using `gdmaneighcrys`.

VII – CBMZPN10 **11.properties_CBMZPN**

DMACRYS can calculate the second derivative properties of the crystal at the lattice energy minimisation, namely the elastic constants¹² and k=0 phonon frequencies¹³. This is done with accurate second derivatives of the lattice energy,

not the estimates made by updating the Hessian matrix used within the lattice energy minimisation. (These estimated second derivatives are used to calculate an approximate elastic constant matrix and eigenvalues of the Hessian to tests whether the Born stability criterion is met, or whether the structure is a transition state, see **15.symmred_PAPTUX**). The elastic tensor is usually aligned so that z is along c , x is parallel to a and y is in the ab plane, but please check fort.21 for higher symmetry space groups. The lowest eigenvalue and eigenvector of the shear submatrix is calculated as a guide to whether the crystal has a particularly weak plane. A range of properties of a microcrystalline aggregate, by various approximate averaging procedures,¹⁴ are also reported.

The example of properties calculation with the FIT potential is for the most stable polymorph of carbamazepine (form III). The example files here are a lattice energy minimum found in a rigid molecule CSP study of carbamazepine.

In order to calculate second derivative properties, it is usual to start at a lattice energy minimum (fort.16 from a previous standard lattice energy minimisation run) to save the time in minimising with the more expensive and accurate 2nd derivatives calculation. This is why the example output has only the lattice energy changes so very little in the fort.12 and why the goodness of fit (F) is so low.

To run a properties calculation, following a NEIGHCRYST run starting from an estimated lattice energy minimum, the *.domain must be edited to change the line that said "STAR PLUT" to say "STAR PROP" and remove the NOPR directive so that the program uses the most accurate second derivatives.

Output from properties calculations		
<pre> Zone Centre Phonon Frequencies THz cm-1 ----- 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 1.2715 42.4141 1.3658 45.5581 1.4236 47.4857 1.5035 50.1501 1.6128 53.7974 1.6132 53.8118 1.7330 57.8069 2.0262 67.5881 2.0910 69.7474 2.2975 76.6369 2.4734 82.5041 2.5333 84.5007 2.6044 86.8744 2.7490 91.6966 3.0035 100.1871 3.0663 102.2823 3.1611 105.4436 3.2440 108.2097 3.8346 127.9073 3.9122 130.4982 4.0298 134.4190 </pre>		The first 3 frequencies should be zero, to within numerical error.
MECHANICAL PROPERTIES CALCULATED FROM HESSIAN MATRIX		
<pre> Elastic stiffness tensor (Cij): GPa (10**10 DYNE/CM**2) 16.85742 7.82589 9.42895 0.00000 -3.48991 0.00000 7.82589 32.49149 3.46721 0.00000 0.33086 0.00000 9.42895 3.46721 13.70514 0.00000 -0.68556 0.00000 0.00000 0.00000 0.00000 5.98553 0.00000 -0.63183 -3.48991 0.33086 -0.68556 0.00000 11.34792 0.00000 0.00000 0.00000 0.00000 -0.63183 0.00000 11.40048 Born stability criteria satisfied. Lowest eigenvalue of shear submatrix of Cij = 5.91278 GPa Corresponding eigenvector 0.99344 0.00000 0.11438) Elastic compliance tensor (Sij): GPa^(-1) (10**(-10) CM**2/DYNE) 0.11653 -0.02056 -0.07337 0.00000 0.03200 0.00000 etc </pre>		
<pre> Mechanical properties calculated for a microcrystalline aggregate. Bulk modulus from elastic constants (Voigt averaging): 11.61091 GPa Bulk modulus from compliance constants (Reuss averaging): 10.51222 GPa Arithmetic mean: 11.06156 GPa Geometric mean: 11.04792 GPa </pre>		

```

Shear modulus from elastic constants (Voigt averaging):      8.56892 GPa
Shear modulus from compliance constants (Reuss averaging):   5.97644 GPa
Arithmetic mean:      7.27268 GPa
Geometric mean:      7.15623 GPa

Young's modulus from elastic constants (Voigt averaging):   20.63139 GPa
Young's modulus from compliance constants (Reuss averaging): 15.07289 GPa
Arithmetic mean:     17.85214 GPa
Geometric mean:     17.63447 GPa

Poisson's ratio from elastic constants (Voigt averaging):   0.20385 GPa
Poisson's ratio from compliance constants (Reuss averaging): 0.26103 GPa
Arithmetic mean:     0.23244 GPa
Geometric mean:     0.23067 GPa

Single crystal Young's modulus along optical axes      x-component:      8.58139 GPa
y-component:      28.34249 GPa
z-component:      8.23443 GPa
arithmetic mean:  15.05277 GPa

```

Experimental elastic constants and phonon frequencies are often not available, and the main reason for calculating these properties is to estimate the zero-point vibrational energy and thermal contribution to the Helmholtz free energy. In this example, the resulting *.dmaout file has been automatically analysed to extract the phonon frequencies¹³ and elastic constants,¹² and the following thermodynamic information calculated, using scripts provided by G.M. Day and not currently included in the release bundle.

```

-----
Average linearly extrapolated Debye frequency:
(scaled by 1.0000000000000000 )
wD (cm-1) = 59.7994633142861

Average sinusoidally extrapolated Debye frequency:
(scaled by 1.0000000000000000 )
wD (cm-1) = 45.4104876562236
!! Using this value for the Debye frequency !!

Zero-Point Energy Calculations:
ZPE from optical modes (kJ/mol) = 2.57125581837337
ZPE from acoustic modes (kJ/mol) = 0.152783664528630
Total ZPE (kJ/mol) = 2.72403948290200
-----

entropy worked out for T (K) = 298.0000000000000
-----
Entropy from optical modes (J/molK) = -87.2014797921121
Debye x = 0.219245423550902
Debye function = 0.920179181281333
kD(x) bit = -1.91271384878878
entropy from acoustical modes (J/molK) :
from Debye fiunction bit (J/molK) = -2.07365235325527
from other bit (J/molK) = -15.7117385516701
Total Entropy (J/molK) = -104.986870697037

thermal energy worked out for T (K) = 298.0000000000000
-----
thermal E from optical modes (kJ/mol) = -15.3601705071603
thermal E from -kTD(x) (kJ/mol) = -0.569988726939055
thermal E from second bit (kJ/mol) = -3.02007482748696
Total Thermal Energy (kJ/mol) = -18.9502340615863
-----
Vibrational Free Energy (including ZPE):
Fvib (kJ/mol) = -16.2261945786843
-----

```

VIII – DCLBEN06 12.properties_DCLBEN

This is an example of a properties calculation for the β triclinic P-1 $Z'=0.5$ polymorph of dichlorobenzene with a custom potential using a non-empirically derived atom-atom repulsion-dispersion potential for anisotropic chlorine.¹⁵ This illustrates the more accurate type of potential that is likely to be needed for studying properties which are very sensitive to the 2nd derivatives, as shown by the comparison with the recorded low temperature spectrum.¹⁶

VIII_12 from .dmaout file	Experimental room temperature spectrum ¹⁶
Zone Centre Phonon Frequencies THz cm-1 ----- -----	cm ⁻¹

0.0000	0.0000	Three zero frequency modes, translating entire crystal 56 65 103 – Fortuitously close!			
0.0000	0.0000				
0.0000	0.0000				
1.4666	48.9189				
1.9984	66.6591				
3.1028	103.4993				
Only one molecule in the unit cell gives few lattice modes, but the triclinic cell has a full elastic tensor					
Elastic stiffness tensor (Cij): GPa (10**10 DYNE/CM**2)					
23.57874	9.55220	5.96077	3.17326	-2.29635	-3.47447
9.55220	17.02894	6.33804	1.94510	-0.82292	-3.71923
5.96077	6.33804	13.71527	-1.57968	0.12684	0.12077
3.17326	1.94510	-1.57968	4.31041	-0.55520	-2.31399
-2.29635	-0.82292	0.12684	-0.55520	3.43367	2.74291
-3.47447	-3.71923	0.12077	-2.31399	2.74291	9.09302

IX - 4-fluorotoluene 14.press_4FT

The starting file in this example is a crystal structure determination where the liquid was forced to crystallize at high pressure and the X-ray data collected under those extreme conditions.¹⁷

Following the NEIGHCRYST run, the .dmain needs to be edited to add a line to include pressure. "PRES 0.5 GPa" after the CONP directive.

The resulting lattice energy from the fort.12 is very high because it includes the PV term.

```
Initial Lattice Energy:      -11.438620 kJ/mol
Final Lattice Energy:      -11.969846 kJ/mol
```

X – OBEQUIJ 15.induction_OBEQUIJ

This illustrates the calculation of induction energy and lattice energy minimisation, including this term. The inclusion of damped induction and dispersion up to C₁₀ are new features of DMACRYST for research work on using non-empirical potentials.

This molecule was set as one of the challenges in the Fifth Blind Test of Crystal Structure Prediction.¹⁸ The example uses the *ab initio* optimised molecular structure and has a non-empirical potential (c.f. SOLEX⁵ derived using CamCASP¹⁹) which has been fitted excluding the induction energy. The modelling of the induction energy using a distributed dipolar polarisability model¹ is the novel feature of this example. The molecular structure, atomic multipole moments, dipolar polarisability tensors and atom-atom isotropic C₆ dispersion coefficients were derived from the PBE0 exchange-correlation functional and the Sadlej pVTZ basis set with the Tozer-Handy asymptotic correction. The CUSTOM repulsion-dispersion model assumed that the parameters were transferable between all hydrogens and the four carbon atoms bonded to hydrogen (see labels file). This proved to be a lousy model potential, giving rise to considerable slippage in the *ab* plane, from deficiencies in the repulsion-dispersion potential. The c vector is large, so a larger cutoff should be used, but this significantly increases the computer time.

It is included here as a severe test of reproducibility, as the induction energy has to be iterated to convergence, and hence the structure optimisation uses numerical gradients.

The distributed dipolar polarisabilities are in the file `dmacrys.dma.pol`, which starts:

```
# Static polarizabilities
1 C C1_1_____ -0.277986 -1.883193 -0.000535 RANK 1
2.46610
0.00000 14.52040
0.00000 4.63450 12.08170
```

```

2      C_C2_2_____ 0.816974 0.674908 -0.000979      RANK 1
2.67470
0.00000      23.67240
0.00000      4.44500      17.25500

```

This is automatically read-in by NEIGHCRYG provided that the need for induction is specified near the start of the dmacryst.mols file by specifying the induction damping coefficient DIND, for example

```

MOLX 1
X LINE C_C2_2_____ N_N1_1_____ 1
Y PLANE C_C2_2_____ N_N1_1_____ 1 O_O1_1_____ 2
DIND 1.0885
ANIS
C_C1_1_____
Z LINE C_C1_1_____ O_O1_1_____ 1
X PLANE C_C1_1_____ O_O1_1_____ 1 C_C2_2_____ 1

```

In the dmacryst.out file, the polarisabilities are not written out, but the phrase “Induction damping has been requested” precedes the damping parameters. The induction calculation at the starting structure reports

```

First order induced moments (atomic units)
Atom Label      Q10      Q1c      Q1s
C_C1_1_____1_____ -0.003618019 0.011915082 0.075723632
C_C1I14_____17_____ 0.003659108 0.012115435 0.075643569
C_C2_2_____2_____ -0.008601462 0.138004038 0.154284011

N_N1_1_____7_____ -0.009497820 0.016845367 0.049625221
N_N1I14_____59_____ 0.009513033 0.016922579 0.049644818
N_N2_2_____8_____ -0.024404194 -0.047145134 0.040705569
N_N2I15_____66_____ 0.024388017 -0.047137808 0.040703261
O_O1_1_____9_____ 0.005452855 -0.012324706 0.096145953
O_O1I14_____73_____ -0.005383297 -0.012226963 0.096193965

H_H1_4_____13_____ -0.003580690 -0.001161334 -0.005492413
H_H1I17_____101_____ 0.003580690 -0.001161334 -0.005492413
First-order induction energy -6.75003928 kJ/mol.
Converged induced moments (atomic units)
Atom Label      Q10      Q1c      Q1s
C_C1_1_____1_____ -0.006423281 0.032454810 0.128510449
C_C1I14_____17_____ 0.006463160 0.032676110 0.128436206
C_C2_2_____2_____ -0.013723857 0.185627239 0.217968361

N_N1_1_____7_____ -0.011619401 0.039442211 0.071658801
N_N1I14_____59_____ 0.011628866 0.039553683 0.071667897
N_N2_2_____8_____ -0.023443637 -0.050708568 0.062899819
N_N2I15_____66_____ 0.023400666 -0.050696022 0.062898751
O_O1_1_____9_____ 0.010593229 -0.011870327 0.151073536
O_O1I14_____73_____ -0.010525595 -0.011761586 0.151121370

H_H1_4_____13_____ -0.002412628 0.001558641 -0.004513140
H_H1I17_____101_____ 0.002415335 0.001564600 -0.004504335
Induction energy converged to -9.67687497 kJ/mol with 16 iterations.

```

The induced dipole moments should be modest, reflecting the atoms which are most polarisable, with the induction energy being stabilising and converge in a reasonable number of iterations. The induction energy is written out as a component of the initial and final lattice energy. The initial energies and induced moments should be well reproduced, but minor discrepancies in the final structure and energy may just reflect numerical noise.

XI – PAPTUX 16.symmred_PAPTUX

Lattice energy minimisation within the constraints of space group symmetry may lead to a structure which is not a true minimum, as detected by considering the eigenvalues of the second derivative matrix (~Born stability criterion). When this happens, then another run in a lower symmetry space-group, usually with more independent molecules in the asymmetric unit cell is required. This example shows the ability of NEIGHCRYG to generate the required new input files and run in lower symmetry.

The anti-inflammatory naproxen was studied because the structure of the marketed enantiopure form was known but not that of the racemate.²⁰ The crystal energy landscape showed that the racemic form was more stable, but experimentally it proved impossible to obtain single crystals, so this structure had to be determined from powder X-ray diffraction. A good match to the experimental data was obtained by the global minimum of the lattice energy

landscape. However this $Z'=1$ structure had a negative eigenvalue of the Hessian, showing that it was a saddlepoint. This example demonstrates how the symmetry was lowered to give a true minimum, requiring a second run of NEIGHCRY and DMACRY to give a $Z'=2$ structure with the small energy lowering (~ 1 kJ/mol). Solid state NMR was used to confirm that structure was indeed $Pbca$ $Z'=1$, confirming the estimate that even the zero-point motions would average over the $Z'=2$ $Pca2_1$ lattice energy minima.

The files in the directory “reasons” are the original NEIGHCRY and DMACRY runs, showing the fort.12 detects that the structure is not a true minimum.

```
Warning - Non-zero eigenvalues found.
A subgroup has a lower energy structure
```

To find the correct eigenvalue (\sim symmetry element) to remove, the *.dmaout must be inspected. The relevant section looks like this.

```
EIGENVALUES FOR REPRESENTATION 1
 0.54650502E+01  0.10481546E+02  0.21290296E+02  0.28917696E+02  0.32665817E+02
 0.58644383E+02
EIGENVALUES FOR REPRESENTATION 2
-0.41450441E-13  0.41518084E+01  0.88544347E+01  0.26923507E+02  0.34152402E+02
 0.40821128E+02
EIGENVALUES FOR REPRESENTATION 3
-0.13300398E+01 -0.32657923E-13  0.84672024E+01  0.15557203E+02  0.22004708E+02
 0.55791236E+02
EIGENVALUES FOR REPRESENTATION 4
 0.80338413E+01  0.26385298E+02  0.30846372E+02  0.39298905E+02  0.63013076E+02
 0.74101157E+02  0.99168983E+02
EIGENVALUES FOR REPRESENTATION 5
-0.97659751E-13  0.10670319E+02  0.14970517E+02  0.24856469E+02  0.29173921E+02
 0.93092617E+02
EIGENVALUES FOR REPRESENTATION 6
 0.91597015E+01  0.24384229E+02  0.39156310E+02  0.39567166E+02  0.50352782E+02
 0.79676533E+02  0.92017084E+02
EIGENVALUES FOR REPRESENTATION 7
 0.75539446E+01  0.20717243E+02  0.32381773E+02  0.42148530E+02  0.48681344E+02
 0.73599869E+02  0.76395535E+02
EIGENVALUES FOR REPRESENTATION 8
 0.93938906E+01  0.20073049E+02  0.28795828E+02  0.39379251E+02  0.45250889E+02
 0.71109111E+02  0.11489723E+03  0.15932457E+03  0.38660931E+03
```

In the next NEIGHCRY run, the eigenvalue that is negative should be removed. In this case, the eigenvalue for representation 3 is negative and is the relevant one. (There are always 3 eigenvalues that are zero to within numerical error, for translation of the entire crystal. These are not exactly zero and so may also be negative, and here are in representations 2, 3 and 5). It can sometimes be the case that there are 2 negative eigenvalues, and it is recommended that you remove the larger magnitude one first, reoptimize the structure, check the output, and run NEIGHCRY again to remove the other if necessary. You should never need to remove the last representation on the list as this is the totally symmetric representation.

The subsequent run (15.symmred_PAPTUX) of NEIGHCRY is distinguished by using this value 3 to answer the questions

```
Input zero for no symmetry subgroup or n to remove representation n
3
CVECTOR
 5.516700000000000

Symmetry reduction for representation 3 complete
input zero to end symmetry reduction or n to remove new representation n
0
```

which produces the files with parameters for two independent naproxen molecules: dmacrys.new.mols as a replacement to be used instead of the dmacrys.mols and dmacrys.new.dma instead of dmacrys.dma. These files are needed as input if it proves necessary to remove another representation. However, in this example, at the end of the run, a true minimum has been reached, with the fort.12 summary file stating

```
Valid minimisation - converged on gradients
```

```
Elastic properties and eigenvalue calculation is exact
```

Change in Hessian matrix during run 16.symmred_PAPTUX				
At the start of the run with reduced symmetry, we have the negative evalue appearing in the totally symmetric repr				
EIGENVALUES FOR REPRESENTATION 1				
0.54650502E+01	0.91597015E+01	0.10481546E+02	0.21290296E+02	0.24384229E+02
0.28917696E+02	0.32665817E+02	0.39156310E+02	0.39567166E+02	0.50352782E+02
0.58644383E+02	0.79676533E+02	0.92017084E+02		
EIGENVALUES FOR REPRESENTATION 2				
-0.10658141E-13	0.41518084E+01	0.80338413E+01	0.88544347E+01	0.26385298E+02
0.26923507E+02	0.30846372E+02	0.34152402E+02	0.39298905E+02	0.40821128E+02
0.63013076E+02	0.74101157E+02	0.99168983E+02		
EIGENVALUES FOR REPRESENTATION 3				
0.63948846E-13	0.75539446E+01	0.10670319E+02	0.14970517E+02	0.20717243E+02
0.24856469E+02	0.29173921E+02	0.32381773E+02	0.42148530E+02	0.48681344E+02
0.73599869E+02	0.76395535E+02	0.93092617E+02		
EIGENVALUES FOR REPRESENTATION 4				
-0.13300398E+01	0.14210855E-13	0.84672024E+01	0.93938906E+01	0.15557203E+02
0.20073049E+02	0.22004708E+02	0.28795828E+02	0.39379251E+02	0.45250889E+02
0.55791236E+02	0.71110911E+02	0.11489723E+03	0.15932457E+03	0.38660931E+03
In the final report of the eigenvalues in symmetry reduction, we have a true minimum (only 3 zero evalues)				
EIGENVALUES FOR REPRESENTATION 1				
0.62680772E+01	0.89952291E+01	0.10903154E+02	0.21908583E+02	0.24681628E+02
0.25629980E+02	0.29330432E+02	0.37671919E+02	0.38987639E+02	0.51046738E+02
0.59844206E+02	0.78535927E+02	0.95165605E+02		
EIGENVALUES FOR REPRESENTATION 2				
0.31974423E-13	0.43703821E+01	0.87931586E+01	0.90192465E+01	0.27052593E+02
0.27245421E+02	0.30550234E+02	0.32999872E+02	0.35867014E+02	0.42662430E+02
0.58564032E+02	0.74675276E+02	0.10538158E+03		
EIGENVALUES FOR REPRESENTATION 3				
0.35527137E-13	0.80485980E+01	0.10746691E+02	0.15317116E+02	0.21028929E+02
0.23662088E+02	0.28288178E+02	0.34125368E+02	0.38653148E+02	0.49171768E+02
0.69782052E+02	0.73530099E+02	0.92088627E+02		
EIGENVALUES FOR REPRESENTATION 4				
0.00000000E+00	0.28642763E+01	0.87958050E+01	0.91281972E+01	0.16181755E+02
0.19060596E+02	0.20481150E+02	0.28147532E+02	0.39877171E+02	0.42059829E+02
0.50375993E+02	0.77332452E+02	0.11656845E+03	0.15452157E+03	0.39131260E+03

Note that in symmetry reduction, although the resulting structure is $Z'=2$, the lattice energy had not been doubled, but is only slightly lower (i.e. lattice energy at the saddle point is -134.14 kJ/mol (Initial energy=Final energy in initial minimisation in `reason`) and at the minimum is -134.714kJ/mol). This is done so that automated symmetry reduction, as part of a CSP study, keeps all the structures on the same energy scale.

XII – TEVSOD 17.pasting_TEVSOD

The NEIGHCRYST / DMACRYST combination is used for minimizing experimental crystal structures holding the conformation of the molecule rigid throughout. It is often desired to minimize a crystal structure with an alternative conformation of the molecule, such as the ab initio optimized conformation that is being used as input into a Crystal Structure Prediction study. NEIGHCRYST was written with the ability to change to a slightly different molecular structure within a crystal structure by aligning the molecule fixed axes of the new and original molecule. This will not work if there is a significant change in the molecular conformation, or the molecules are not identical. The use of a separate program to produce a crystal structure which optimises the overlay of the two molecules is recommended in preference to this option.

The example chosen for this is Cyheptamide. Before beginning, NEIGHCRYST is run to set up the molecule in the local axis system. Text from the `fort.21` is then used for the GAUSSIAN input file, and GAUSSIAN is run specifying that the output should be written in atomic units. The coordinates of the optimized geometry in atomic units are put into the `coord_to_paste_au` file with the atom labels generated by NEIGHCRYST. EVERY molecule in the crystal structure needs to appear in this file, so it will look very similar to the end of the `fort.21` file.

When NEIGHCRYST is run pasting in a new molecule, the end of the `fort.21` file is first written out with the original coordinates and then with the new pasted coordinates.

This example uses the same NEIGHCRYST input files as for **02.lem_will01_AXOSOW** but all the filenames have been changed. When NEIGHCRYST is run, d should be the answer to the first question, and most of the rest of the questions do not need any answers as the filenames are picked up automatically.

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