ESI

**Crystals formation of 1D coordination polymers based on chiral, achiral and racemic 1,2 cyclohexane scaffold**

Abdelaziz Jouaiti, Philippe Grosshans, Nathalie Kyritsakas, Sylvie Ferlay, Marc Henry, Mir Wais Hosseini

**Characterization**

**Compound c, Bis-pyridin, 4,4'-[cis-1,2-cyclohexanediylbis(oxyl)]**

$^1$H-RMN (300 MHz, CDCl$_3$, 25 °C)

![$^1$H-RMN spectrum](image)

$^{13}$C-RMN (125 MHz, CDCl$_3$, 25 °C)

![$^{13}$C-RMN spectrum](image)
PACHA: General considerations

The PACHA formalism is a very useful method for probing intermolecular interaction energies in a perfectly non-empirical way that do not follow the usual decomposition of the total energy into coulombic, polarization, dispersion, repulsive, H-bonding terms. The crucial physical reason for not relying on such a partition of the total energy in PACHA is that all these terms depend on the same electromagnetic interaction involving electrons and protons.

However, for such an approach to be reliable, three requirements should imperatively be met:

i) The partial charges distributions should be self-consistent and should not involve empirical scalings. With PACHA this requirement is met using an electronegativity equalization principle coupled to the universal Allen’s scale and to atomic radii computed using relativistic wavefunctions solutions of the Dirac equations.

ii) The SE (Self-Energy)-term should be at least one order of magnitude large than the F-term meaning that the method is not well-suited for completely apolar compounds. In practice this requirement is met as soon as it exists one oxygen or nitrogen atom in the investigated compound. This means that crystalline elements and pure hydrocarbons characterized by a null or rather small electronegativity differences between constituting atoms are not well-handled by PACHA and should be treated by other methods.

iii) Compounds displaying an energy difference between the ground state and the first excited electronic state less than 1 eV (semi-conductors, semi-metals, metals, radicals, etc...) should be considered with extreme care as in this case the adiabatic approximation may not apply. For such compounds, a full quantum-mechanical treatment becomes mandatory.
One of the big advantages of the PACHA approach is that hydrogen-bonded systems may be easily and rigorously treated on the same theoretical ground as non-hydrogen-bonded systems. This is crucial as in most other methods, hydrogen bonding is usually considered as a very difficult problem needing ad hoc potentials. In PACHA, hydrogen bonding is automatically included as a consequence of the validity of the Hellman-Feynman theorem and is just a particular case of the universal electromagnetic interaction that is easily handled by the SE (Self-Energy) term.

Table 1 gives the atomic parameterization that has been used in this paper. As packing energies are very sensitive to H-atom positions in PACHA, coordinates for H-atoms derived from X-ray structures cannot be used owing to the large errors made on these atomic positions. In order to avoid introducing unphysical values, all C-H bond lengths have been fixed at the standard value of 108 pm allowing performing reliable comparisons between crystal structures derived from single-crystal X-ray diffraction.

<table>
<thead>
<tr>
<th>Element</th>
<th>H</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>Cl</th>
<th>Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>van der Waals radius /pm</td>
<td>120</td>
<td>170</td>
<td>155</td>
<td>152</td>
<td>175</td>
<td>155</td>
</tr>
<tr>
<td>Electronegativity /eV</td>
<td>13.61</td>
<td>15.05</td>
<td>18.13</td>
<td>21.36</td>
<td>16.97</td>
<td>10438</td>
</tr>
<tr>
<td>Atomic radius /pm</td>
<td>53.0</td>
<td>62.0</td>
<td>52.1</td>
<td>45.0</td>
<td>72.4</td>
<td>112.6</td>
</tr>
</tbody>
</table>

Table 1: Standard sets of van der Waals radii † used for the computation of packing coefficients, with associated atomic electronegativities ‡ and radii § used for partial charges evaluation in PACHA.


**Calculations**

**Calculation of Packing Energy (PE)**

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In the crystalline state, the Packing Energy may depend on the different crystallographic directions. In this case, we propose to introduce three structure descriptors, reflecting the anisotropy of the molecular packing. The basic idea is to use three partial space-group symmetries (packing sub-groups) creating large voids in the structure that lead to a strong reduction of the Packing Energy. The three Partial Packing Energy (PPE), reflecting the packing anisotropy, are assumed to be in the order \( \text{PPE}_1 < \text{PPE}_2 < \text{PPE}_3 \), one may define the isotropic Partial Packing Energy \(<\text{PE}>:\)

\[
<\text{PE}> = \frac{(\text{PPE}_1 + \text{PPE}_2 + \text{PPE}_3)}{3}
\]

And the Packing Energy span \( \Delta\text{PE}: \)

\[
\Delta\text{PE} = \text{PPE}_1 - \text{PPE}_3
\]

And the Packing Energy skew \( \eta\text{PE}: \)

\[
\eta\text{PE} = 3(\text{PPE}_2 -<\text{PE}>)/\Delta\text{PE}
\]

(with \( \eta = 0 \) in the case of spherical symmetry when \( \Delta = 0 \)).

\(-1 < \eta\text{PE} < +1\) (tri-axial ellipsoid) is measuring the deviation from pure axial symmetry characterized by \( \eta\text{PE} = +1 \) (oblate ellipsoid) and \( \eta\text{PE} = -1 \) (prolate ellipsoid).

**Calculation of Cooperativity Index (CI)**

A last structure descriptor would then be the CI cooperativity index:

\[
\text{CI} = 3<\text{PE}> - \text{PE}
\]

reflecting the cooperativity (\( \text{CI} < 0 \)) or anti-cooperativity (\( \text{CI} > 0 \)) of the stacking of the layers generated by each sub-group.

On purely intuitive grounds, one may expect low packing anisotropies for achiral space-groups and large packing anisotropies for chiral space-groups.

**Calculations for 1a-HgCl\(_2\), 1b-HgCl\(_2\), 1c-HgCl\(_2\) and 1a\(_{0.5}\)1b\(_{0.5}\)-HgCl\(_2\)**

Table 1 shows the results obtained by applying the PACHA approach to 1a-HgCl\(_2\), 1b-HgCl\(_2\), 1c-HgCl\(_2\) and 1a\(_{0.5}\)1b\(_{0.5}\)-HgCl\(_2\). The evaluation of \( \text{PE} \) is performed step by step: the Self-Energies (\( SE \) in kJ·mol\(^{-1}\)) for mercury dichloride HgCl\(_2\), the free ligand and a molecular chain generated by complexation between HgCl\(_2\) and the ligands. Then «\( \text{Net} \)» corresponds to the self-energy of the fully interacting chains in kJ·mol\(^{-1}\), from which a Packing Energy may be evaluated as

\[
\text{PE} = (\text{Net} - \text{Chain}*4)
\]

For the solvated network (1a\(_{0.5}\)1b\(_{0.5}\)-HgCl\(_2\)) this Packing Energy corresponds to Packing = \([\text{Net} - (\text{Chain}+\text{CHCl}_3)*4]\) with CHCl\(_3\) = -6 kJ·mol\(^{-1}\).

Then, the average Hg-N bond energy (kJ·mol\(^{-1}\)) has been evaluated according to:

\[
\text{Hg-N} = (\text{Chain} - \text{HgCl}_2 - \text{ligand})/2.
\]

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Group</th>
<th>HgCl(_2)</th>
<th>Ligand</th>
<th>Chain</th>
<th>Net</th>
<th>PE</th>
<th>CI</th>
<th>Hg-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a-HgCl(_2)</td>
<td>P2(_1)2(_1)2(_1)</td>
<td>-150(2)</td>
<td>-299(2)</td>
<td>-536(2)</td>
<td>-2267(9)</td>
<td>-123(9)</td>
<td>-2(2)</td>
<td>-43(2)</td>
</tr>
</tbody>
</table>
As mentioned above, the three different PPE (Partial Packing Energies) have to be evaluated considering the symmetry associated with different space groups of the coordination networks and their associated sub-space groups.

**1a-HgCl$_2$ or 1b-HgCl$_2$ (Space group P2$_1$2$_1$2$_1$)**

These compounds crystallise in the P2$_1$2$_1$2$_1$ space-group, the choice of subgroups is obvious (P2$_1$.1.1, P1.2$_1$.1 and P1.1.2$_1$) as this group contains only twofold screw axes that all act as packing operators. The three partial packing energies (PPE) have been calculated as:

- **PPE1** = SE (P1.2$_1$.1/2) - SE = -23(2) kJ·mol$^{-1}$ for 1b-HgCl$_2$
- and = -22(2) kJ·mol$^{-1}$ for 1a-HgCl$_2$

- **PPE2** = SE (P1.1.2$_1$.1/2) - SE = -7(2) kJ·mol$^{-1}$ for 1b-HgCl$_2$
- and = -7(2) kJ·mol$^{-1}$ for 1a-HgCl$_2$

- **PPE3** = SE (P2$_1$.1.1/2) - SE = -2(2) kJ·mol$^{-1}$ for 1b-HgCl$_2$
- and = -2(2) kJ·mol$^{-1}$ for 1a-HgCl$_2$

\[
<\text{PE}> = -11 \text{ kJ·mol}^{-1}, \Delta \text{PE} = -21(9) \text{ kJ·mol}^{-1} \text{ and } \eta \text{PE} = -0.57
\]

The Cooperativity Index (CI) reflecting the cooperativity between the chains is:

\[
\text{CI} = 3<\text{PE}> - \text{PE}/4 = 31 - 33 = -2(2) \text{ kJ·mol}^{-1} \text{ for 1a-HgCl}_2 \text{ or 1b-HgCl}_2
\]

**1c-HgCl$_2$ (Space group P2$_1$2$_1$2$_1$)**

This compound crystallizes in the P2$_1$2$_1$2$_1$ space-group, the twofold axis acts as an intramolecular symmetry operator that has no effect on the packing efficiency. In order to be able to discuss the packing anisotropy in this compound, we have considered a supercell of the P2$_1$2$_1$2$_1$ space-group, obtained by doubling the c-parameter leading to a new space group displaying 8 symmetry operators instead of 4:

- #1 = x,y,z -> 1
- #2 = x,y,1/2+z -> 1(0,0,1/2)
- #3 = -x,-y,z -> 2 0,0,z
- #4 = 1/2-x,1/2+y,-z -> 2(0,1/2,0) 1/4,y,0
- #5 = -x,-y,1/2+z -> 2(0,0,1/2) 0,0,z
- #6 = 1/2-x,1/2+y,1/2-z -> 2(0,1/2,0) 1/4,y,1/4
- #7 = 1/2+x,1/2-y,-z -> 2(1/2,0,0) x,1/4,0
- #8 = 1/2+x,1/2-y,1/2-z -> 2(1/2,0,0) x,1/4,1/4

It is then possible to generate three packing sub-groups: P112$_1$(2) by choosing operators #(1,2,3,5), P2$_1$2$_1$2 (screw axes at z = 0) using operators #(1,3,4,7) and P’2$_1$2$_1$2
(screw axes at z = 1/4) using operators #(1,3,6,8). The three partial packing energies (PPE) have been then calculated as:

\[
\begin{align*}
\text{PPE}_1 &= \text{SE} \left[ \text{P}1.1.2(2_1) \right] / 4 - \text{SE} = -30(2) \text{ kJ}\cdot\text{mol}^{-1} \\
\text{PPE}_2 &= \text{SE} \left( \text{P}'2_1.2_1.2 \right) / 4 - \text{SE} = -25(2) \text{ kJ}\cdot\text{mol}^{-1} \\
\text{PPE}_3 &= \text{SE} \left( \text{P}2_1.2_1.2 \right) / 4 - \text{SE} = -24(2) \text{ kJ}\cdot\text{mol}^{-1}
\end{align*}
\]

\[
<\text{PE}> = -26 \text{ kJ}\cdot\text{mol}^{-1}, \Delta\text{PE}_{SR} = -6(2) \text{ kJ}\cdot\text{mol}^{-1} \text{ and } \eta_{\text{PE}} = -0.5.
\]

The computed Cooperativity Index CI is then:

\[
\text{CI} = 3<\text{PE}> - \text{PE}/4 = 45 - 78 = -33(2) \text{ kJ}\cdot\text{mol}^{-1}
\]

\[1a_{0.5}1b_{0.5}\cdot\text{HgCl}_2 \text{ (Space group } P2_1/n)\]

In this case, the choice of subgroups is obvious (P2_1, P-1and Pn) since all symmetry operators are used for packing molecular chains. The three partial packing energies (PPE) have been calculated as:

\[
\begin{align*}
\text{PPE}_1 &= \text{SE}(\text{P}2_1)/4 - \text{SE} = -23(2) \text{ kJ}\cdot\text{mol}^{-1} \\
\text{PPE}_2 &= \text{SE}(\text{P}-1)/4 - \text{SE} = -10(2) \text{ kJ}\cdot\text{mol}^{-1} \\
\text{PPE}_3 &= \text{SE}(\text{P}n)/4 - \text{SE} = -2(2) \text{ kJ}\cdot\text{mol}^{-1}
\end{align*}
\]

\[
<\text{PE}> = -12 \text{ kJ}\cdot\text{mol}^{-1}, \Delta\text{PE} = -21(2) \text{ kJ}\cdot\text{mol}^{-1} \text{ and } \eta_{\text{PE}} = -0.29
\]

The computed Cooperativity Index CI is then:

\[
\text{CI} = 3<\text{PE}> - \text{PE}/4 = 33 - 36 = -3(2) \text{ kJ}\cdot\text{mol}^{-1}
\]
Reflections were merged by SHELXL according to the crystal class for the calculation of statistics and refinement.

_computing_structure_refinement 'SHELXL-2014/6 (Sheldrick, 2014)'
_computing_molecular_graphics 'Bruker SHELXTL'
Bruker SHELXTL

_refine_ls_structure_factor_coefficient Fsqd
_refine_ls_matrix_type full
_refine_ls_weighting_scheme calc
_refine_ls_weighting_details
\[ w = 1 / \left( s^2(Po^2) + (0.0102P)^2 + 11.6797P \right) \] where \( P = (Po^2 + 2Pc^2)/3 \)

_refine_ls_hydrogen_treatment constr
_refine_ls_extinction_method none
_refine_ls_extinction_coefficient .

_refine_ls_number_reflections 5182
_refine_ls_number_parameters 256
_refine_ls_number_restraints 0

_refine_ls_R_factor_all 0.1137
_refine_ls_R_factor_gt 0.0477
_refine_ls_wrfactor_ref 0.1085
_refine_ls_wrfactor_gt 0.0862

_refine_ls_goodness_of_fit_ref 0.823
_refine_ls_restrained_S_all 0.823

_refine_ls_shift/su_max 0.002

_refine_diff_density_max 1.311
_refine_diff_density_min -1.158

ENDCIF

CELL
Vol= 2390.06 VÖ=> 2= 4
SPGR ITC= 14 HM= P 21/n HALL= -P 2yn
NHKL 2 EWD= 0 KIN= -0.090 INC=0.01 ESIG=1000 DMP=0 GKR=1
QTOT =0

OPTM EPS=3 ANG=360 RTE=0.99 ANL=10 MOV=0 MIX=1
RVDW H=120 C=170 N=155 O=152 Cl=175 Hg=155
ANAL DMIN=1.080 FIRST=238 OCF=0.93 RESI=200
BNDS (1-1)=60(40) (1-6)=107(60) (1-7)=100(60) (1-8)=100(60) (1-8)=96(60) (1-17)=132(60)
(1-80)=177(60) (6-6)=154(40) (6-7)=114(60) (6-8)=107(60) (6-17)=134(60)
(6-80)=175(60) (7-7)=140(40) (7-8)=97(60) (7-17)=124(60) (7-80)=165(60)
(8-8)=132(40) (8-17)=117(60) (8-80)=158(60) (17-17)=204(40) (17-80)=185(60)
(80-80)=274(0)
EBND

\( \nabla \)
Partial Charge Distribution Evaluation -> e1450

_CELL   Vol= 2390.06 \( \text{\textdegree} \) Z= 4

[\text{H19 C19 N2 O4 Cl5 Hg }]^4 = 2868.96 \text{ amu}

Madelung summation details
Ewald parameter for 1/R summation was \( K = 0.129 \) \( \text{\textdegree} \) (accuracy = 4e-010)
Reciprocal space exploration: \(-2 \leq (h, k, l) \leq 2\)
\( \text{min} = 8.89860 \text{ eV} < \text{mean} = 16.42282 \text{ eV} < \text{max} = 125.45198 \text{ eV} \)
Madelung constant \( A = 147.94740204 = 36.9868505 \) (dmin = 0.94945 \( \text{\textdegree} \))
Orbital compression factor was \( \text{OCF} = 82.00\% \)
Total electrostatic balance = \(-2243.8149 \text{ eV} = -216495.2 \text{ kJ.mol}^{-1} \)

***Atomic electronegativies (eV) and radii (pm) ***
\begin{align*}
\text{Hg} & : (10.438, 112.6) \\
\text{Cl} & : (16.970, 72.4) \\
\text{N} & : (18.130, 52.1) \\
\text{C} & : (15.050, 62.0) \\
\text{H} & : (13.610, 53.0) \\
\text{O} & : (21.360, 45.0)
\end{align*}

Level of significance for Madelung elements eps = 5.292126e-009
Convergence criterion \( |Ax - b|/|b| < \text{eps} \)
Estimated error on charges after 24 iterations = 2.058074e-010

*** PACHA signature ***
Mean electronegativity \( \langle EN \rangle = 15.0369 \text{ eV} \)
Partial electrostatic balance: \( \langle EB \rangle = -24.5298 \text{ eV} = -2366.8 \text{ kJ.mol}^{-1} \)
Reduced electrostatic balance: \( \langle EB/4 \rangle = -6.1324 \text{ eV} = -591.7 \text{ kJ.mol}^{-1} \)
Global ionicity: \( \langle GI \rangle = 10.4557 \% \)
\begin{tabular}{cccc}
\# & \text{Label(-tox)[CN]} & \text{Charge \(-q\)} & \\
\hline
33 & O3(-2)[2] = & -0.27664 & 10.12 V \\
35 & O4(-2)[1] = & -0.27600 & 10.03 V \\
16 & O2(-2)[2] = & -0.27297 & 9.65 V \\
15 & O1(-2)[1] = & -0.26867 & 9.10 V \\
2 & C11(-1)[1] = & -0.23061 & 10.61 V \\
3 & C12(-1)[1] = & -0.22614 & 10.26 V \\
4 & N1(-2)[2] = & -0.20969 & 10.81 V \\
41 & N2(-2)[2] = & -0.20772 & 10.59 V \\
50 & C15(-1)[1] = & -0.13267 & 2.82 V \\
48 & C13(-1)[1] = & -0.12359 & 2.10 V \\
49 & C14(-1)[1] = & -0.11652 & 1.54 V \\
27 & C11(-2)[4] = & -0.07887 & 7.28 V \\
21 & C9(-2)[4] = & -0.07799 & 7.19 V \\
24 & C10(-2)[4] = & -0.07759 & 7.16 V \\
30 & C12(-2)[4] = & -0.07714 & 7.11 V \\
44 & C18(-1)[3] = & -0.04063 & 3.72 V \\
7 & C2(-1)[3] = & -0.03912 & 3.58 V \\
10 & C4(-1)[3] = & -0.03712 & 3.40 V \\
37 & C15(-1)[3] = & -0.03289 & 3.00 V \\
9 & C3(+0)[3] = & +0.00235 & -0.27 V \\
36 & C14(+0)[3] = & +0.00441 & -0.46 V \\
5 & C1(+0)[3] = & +0.00717 & -0.72 V \\
42 & C17(+0)[3] = & +0.00908 & -0.90 V \\
12 & C5(+0)[3] = & +0.01174 & -1.14 V \\
39 & Cl6(+0)[3] = & +0.01623 & -1.56 V \\
19 & C8(+0)[4] = & +0.03405 & -3.22 V \\
\end{tabular}
Total sum for Charge = 0.0

Statistical report:
<Atom>[num] = mean ± 3√óstdev (stdev) <avdev>
?q(H) = 0.08159 (0.01663) <0.01354>
?q(C) = 0.00320 (0.07363) <0.05135>
?q(N) = -0.20870 (0.00139) <0.00098>
?q(O) = -0.27357 (0.00364) <0.00275>
?q(Cl) = -0.16590 (0.05734) <0.04998>
?q(Hg) = 0.73017 (0.00000) <0.00000>

Statistical report:
<Atom>[num] = mean ± 3√óstdev (stdev) <avdev>
?q(black) = 0.00320 (0.07363) <0.05135>
?q(royal_blue) = -0.20870 (0.00139) <0.00098>
?q(green) = -0.16590 (0.05734) <0.04998>
?q(red) = -0.27357 (0.00364) <0.00275>
?q(silver) = 0.08159 (0.01663) <0.01354>
?q(wood) = 0.73017 (0.00000) <0.00000>
Steric Energy Evaluation
After summing over 3x3x3 cells
Distance threshold for bonded atoms was 4.596 Å
Total steric energy = 10099.7 kJ.mol⁻¹
Bonded steric energy = 9991.6 kJ.mol⁻¹
Steric energy = 108.1 kJ.mol⁻¹

Bond Valence Sum Evaluation
#1 Hg(+2) [2] = 1.57 -> C12 C11
#2 C11(-1) [1] = 0.78 -> Hg
#3 C12(-1) [1] = 0.79 -> Hg
#4 N1(-2) [2] = 2.80 -> C1 C5
#5 C1(+0) [3] = 3.51 -> H1 N1 C2
#6 H1(+1) [1] = 1.06 -> C1
#7 C2(-1) [3] = 3.13 -> H2 C1 C3
#8 H2(+1) [1] = 1.06 -> C2
#9 C3(+0) [3] = 2.78 -> C2 C4 C6
#10 C4(-1) [3] = 3.12 -> H4 C5 C3
#11 H4(+1) [1] = 1.06 -> C4
#12 C5(+0) [3] = 3.51 -> H5 N1 C4
#13 H5(+1) [1] = 1.06 -> C5
#14 C6(+3) [3] = 3.63 -> O1 O2 C3
#15 O1(-2) [1] = 1.70 -> C6
#16 O2(-2) [2] = 1.97 -> C6 C7
#17 C7(+0) [4] = 3.32 -> H7 O2 C8 C12
#18 H7(+1) [1] = 1.06 -> C7
#19 C8(+0) [4] = 3.26 -> H8 O3 C7 C9
#20 H8(+1) [1] = 1.06 -> C8
#21 C9(-2) [4] = 3.50 -> H9B H9A C10 C8
#22 H9A(+1) [1] = 1.06 -> C9
#23 H9B(+1) [1] = 1.06 -> C9
#24 C10(-2) [4] = 3.55 -> H10B H10A C11 C9
#25 H10A(+1) [1] = 1.06 -> C10
#26 H10B(+1) [1] = 1.06 -> C10
#27 C11(-2) [4] = 3.51 -> H11B H11A C10 C12
#28 H11A(+1) [1] = 1.06 -> C11
#29 H11B(+1) [1] = 1.06 -> C11
#30 C12(-2) [4] = 3.51 -> H12B H12A C7 C11
#31 H12A(+1) [1] = 1.06 -> C12
#32 H12B(+1) [1] = 1.06 -> C12
#33 O3(-2) [2] = 1.95 -> C13 C8
#34 C13(+3) [3] = 3.65 -> O4 O3 C14
#35 O4(-2) [1] = 1.72 -> C13
#36 C14(+0) [3] = 2.87 -> C15 C18 C13
#37 C15(-1) [3] = 3.17 -> H15 C14 C16
#38 H15(+1) [1] = 1.06 -> C15
#39 C16(+0) [3] = 3.57 -> H16 N2 C15
#40 H16(+1) [1] = 1.06 -> C16
#41 N2(-2) [2] = 2.79 -> C16 C1