

Multicomponent titanium(IV)-based helicates incorporating the *ortho*-phenylenediamine ligand: a structural and a computational investigation

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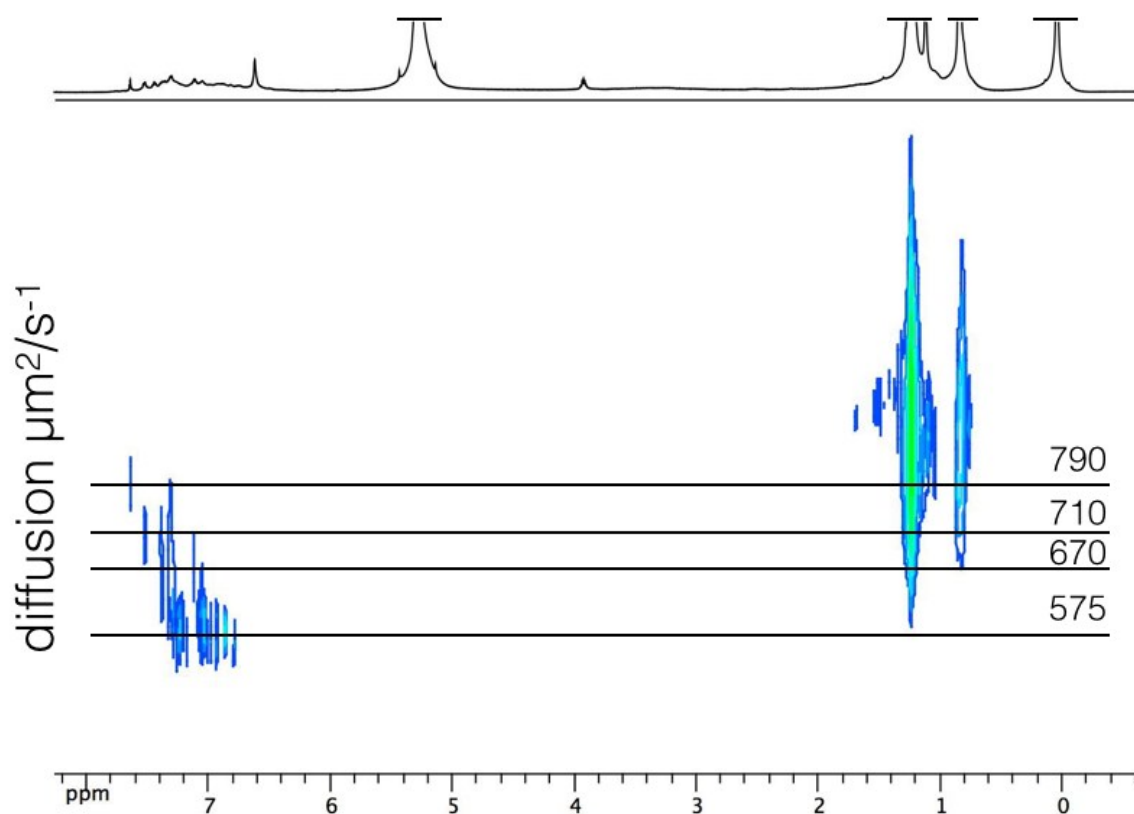


Figure 1: DOSY map analysis of the $L^2H_4 + Ti(OPr^i)_4 + opda$ reaction performed in situ (CD_2Cl_2).

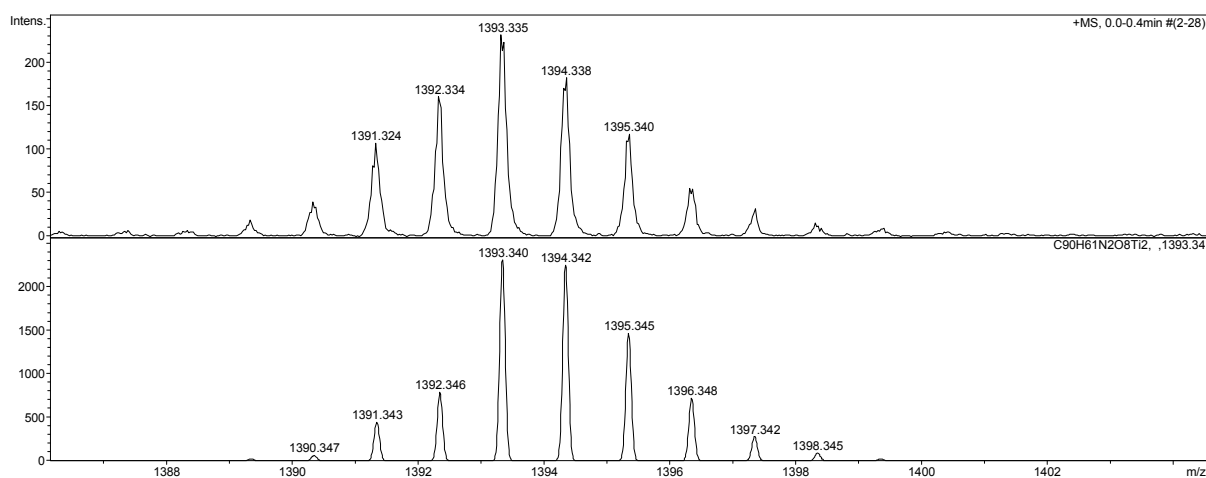


Figure 2 : Enlargement at $m/z = 1393.335$ of the $Ti_2(L^2)_2(opda)_2$ mass spectrum (top). The simulated isotopic profile (down) corresponds to $[Ti_2(L^2)_2(opda) + H]^+$.

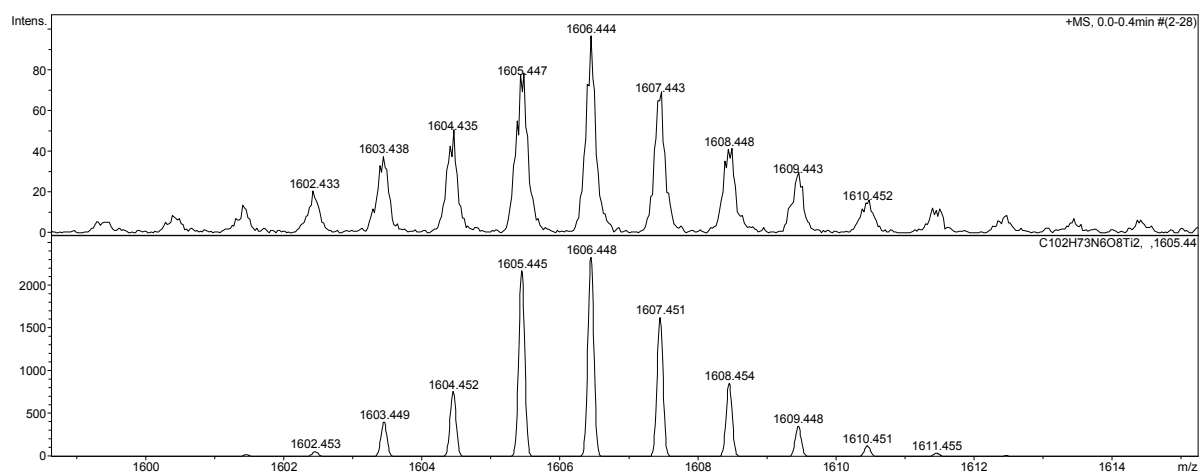


Figure 3 : Enlargement at $m/z = 1605.447$ of the $Ti_2(L^2)_2(opda)_2$ mass spectrum (top). The simulated isotopic profile (down) corresponds to $[Ti_2(L^2)_2(opda)_2(bqdi) + H]^+$.

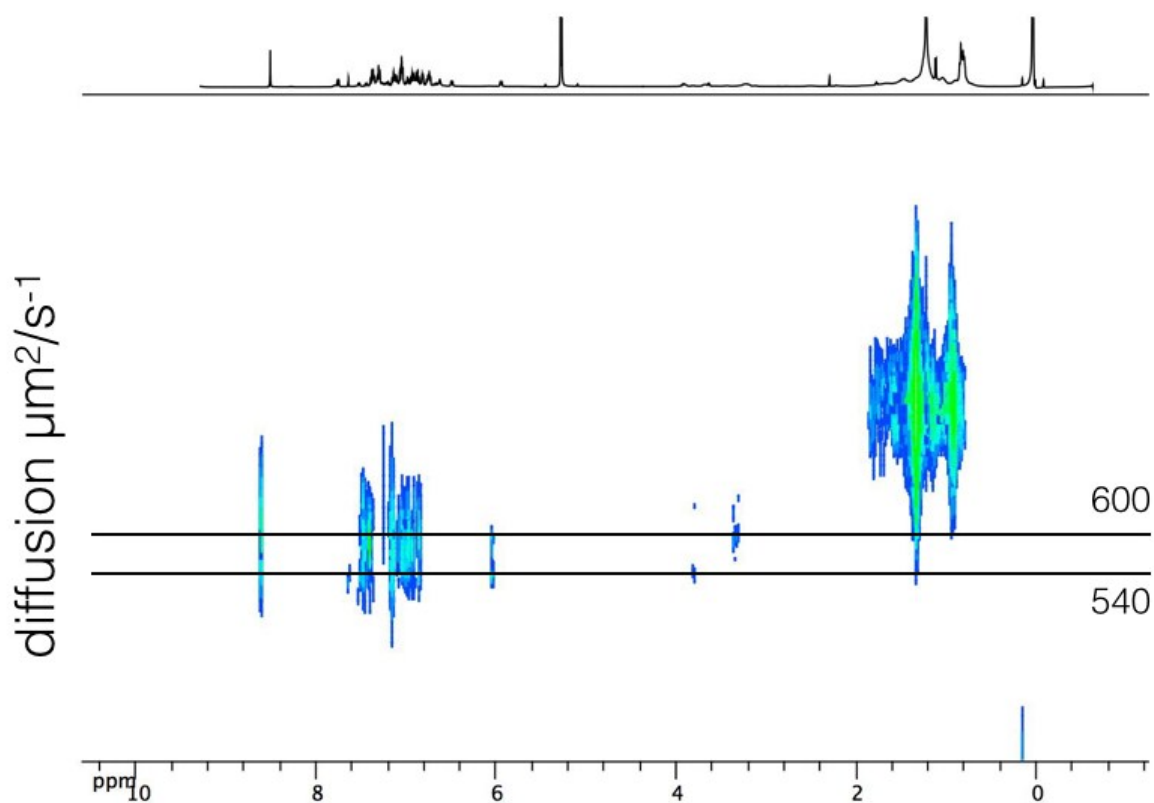


Figure 4: DOSY map analysis of the $Ti_2(L^2)_2(opda)_2$ crystals dissolved in CD_2Cl_2 .

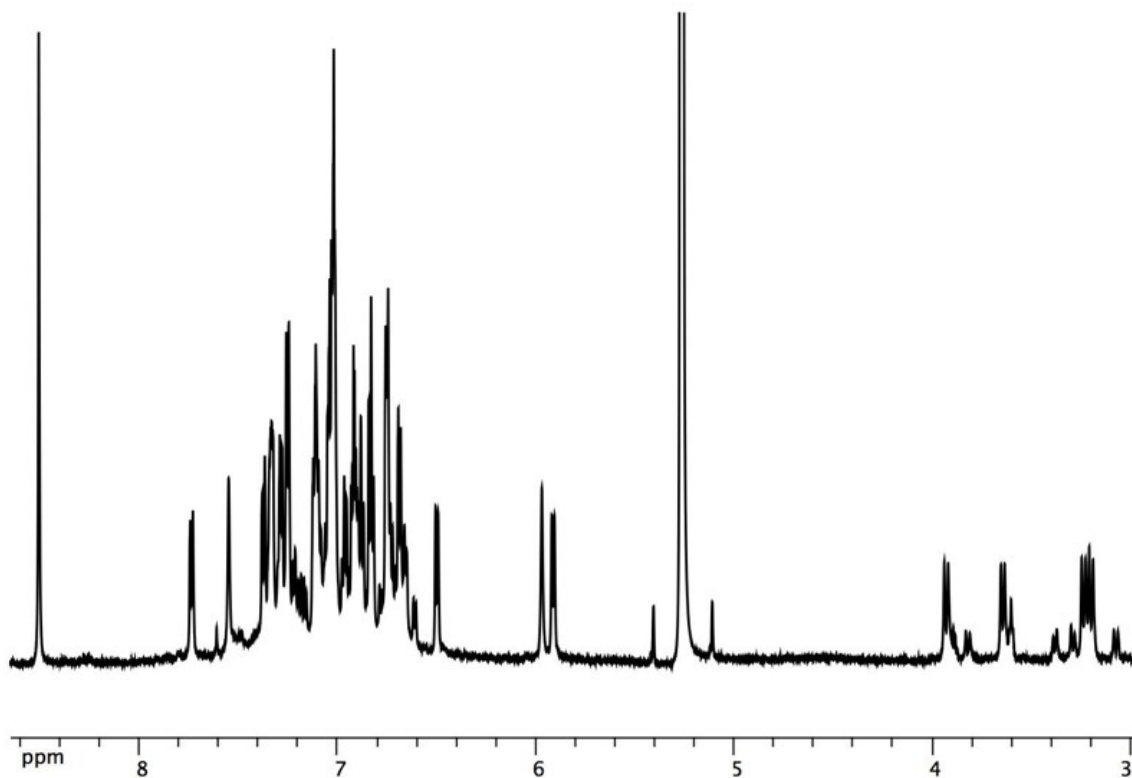


Figure 5: ^1H NMR spectrum at 260 K (from 3 ppm to 9 ppm) of the $\text{Ti}_2(\text{L}^2)_2(\text{opda})_2$ crystals dissolved in CD_2Cl_2 .

The Partial Charges Model (PCM)

The partial charges model is based on a functional approach of chemical bonding using atomic charges q and their associated potentials v , which are both first derivatives of the total energy of the system E :

$$q \propto \frac{\partial E}{\partial v} \text{ et } v \propto \frac{\partial E}{\partial q}$$

For a chemical system, $q = Z - N$, with Z atomic number and N non-integral number of electrons around the nucleus, while v becomes a measure of its electronegativity χ . This may be readily understood by looking at a diatomic molecule A-B constrained to have $N = Z_A + Z_B = N_A + N_B$ [1]. For any electron transfer dN from B to A ($dN_A = -dN_B = dN > 0$) at the internuclear distance R , the change in the total energy should be:

$$E = f(N_A, N_B, Z_A, Z_B, R) \Rightarrow dE = \left[\left(\frac{\partial E}{\partial N_A} \right)_{N_B, R} - \left(\frac{\partial E}{\partial N_B} \right)_{N_A, R} \right] dN + \left(\frac{\partial E}{\partial R} \right)_{N_A, N_B} dR \quad (1)$$

For a given R distance ($dR = 0$) a spontaneous transfer will occur if $dE < 0$:

$$\Rightarrow \left(\frac{\partial E}{\partial N_A} \right)_{N_B, R} < \left(\frac{\partial E}{\partial N_B} \right)_{N_A, R} \Leftrightarrow \chi_A > \chi_B \text{ if } \chi = - \left(\frac{\partial E}{\partial N} \right) = \left(\frac{\partial E}{\partial q} \right) = -\mu_e \quad (2)$$

The last equalities coming from the fact that electronegativity measures the affinity of atoms for electrons [2]. Another consequence of (1) is that if $R = R_e$, internuclear equilibrium distance, then $dE = dR = 0$ i.e. $\chi_A = \chi_B$. This is the electronegativity equalization principle of R.T. Sanderson [3] meaning that electronegativity should be considered as the opposite of an electronic chemical potential $\mu_e = \partial E / \partial N$ [4]. The relation between this electronic chemical potential and the empirical electronegativity introduced by L. Pauling in the thirties is immediate if we introduce the chemical hardness $\eta = \partial^2 E / \partial N^2$ of the system (its chemical softness being $\sigma = 1/\eta$):

$$E(N) = E^\circ(Z) + (N - Z) \left(\frac{\partial E}{\partial N} \right)_{N=Z} + \frac{(N - Z)^2}{2!} \left(\frac{\partial^2 E}{\partial N^2} \right)_{N=Z} = E^\circ(Z) + q\chi^\circ + \frac{q^2}{2} \eta \quad (3)$$

With $\chi = -\partial E / \partial N = \chi^\circ + \eta \times q$, and $\chi_A = \chi_B = \langle \chi \rangle$ for a diatomic molecule, it comes:

$$\chi_A = \chi_A^\circ - \eta_A q = \chi_B^\circ + \eta_B q = \chi_B = \langle \chi \rangle \Leftrightarrow q = \frac{\chi_A^\circ - \chi_B^\circ}{\eta_A + \eta_B} \quad (4)$$

leading to a stabilization energy $\Delta = (E_A - E_A^\circ) + (E_B - E_B^\circ) = q(\chi_B^\circ - \chi_A^\circ) + q^2(\eta_A + \eta_B)/2$:

$$\Delta = - \frac{(\chi_A^\circ - \chi_B^\circ)^2}{\eta_A + \eta_B} + \frac{1}{2} \frac{(\chi_A^\circ - \chi_B^\circ)^2}{\eta_A + \eta_B} = - \frac{1}{2} \frac{(\chi_A^\circ - \chi_B^\circ)^2}{\eta_A + \eta_B} < 0 \quad (5)$$

in full agreement with the original Pauling definition [2] assuming that $\eta_A + \eta_B \sim \text{cste}$. Relation (5) provides also a firm theoretical justification of the empirical HSAB principle (Hard and Soft Acids and Bases) introduced empirically by R.G Pearson [5]:

$$\eta_A(\text{soft}) + \eta_B(\text{soft}) < \eta_A(\text{soft}) + \eta_B(\text{hard}) \Leftrightarrow \Delta(\text{soft-soft}) < \Delta(\text{hard-soft})$$

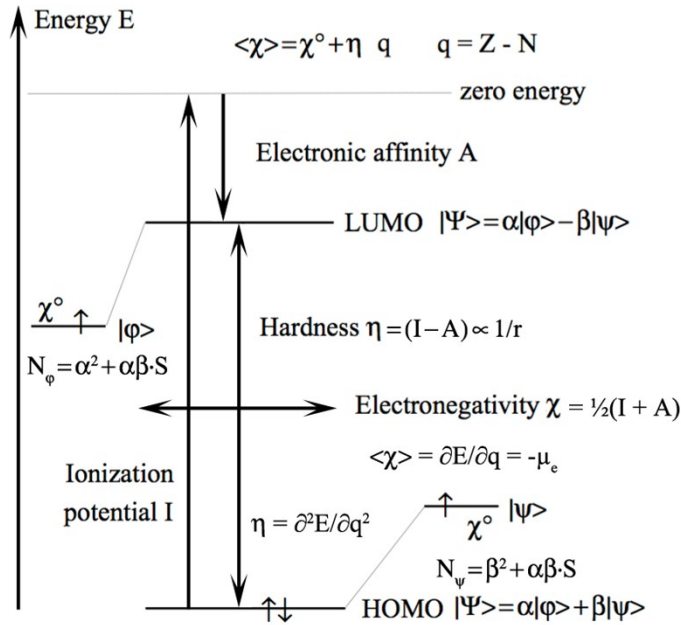
The other part of the HSAB principle [$\Delta(\text{hard-hard}) < \Delta(\text{hard-soft})$] comes rather from the contraction of atomic orbitals in response to an increase in the nuclear effective charge Z^* [6], as with $dZ^* > 0$ and $(\partial E/\partial Z^*) < 0 \Rightarrow \Delta E = (\partial E/\partial Z_A^*)dZ_A^* + (\partial E/\partial Z_B^*)dZ_B^* < 0$.

The problem of the quantitative evaluation of the hardness parameter may be solved by treating an atom as a sphere having a uniformly distributed electric charge q . If this sphere has a characteristic radius r , then:

$$E(q) = \frac{e^2 q^2}{8\pi\epsilon_0 r} \Leftrightarrow \chi = \left(\frac{\partial E}{\partial q} \right) = \frac{e^2 q}{4\pi\epsilon_0 r} \text{ et } \eta = \left(\frac{\partial^2 E}{\partial q^2} \right) = \frac{e^2}{4\pi\epsilon_0 r} \quad (6)$$

The chemical hardness is then known as soon as some atomic radius has been defined [7].

The link between this functional approach of chemical bonding and the more conventional molecular orbital theory is as follows:



where we have used the Koopmans theorem $I \sim -E_{\text{HOMO}}$ and $A \sim -E_{\text{LUMO}}$. For a sphere of charge q and characteristic radius r , we have $I = E(q+1) - E(q)$ and $A = E(q) - E(q-1)$:

$$I = \frac{e^2(2q+1)}{8\pi\epsilon_0 r} ; A = \frac{e^2(2q-1)}{8\pi\epsilon_0 r} \Rightarrow \chi = \frac{I+A}{2} ; \eta = I - A$$

in full agreement with Mulliken's definition of orbital electronegativity [8]. Consequently, if electronegativity corresponds to the Fermi level of the electrons in a given chemical system [9][10], its chemical hardness η measures its HOMO-LUMO gap [11].

From a practical point of view, given any system resulting from the association of n atoms and carrying a total electrical charge z , it is possible to write its electronegativity as [12-16]:

$$\chi_i = \langle \chi \rangle = \chi_i^0 + \frac{e}{4\pi\epsilon_0 r_i} q_i + \frac{1}{4\pi\epsilon_0} \sum_{j=1}^n M_{ij} e q_j \quad \forall i = 1, \dots, n \text{ et } \sum_{i=1}^n q_i = z \quad (7)$$

where χ_i° are Mulliken-type electronegativities, r_i atomic radii modelling the spatial extent of valence orbitals and M_{ij} Madelung contributions which are readily evaluated as $1/R_{ij}$ for a molecular compound or computed with an Ewald summation for a crystalline network [17]:

$$M_{ij} = \frac{\pi}{V} \sum_{\substack{\vec{h}=\vec{h}\vec{a}^*+\vec{k}\vec{b}^*+\vec{h}\vec{c}^* \neq 0 \\ \vec{x}=\vec{x}\vec{a}+\vec{y}\vec{b}+\vec{z}\vec{c}}} \frac{\exp\left[2\pi\vec{h}(\vec{x}_j - \vec{x}_i)\right]}{|\vec{h}|^2} \exp\left(\frac{\pi^2|\vec{h}|^2}{K^2}\right) + \sum_{\substack{\vec{l}=\vec{u}\vec{a}+\vec{v}\vec{b}+\vec{w}\vec{c} \neq \vec{0} \\ \vec{x}=\vec{x}\vec{a}+\vec{y}\vec{b}+\vec{z}\vec{c}}} \frac{\operatorname{erfc}(K|\vec{l} + \vec{x}_j - \vec{x}_i|)}{|\vec{l} + \vec{x}_j - \vec{x}_i|} - \frac{2K}{\sqrt{\pi}} \delta_{ij}$$

with $\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^{+\infty} \exp(-t^2) dt$

Here V is the unit-cell volume and K is an adjustable parameter ruling the convergence speed of this double summation process.

In the case of the PACHA formalism, great care has been taken to define the atomic (χ, η) parameterization needed for computing partial charges q . Concerning atomic electronegativity χ , the Allen scale was selected owing to its clear definition based on the average one-electron energy of the valence-shell electrons in ground state free atoms [18]. This scale is attractive because it can be indifferently based on high-resolution experimental values concerning atomic energy levels or on high accuracy numerical Dirac-Hartree-Fock solutions. This double check both experimental and theoretical is thus a solid guarantee that we are not using in the model arbitrary values. Moreover, as Allen's electronegativities are given in energy units (eV), it solves also a very troublesome physical unit problem coming from the failure of L. Pauling to recognize that the polarity of a bond was not only a consequence of the difference in electronegativity but also a matter of matching between chemical hardness of both partners. The only problem with the Allen's scale is that it is defined only for main group and d-block elements, values for the f-block being not yet available. In the PACHA formalism this problem is solved thanks to (6) recalling that energy and size are two perfectly equivalent ways of dealing with the electromagnetic interaction. This particularly means that atomic electronegativity should also correlates with the volume density of the valence electrons, as originally stated by the pioneering work of R.T. Sanderson who was the first to recognize the importance of the electronegativity equalization principle in chemistry [3]. Based on the knowledge of the maxima of the electron density of the electrons of the valence orbitals, it was possible to derive Pauling-type atomic electronegativities for f-elements [19] that may be converted into eV-values after adequate scaling: $\chi(\text{Allen}) = (13.605/2.30016) \times \chi(\text{Pauling})$ [20]. By coherence with (6) the chemical hardness may not arbitrarily defined but approximated by the radius corresponding to the most diffuse principal maxima in the radial distribution function $r^2\psi^2(r)$, computed using relativistic wavefunctions solutions of the Dirac equations [21]. In order to keep coherence with the chosen units for measuring electronegativities all radii and distances (structure) are scaled by the non empirical factor $k = e^2/(4\pi\epsilon_0) = 14.4 \text{ eV}\cdot\text{\AA}$, where e is the elementary charge ($1.60219 \cdot 10^{-19} \text{ C}$) and ϵ_0 the permittivity of the vacuum ($8.85419 \cdot 10^{-12} \text{ C}\cdot\text{V}^{-1}\cdot\text{m}^{-1}$).

Relation (7) allows us to switch very quickly between a set of chemical parameters (electronegativities, sizes and spatial positions) and the associated partial charge distribution q_i . From this distribution, it is possible to define two kinds of self-energies SE:

$$SE = \frac{e^2}{8Z\pi\epsilon_0} \sum_{i=1}^n \sum_{j=1}^n M_{ij}(K)(q, z)_i (q, z)_j = \frac{694.68}{Z} \sum_{i=1}^n \sum_{j=1}^n M_{ij}(K) [\text{\AA}^{-1}] (q, z)_i (q, z)_j \text{ kJ}\cdot\text{mol}^{-1}$$

one SE(q) using the partial charge distribution q_i , and the other one SE(z) computed using integral oxidation states z_i . The ratio of these two self-energies defines the global ionicity I of the structure: $I(\%) = 100\sqrt{SE(q)/SE(z)}$. Moreover, given a characteristic distance R_0 , the Madelung constant A is readily obtained as: $A = 4\pi\epsilon_0 R_0 \times SE(z)/e^2$.

The Madelung tensor M_{ij} allows also to get a set of strictly positive numbers $f_i = \partial^2 E / \partial q_i \partial v_i \Leftrightarrow \partial \rho_{\text{HOMO/LUMO}} / \partial N$, called frontier indexes [22], and showing where the variation of μ_e should be the largest [23]:

$$\eta = \frac{e}{4\pi\epsilon_0 r_i} f_i + \frac{1}{4\pi\epsilon_0} \sum_{j=1}^n M_{ij} f_j \quad \forall i = 1, \dots, n \quad \text{et} \quad \sum_{i=1}^n f_i = 1 \quad (8)$$

Where η is the global hardness of the system i.e. its HOMO-LUMO gap.

Here is an example for an input file used for computing partial charges distributions directly from crystalline data. As shown, some atoms (#108-115) are defined using internal coordinates instead of triclinic coordinates allowing performing rotation of a phenyl group as explained in the paper. The following table gather the values used for atomic electronegativities and chemical hardnesses in the paper:

Element	H	C	N	O	Ti
Electronegativity /eV	13.61	15.05	18.13	21.36	16.97
Atomic radius /pm	53.0	62.0	52.1	45.0	72.4

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2 Ti2 0.52312(5) 0.72378(4) 0.35945(3) c101 @22 :2a
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5 H2 -0.37104 0.05082 0.04732 z1 c89 rLIG3A @1 :2a
6 Cc3 -0.2848(5) -0.0176(3) -0.0163(4) c2 rLIG3A @6 :2a
7 H3 -0.30673 -0.06465 0.00097 z1 c89 rLIG3A @1 :2a
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84 Cc48 -0.3765(3) 0.1193(2) 0.2180(2) c2 rLIG4A @6 :2a
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92 Cc53 -0.0690(3) 0.1902(3) 0.3751(2) c2 rLIG4A @6 :2a
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101 H58 0.39501 0.28491 0.23105 z1 c89 rLIG4A @1 :2a
102 Cc105 0.2780(3) 0.2085(2) 0.2537(2) c2 rLIG4A @6 :2a
103 H105 0.32771 0.17161 0.25665 z1 c89 rLIG4A @1 :2a
104 Cc60 0.1770(3) 0.1921(2) 0.2666(2) c2 rLIG4A @6 :2a
105 H60 0.14968 0.14281 0.28026 z1 c89 rLIG4A @1 :2a
106 Cc61 0.2913(3) 0.3823(2) 0.2078(2) c2 rLIG4A @6 :2a
107 Cc62 0.3657(3) 0.3778(2) 0.1655(2) c2 rLIG4A @6 :2a
10800300 Cc65 1.38400 !10555001 121.70000 !10655001 33.2 !10755001 c2 rLIG2A @6
10900000 Cc66 1.38400 !10855001 121.50000 !10555001 -176.80000 !10655001 c2 rLIG2A @6

11000000 Cc63 1.38700 !105555001 117.40000 !108555001 2.30000 !109555001 c2 rLIG2A @6
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11300000 H66 1.08000 !109555001 119.1000 !108555001 176.5000 !105555001 z1 c89 rLIG2A @1
11400000 H63 1.08000 !110555001 119.3000 !105555001 -179.4000 !108555001 z1 c89 rLIG2A @1
11500000 H65 1.08000 !108555001 119.2000 !105555001 -177.6000 !110555001 z1 c89 rLIG2A @1
116 Cc67 0.4269(3) 0.5748(2) 0.1518(2) c2 rLIG4A @6 :2a
117 Cc68 0.4446(3) 0.6544(2) 0.19980(19) c2 rLIG4A @6 :2a
118 Oo7 0.42126(19) 0.67293(13) 0.26539(12) z-2 c84 rLIG4A @8 :2a
119 Cc69 0.4885(3) 0.7164(2) 0.1808(2) c2 rLIG4A @6 :2a
120 Cc70 0.5196(3) 0.6981(3) 0.1160(2) c2 rLIG4A @6 :2a
121 H70 0.55460 0.74549 0.10168 z1 c89 rLIG4A @1 :2a
122 Cc71 0.5062(4) 0.6201(3) 0.0695(2) c2 rLIG4A @6 :2a
123 H71 0.53374 0.60679 0.02023 z1 c89 rLIG4A @1 :2a
124 Cc72 0.4576(3) 0.5587(3) 0.0861(2) c2 rLIG4A @6 :2a
125 H72 0.44304 0.49749 0.04776 z1 c89 rLIG4A @1 :2a
126 Cc73 0.4937(3) 0.8005(2) 0.2236(2) c2 rLIG4A @6 :2a
127 Cc74 0.5402(3) 0.8446(2) 0.2994(2) c2 rLIG4A @6 :2a
128 Oo8 0.5811(2) 0.81139(14) 0.34175(13) z-2 c84 rLIG4A @8 :2a
129 Cc75 0.5523(3) 0.9276(2) 0.3338(3) c2 rLIG4A @6 :2a
130 Cc76 0.5109(4) 0.9608(3) 0.2900(3) c2 rLIG4A @6 :2a
131 H76 0.51796 1.02341 0.31516 z1 c89 rLIG4A @1 :2a
132 Cc77 0.4618(4) 0.9168(3) 0.2164(3) c2 rLIG4A @6 :2a
133 H77 0.42993 0.94457 0.18441 z1 c89 rLIG4A @1 :2a
134 Cc78 0.4529(4) 0.8371(3) 0.1831(3) c2 rLIG4A @6 :2a
135 H78 0.41391 0.80254 0.12489 z1 c89 rLIG4A @1 :2a
136 Cc79 0.6102(4) 0.9803(2) 0.4110(3) c2 rLIG4A @6 :2a
137 Cc80 0.6780(5) 1.0559(3) 0.4266(3) c2 rLIG4A @6 :2a
138 H80 0.69163 1.07169 0.38240 z1 c89 rLIG4A @1 :2a
139 Cc81 0.7282(5) 1.1113(3) 0.5003(4) c2 rLIG4A @6 :2a
140 H81 0.78025 1.16982 0.51223 z1 c89 rLIG4A @1 :2a
141 Cc82 0.7129(5) 1.0928(3) 0.5561(4) c2 rLIG4A @6 :2a
142 H82 0.75269 1.13612 0.61238 z1 c89 rLIG4A @1 :2a
143 Cc83 0.6472(4) 1.0197(3) 0.5415(3) c2 rLIG4A @6 :2a
144 H83 0.63415 1.00494 0.58634 z1 c89 rLIG4A @1 :2a
145 Cc84 0.5962(4) 0.9631(2) 0.4688(2) c2 rLIG4A @6 :2a
146 H84 0.54494 0.90479 0.45812 z1 c89 rLIG4A @1 :2a
147 N1 0.0177(2) 0.21630(18) 0.08264(17) z-3 c5 rOPD1A @7 :2a
148 H1A 0.06149 0.19815 0.11356 z1 c89 rOPD1A @1 :2a
149 H1B -0.04379 0.16850 0.04620 z1 c89 rOPD1A @1 :2a
150 Cc85 0.0845(3) 0.2459(2) 0.0425(2) c2 rOPD1A @6 :2a
151 Cc86 0.0964(3) 0.3239(2) 0.0512(2) c2 rOPD1A @6 :2a
152 N2 0.0442(2) 0.36974(18) 0.10121(18) z-3 c5 rOPD1A @7 :2a
153 H2A -0.00604 0.38699 0.07336 z1 c89 rOPD1A @1 :2a
154 H2B 0.10050 0.41904 0.14055 z1 c89 rOPD1A @1 :2a
155 Cc87 0.1587(3) 0.3556(3) 0.0138(2) c2 rOPD1A @6 :2a
156 H87 0.16700 0.41542 0.01949 z1 c89 rOPD1A @1 :2a
157 Cc88 0.2095(4) 0.3094(3) -0.0304(3) c2 rOPD1A @6 :2a
158 H88 0.25981 0.33416 -0.05834 z1 c89 rOPD1A @1 :2a
159 Cc89 0.1974(4) 0.2325(3) -0.0399(3) c2 rOPD1A @6 :2a
160 H89 0.23673 0.19681 -0.07559 z1 c89 rOPD1A @1 :2a
161 Cc90 0.1337(3) 0.2004(3) -0.0027(2) c2 rOPD1A @6 :2a
162 H90 0.12370 0.13992 -0.00986 z1 c89 rOPD1A @1 :2a
163 N3 0.4788(2) 0.60502(17) 0.36426(16) z-3 c5 rOPD2A @7 :2a
164 H3A 0.48021 0.61435 0.41617 z1 c89 rOPD2A @1 :2a
165 H3B 0.40330 0.57317 0.33312 z1 c89 rOPD2A @1 :2a
166 Cc91 0.5498(3) 0.55858(19) 0.33940(18) c2 rOPD2A @6 :2a
167 Cc92 0.5409(3) 0.4874(2) 0.3445(2) c2 rOPD2A @6 :2a
168 H92 0.48082 0.46533 0.36839 z1 c89 rOPD2A @1 :2a
169 Cc93 0.6093(4) 0.4443(3) 0.3189(3) c2 rOPD2A @6 :2a
170 H93 0.60384 0.38936 0.32402 z1 c89 rOPD2A @1 :2a
171 Cc94 0.6839(4) 0.4718(3) 0.2870(3) c2 rOPD2A @6 :2a
172 H94 0.73543 0.43733 0.26573 z1 c89 rOPD2A @1 :2a
173 Cc95 0.6936(3) 0.5431(2) 0.2820(2) c2 rOPD2A @6 :2a
174 H95 0.75328 0.56504 0.25778 z1 c89 rOPD2A @1 :2a
175 Cc96 0.6261(3) 0.5860(2) 0.30833(19) c2 rOPD2A @6 :2a
176 N4 0.6328(2) 0.66211(17) 0.30575(16) z-3 c5 rOPD2A @7 :2a
177 H4A 0.61607 0.65286 0.25300 z1 c89 rOPD2A @1 :2a
178 H4B 0.70879 0.69852 0.33005 z1 c89 rOPD2A @1 :2a
179 C97 0.8387(6) 0.0244(4) 0.1737(4) z0 c2 @6 :2a
180 H97A 0.81393 0.06695 0.15766 z1 c89 @1 :2a
181 H97B 0.86922 0.05285 0.23299 z1 c89 @1 :2a
182 C11 0.94045(17) 0.00560(17) 0.1377(2) z-1 c41 @17 :2a
183 C12 0.72301(14) -0.05825(9) 0.14926(12) z-1 c41 @17 :2a
184 C98 0.7970(6) 0.8822(5) 0.3035(5) z0 c2 @6 :2a
185 H98A 0.72379 0.89157 0.28236 z1 c89 @1 :2a
186 H98B 0.79405 0.88133 0.35586 z1 c89 @1 :2a

187 C13 0.8994(2) 0.9589(2) 0.3181(3) z-1 c41 @17 :2a
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