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Interpreting molecular crystal disorder in plumbocene, Pb(C5H5)2: Insight from theory

Interpreting Molecular Crystal Disorder in Plumbocene, $Pb(C_5H_5)_2$: Insight from Theory**

Carole A. Morrison,[1,]* Dominic S. Wright[2] and Richard A. Layfield[2]

[1]EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

[2]Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK.

[*]Corresponding author; e-mail: c.morrison@ed.ac.uk

Abstract:
Plane-wave density functional theory has been applied in a novel way to help interpret the molecular crystal structure disorder observed in the orthorhombic zigzag phase of plumbocene, $Pb(C_5H_5)_2$. A crystal lattice comprising uniformly staggered C_5H_5 rings was found to be lower in energy by 2.8 kJ mol^{-1} per unit cell, compared to a uniformly eclipsed packing arrangement. This energy difference has been attributed to the difference in the strength of intermolecular interactions between the $Pb(C_5H_5)_2$ chains for the two different lattices. The calculations performed allowed the determination of the crystallographic occupancy factors by a quantum mechanical technique for the first time.

Keywords:
Plane-wave density functional theory, crystal structure disorder, plumbocene.

Introduction

It is hard to underestimate the impact computational chemistry has had over the last 15 years. The chemist's understanding of structure, reaction mechanism and vibrational properties to name but a few have all benefited enormously as a consequence of collaboration between theory and experiment. To-date the traditional *ab initio* modeling codes that have been employed (*e.g.* GAUSSIAN[1]) simulate isolated molecules, but whilst this style of calculation is clearly relevant to studying gas-phase systems, it is not nearly so applicable to the condensed state. Many properties of the solid state could be amenable to calculation if an alternative modeling approach capable of handling periodic systems were adopted.

One example of a style of modeling suitable for the solid state is plane-wave density functional theory (DFT),[2] which can simulate a repeating unit such as a crystallographic unit cell. The lattice parameters and atomic positions can all be varied to minimize the crystal lattice energy, atomic forces and unit cell stress. As the two different styles of calculation are both quantum mechanical in nature, they share many common features in their calculation procedure. After periodicity, the biggest difference between the two calculation approaches relates to the construction of the molecular wavefunction, Ψ. The periodic method requires a periodic wavefunction, and therefore uses a set of plane waves and a series of pseudopotentials (in effect describing $\Psi_{valence}$ and Ψ_{core}, respectively) rather than a set of Gaussian-type functions centred on each atom, as in the isolated molecule approach. In practice, increasing the energy threshold applied to the repeating unit model-system increases the number of plane waves that are included in the calculation. This offers the advantage of constructing a wavefunction that can be

systematically improved, rather than a truncated one, and thus helps to reduce possible error in the calculation due to an incomplete basis set.

With the ability to calculate properties of molecular crystal lattices quantum mechanically, many interesting questions on structure and bonding in the solid state can now be addressed. One area that can in principle be tackled is molecular crystal disorder, a cause of frustration commonly encountered in X-ray crystallography, where the arrangement of atoms in different unit cells are not all identical. The problem of disorder is a complex one. It is a random effect; that is the several different arrangements of atoms in an asymmetric unit can be assembled randomly to create an infinite number of different packing arrangements. All arrangements, however, must have similar energies to have reasonable probabilities of occurring, and similar unit cell dimensions in order that all the random unit cells can pack together efficiently in an infinite superlattice. Several different classifications of disorder exist. For example, in site occupancy disorder it is impossible to differentiate between two elements that scatter X-rays to a very similar degree (*e.g.* C and N). This could give rise to a simple wrong assignment of ligands such as CO and NO, or fail to assign the position of a heteroatom in an aromatic ring. Alternatively, in positional or orientational disorder a whole molecule or, more confusingly, just part of the molecule, can be distributed over different sites, which are usually related by rotation, reflection or inversion. Moreover, the disorder can be static (*i.e.* the disordered atoms have two or more 'rest' positions, about which they vibrate) or dynamic (*i.e.* with sufficient thermal energy, the atomic positions can switch back and forth between the different positions). Although it is not possible to distinguish between static and dynamic disorder based on the results obtained from one data set collection, by carrying out investigations at lower temperatures, it may be possible to 'freeze out' dynamic disorder and observe, for example, a freely rotating group settle into a single position. Alternatively, upon cooling dynamic disorder may pass smoothly over into static disorder, at which point the disorder will be 'locked in' and no further significant change in the diffraction pattern will be observed.

If the disorder is, for example, between two positions in the cell, then in the data analysis the system is modelled with the disordered unit in both positions, and an occupancy factor dictates the weighting or probability of each position. Clearly for dynamic and static disorder the occupancy factor has a slightly different meaning, implying the fractions of time spent in each position for the former, or the fractions of molecules in each position in the latter. In either case if the occupancy factor is not known an initial value of 0.5 is assumed, and with good quality data it is then refined.

Disorder, whether occurring for whole molecules or just part of a molecule, may result in a shortage of high-angle data of significant intensity being collected, which inevitably results in a structure with lower precision. Thus, refined parameters may have larger uncertainties than would otherwise occur for a system free from disorder, and finer structural details may be lost. It is a common condition: over 16% of entries in the Cambridge Structural Database report problems associated with disorder.[3]

The application of periodic quantum mechanical calculations can offer valuable help in interpreting all types of crystal structure disorder. Due to the random nature of disorder, the number of possible different packing arrangements is infinite, and therefore by definition presents an intractable problem. However, calculations on a series of sensibly constructed models can give insight into the principles that are important in driving the crystal lattice packing. This in turn can result in calculated values for occupancy factors, which can assist the crystal structure determination. Moreover, as the precision of the simulation may be better than that of the experimental structure, the calculations can form a basis for the construction of geometric parameter restraints to be used in the least-squares refinement. This offers the advantage that all parameters are then able to refine (including, for example, H atom positions), thereby giving structures that are as accurate as possible and have realistic estimates of standard deviations for all parameters. This principle of including structural information calculated quantum mechanically to assist in the refinement of experimental structural data was recently reported for gas-phase electron diffraction, where its application has revolutionised the structure determination for small molecules.[4]

However, such an approach has hitherto never been applied to the problem of disorder in solid-state periodic lattices.

Like their transition metal counterparts,[5] main group metallocenes are some of the oldest metallocene compounds known.[6] In contrast to all other Group 14 (Si-Pb) complexes of this type, which are monomeric in the solid state, gas phase and solution, plumbocene exhibits a rich diversity of polymeric solid-state polymorphism. The orthorhombic, zigzag polymorph is one of the classic, text-book structures in organometallic chemistry, and was first prepared by Fischer *et al*. in 1956.[7] The molecular structure of this phase was determined some 10 years later.[8] However, owing to the poor quality of the X-ray diffraction data at that time, an ambiguity transpired over assignment of the correct space group; the choice of *Pnma* or *Pna*2_1 was only resolved in a recent, more accurate redetermination of the structure, which revealed that only the former space group could fit the crystal data and structure refinement.[9] Nonetheless, this polymorph shows orientational disorder, such that the bridging C_5H_5 rings comprising the two columns in the unit cell are assigned randomly to two different positions, which in the redetermination were assumed to be of equal weight (*i.e.* an occupancy factor of 0.5 for both orientations). In the past 10 years or so there has been renewed interest in the structures and reactivities of main group metallocenes, paralleling in many ways the earlier surge in interest in their transition metal counterparts.[10] The particular interest in plumbocene stems from the observation of other solvent-free polymorphs whereby the structure adopted depends on the medium and temperature of crystallisation; a cyclic hexagonal oligomer[11] and a tetragonal, helical phase[12] have been structurally characterised. The observed structural flexibility of plumbocene and its fundamental importance to organometallic chemistry make it an ideal candidate for quantum mechanical investigations of the solid state.

The main purpose of this paper is to demonstrate the complementary nature of plane-wave density functional theory and X-ray diffraction for the determination of molecular structures when an

inconclusive result is obtained on the basis of experimental data alone. In this paper we present the results obtained by plane-wave DFT for two idealised packing arrangements of the orthorhombic, zigzag polymorph of plumbocene. These 'extreme-case' models are constructed from a $1 \times 1 \times 1$ lattice [*i.e.* one unit cell containing four $Pb(C_5H_5)_2$ molecules] where the C_5H_5 rings in the columns are either all-eclipsed in one position or all-staggered over two positions (see Figure 1). The purpose of running these calculations was to determine the absolute energies of these two conformations and the factors upon which the energies depend. In addition to simulating the two different crystal lattices, further calculations were performed on one-dimensional infinite chains of $[Pb(C_5H_5)_2]_\infty$ in the eclipsed and staggered conformations. This demonstrates another useful facet of periodic quantum mechanical calculations; namely the periodic cell can take any size or shape. Removing half the atoms from the unit cell to leave one intact $Pb(C_5H_5)_2$ chain and preserving periodicity in the *b* lattice vector direction only, will allow a one-dimensional calculation on an infinite chain to be performed. As the same basis set and level of theory is employed for both the three-dimensional and one-dimensional periodic calculations it is therefore possible to apply plane-wave DFT to investigate the energetics of intermolecular interactions between neighboring molecular fragments.

a

(a)

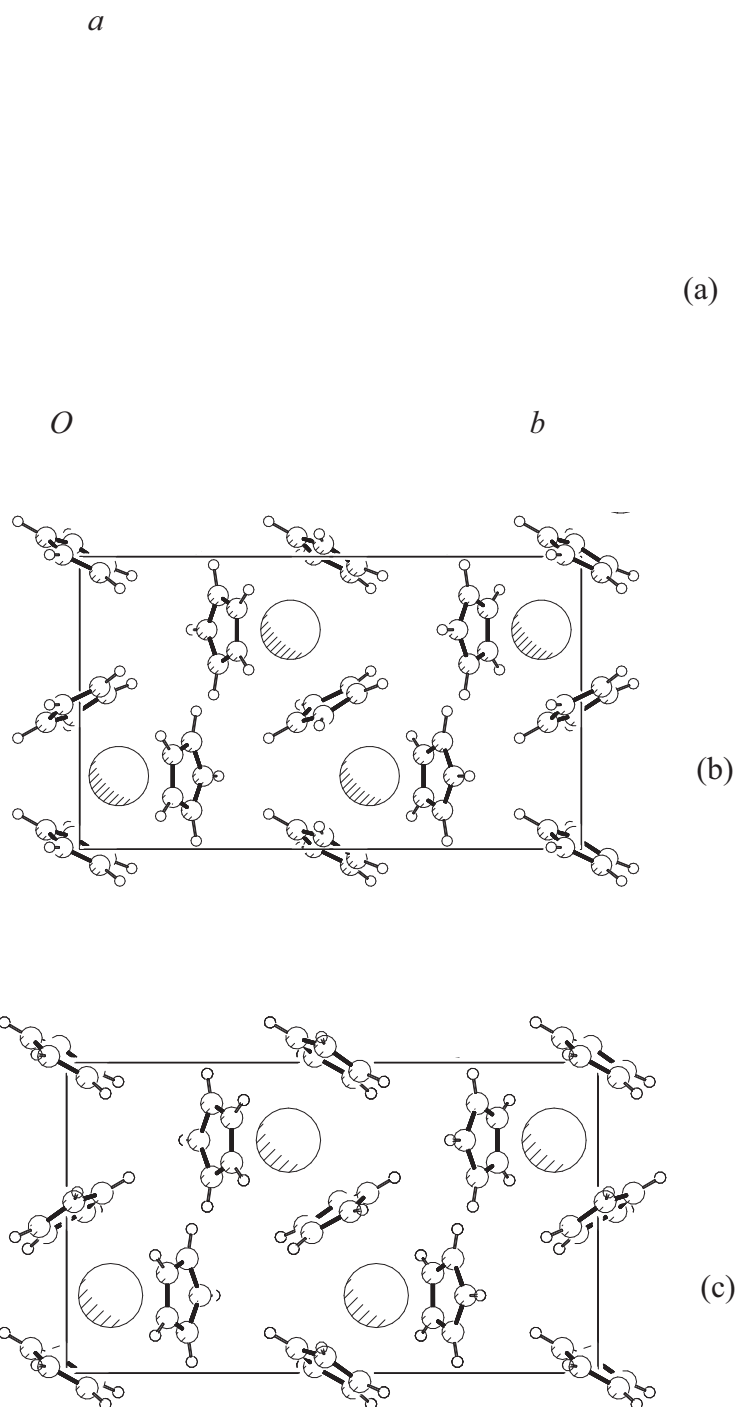*O*   *b*

(b)

(c)

Figure 1 Figure Caption: Crystal lattice diagrams of the orthorhombic phase of plumbocene.

(a) The disordered cell (viewed along the *b* axis, the C_5H_5 rings that give rise to columns are

disordered over two possible sites). From this, two extreme-case models have been resolved:

(b) eclipsed and (c) staggered.

Theoretical Calculations

Crystal lattices. A set of plane-wave DFT calculations was undertaken using the CASTEP 4.2 simulation code.[2] A generalised gradient approximation (PW91) was used for the exchange and correlation potential,[13] and an energy cut-off of 450 eV generated a basis set that allowed the total energy of the system to converge to 0.1 eV atom^{-1}. For the two different crystal lattices integrations over the symmetrised Brillouin zone were performed using two k-points generated *via* the Monkhurst-Pack scheme.[14] Simultaneous optimisation of crystal lattice parameters and atomic relaxation were performed under the space group symmetry constraints in line with the experimental structure determination (see Figures 2 and 3). Note that the two disordered rings are non-centrosymmetric. Therefore, depending on which ring position is chosen, two different Cp_{cent}-Pb-μ-Cp_{cent} angles (where Cp_{cent} denotes the centroid of the C_5H_5 ring) can arise. Thus in the eclipsed lattice, the two different conformations for the [Pb(C_5H_5)$_3$] units present in the unit cell both possess C_s symmetry, having been constructed from disordered C_5H_5 rings in the same orientation. This is described as a 'duu' (or the opposite 'udd') orientation, or 'ddd' ('uuu'), where 'd' and 'u' pertain to the disordered column C_5H_5 rings, 'up' (u) denoting a C_5H_5 ring pointing directly out of the [Pb(C_5H_5)$_3$] molecular plane, 'down' (d) a ring pointing in the opposite direction. Conversely, in the staggered lattice the [Pb(C_5H_5)$_3$] units are constructed from C_5H_5 rings disordered over both positions, and thus only one unique [Pb(C_5H_5)$_3$] structure 'ddu' ('uud') exists in the unit cell, and it has C_1 symmetry.

[Pb(C_5H_5)$_2$]$_\infty$ (one-dimensional periodic). One Pb(C_5H_5)$_2$ chain was selected from each of the two fully optimised crystal lattices and placed in a periodic cell (box size $a = c = 16.000$, $b = 9.582$ and 9.673 Å for eclipsed and staggered respectively, *i.e.* periodic in lattice parameter b only) (see Figure 2), and subjected to a single-point energy calculation. Values for lattice parameters a and c were chosen so that they gave rise to not overly-long calculation times and could still be considered to generate isolated model-systems (the closest contact between neighbouring molecules exceeding 9 Å). The same energy

cut-off was used as for the crystal lattice calculations to generate the same quality basis set, thus allowing direct comparison of the absolute energies obtained. Calculations were performed using 1 k-point located at the Γ position (0,0,0) in the Brillouin zone.
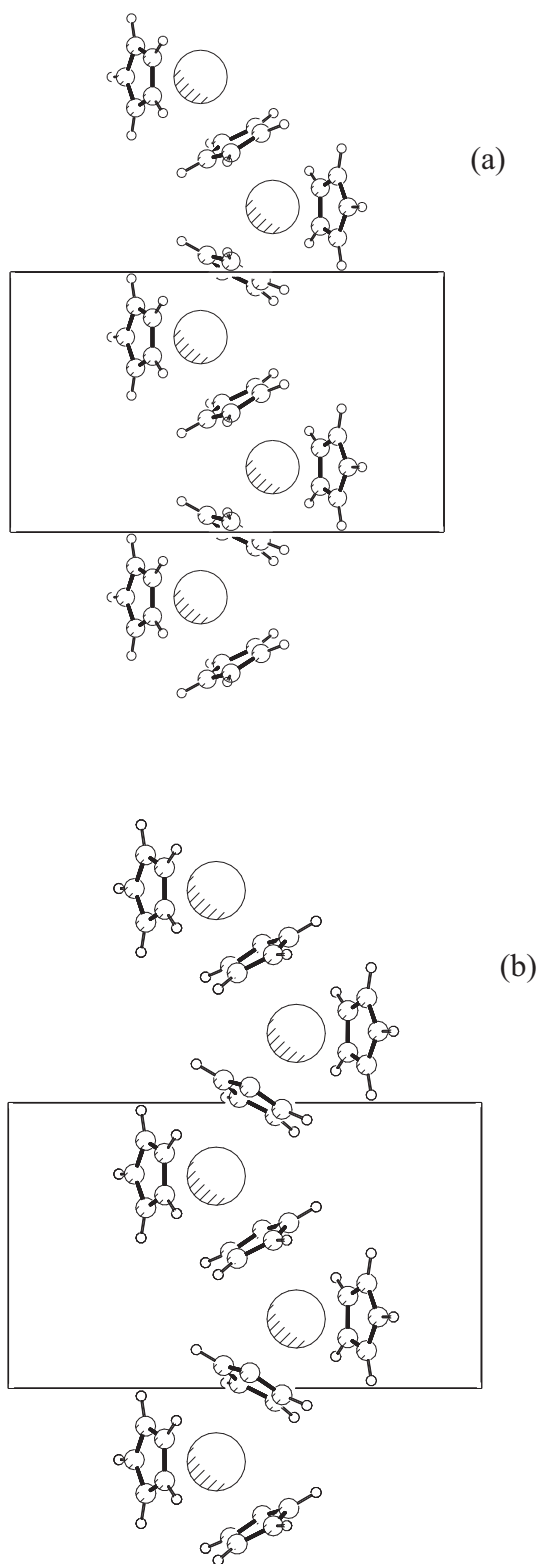
(a)

(b)

Figure 2 Figure Caption: Lattice diagrams of the $[Pb(C_5H_5)_2]_\infty$ periodic cells (a) eclipsed and (b) staggered.

Results and Discussion

Crystal lattices. The results obtained in the simultaneous optimisation of unit cell parameters and atomic positions for the two lattices are given in Table 1 and Figures 3 and 4.

The two models give calculated unit cells with very similar dimensions, indicating that they could pack together efficiently to create a disordered superstructure. Both cells are, however, slightly bigger than the experimentally determined lattice, with lattice parameters a, b and c overestimated by 3, 2, and 10%, *i.e. ca.* 0.5, 0.2 and 0.7 Å, respectively. These discrepancies are not due to a weakness in the calculation to simulate intramolecular bonding, but rather are due to underestimation of the weak interactions between the $Pb(C_5H_5)_2$ chains. Thus in the a direction, whilst rPb-Cp$_{cent}$ is reproduced to within 0.05 Å, the distance between the chains in this direction is overestimated by *ca.* 0.2 Å for the two lattices. Similarly, in the c direction the stacking distance between identical $Pb(C_5H_5)_2$ chains is overestimated by as much as 0.7 Å. The direction along the $Pb(C_5H_5)_2$ chains is represented by b, and with no intermolecular chain interactions to model, is the most accurately determined of the three lattice parameters, with the simulation overestimating the chain length by just 0.04 and 0.13Å (eclipsed and staggered, respectively).

Considering the molecular parameters in more detail, the two calculated structures return near-identical values for the average C-C ring distance (1.408 Å, *c.f.* 1.395 Å by experiment). The Pb-Cp$_{cent}$ distance, which was assumed in the experiment to be unaffected by the nearby disordered C_5H_5 rings, was found to be slightly longer in the calculation compared to the X-ray structure (by 0.03 – 0.05 Å), but crucially not identical in the two lattices. The disordered distance Pb-μ-Cp$_{cent}$ was much more variable in the calculations, differing by –0.06 - +0.12 Å from the experimental values. However, whilst it is true that any improvement in the calculation to correct for an incomplete basis set or weakness in the DFT functional is likely to improve the absolute values *vs.* experiment, if the bond lengths in question are

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electronically similar the discrepancies in the *differences* between bond lengths would be expected to be much smaller. This is indeed the case, with the calculations reproducing rPb-μ-Cp$_{cent}$ − rPb-Cp$_{cent}$ to within 0.10 Å of the experimental value. This information could form the basis for the construction of geometric parameter restraints to use in a re-refinement of the original X-ray data to allow subtle structural differences to be revealed in the region of the molecule assumed to be unaffected by the disorder; information that is detectable by quantum mechanics but lost to large thermal ellipsoids in the experiment.

From the solid-state calculations, the staggered lattice arrangement is found to be lower in energy than the eclipsed conformation by 2.8 kJ mol^{-1} per unit cell, or 0.7 kJ mol^{-1} per Pb(C$_5$H$_5$)$_2$ molecule. Assuming that there is no interaction between cells (*i.e.* a superlattice of alternating staggered and eclipsed cells would generate an energy per unit cell exactly midway between the two extremes) and the entropy of the two lattices is the same, then it is possible to predict a Boltzmann distribution for the molecular arrangement of Pb(C$_5$H$_5$)$_2$ molecules in an averaged, randomised unit cell, in effect generating a calculated occupancy factor. Thus, at the temperature of crystal growth (300 K),[9] the Boltzmann distribution gives an occupancy of *ca.* 43:57 (eclipsed to staggered), compared to the experimentally assumed value of 50:50. If the disorder is a function of temperature (*i.e.* dynamic, not static; the molecules can rearrange in the crystal) then at the temperature of X-ray data collection (173 K), this balance should shift to *ca.* 38:62. At temperatures below 40 K, quantum mechanics predicts that less than 10% of molecules will occupy the eclipsed position, and thus the lattice would tend towards the non-disordered, fully staggered arrangement. In principle at least, a series of low-temperature X-ray data collections could be employed to confirm or deny the variation in occupancy factors predicted by quantum mechanics, assuming that no phase transitions to other polymorphs of plumbocene would occur over such a broad range of temperature.

[Pb(C₅H₅)₂]∞ (one-dimensional periodic). With a statistically significant difference in crystal lattice energy identified, the remaining question to address is why the staggered arrangement is lower in energy than the eclipsed. To this end, a further series of calculations was performed on the two different $[Pb(C_5H_5)_2]_\infty$ molecular chain conformations (see Figure 2 and Table 2), with coordinates frozen in positions obtained from the full crystal lattice optimisations. From this, an interesting result emerges. The absolute energy for the eclipsed chain is slightly lower than that for the staggered (by *ca.* 0.01 eV or 1.0 kJ mol^{-1}). Therefore the conformations of the individual $Pb(C_5H_5)_2$ molecules in the chains are not directly responsible for the difference in packing energy in the two idealised crystal lattices. This is consistent with *ab initio* calculations reported recently for different conformations of the isolated molecule using Gaussian basis sets.[15,16]

However, by comparing the energy obtained for the isolated chain with the value per chain in the corresponding crystal lattice it is possible to obtain the energy of interaction between the chains in the crystal lattice. Thus, the chain intermolecular interactions are assigned an energy of 27.7 kJ mol^{-1} in the eclipsed lattice, and 30.2 kJ mol^{-1} in the staggered lattice. The difference in intermolecular energy (2.5 kJ mol^{-1}) is very close to the difference in packing energies observed between the two idealised lattices (2.8 kJ mol^{-1}). It can therefore be concluded that the stronger chain interactions in the staggered lattice offer it a slight increase in stability, compared to the eclipsed case.

Table 1 Table Title: Experimental and calculated crystal parameters of the orthorhombic phase of $Pb(C_5H_5)_2$

Parameters (Å, º)	Experimental	Calculated	
Lattice		eclipsed	staggered
a	16.294	16.722	16.764
b	9.539	9.582	9.673
c	5.896	6.564	6.547
V	916.4	1051.8	1061.6
Calculation			
E (eV)	-	-13544.44329	-13544.47255
ΔE (kJ mol^{-1})	-	+2.8	0.0
(per unit cell)			

Table 2 Table Title: Calculated single-point energies for one-dimensional $Pb(C_5H_5)_2$ isolated chains

Parameter	eclipsed	staggered
Lattice (Å)		
a	16.000	16.000
b	9.582	9.673
c	16.000	16.000
Calculation		
E(eV)	-6771.93424	-6771.92375
ΔE (lattice/2 – chain) (kJ mol^{-1})	27.7	30.2

(a)   (b)
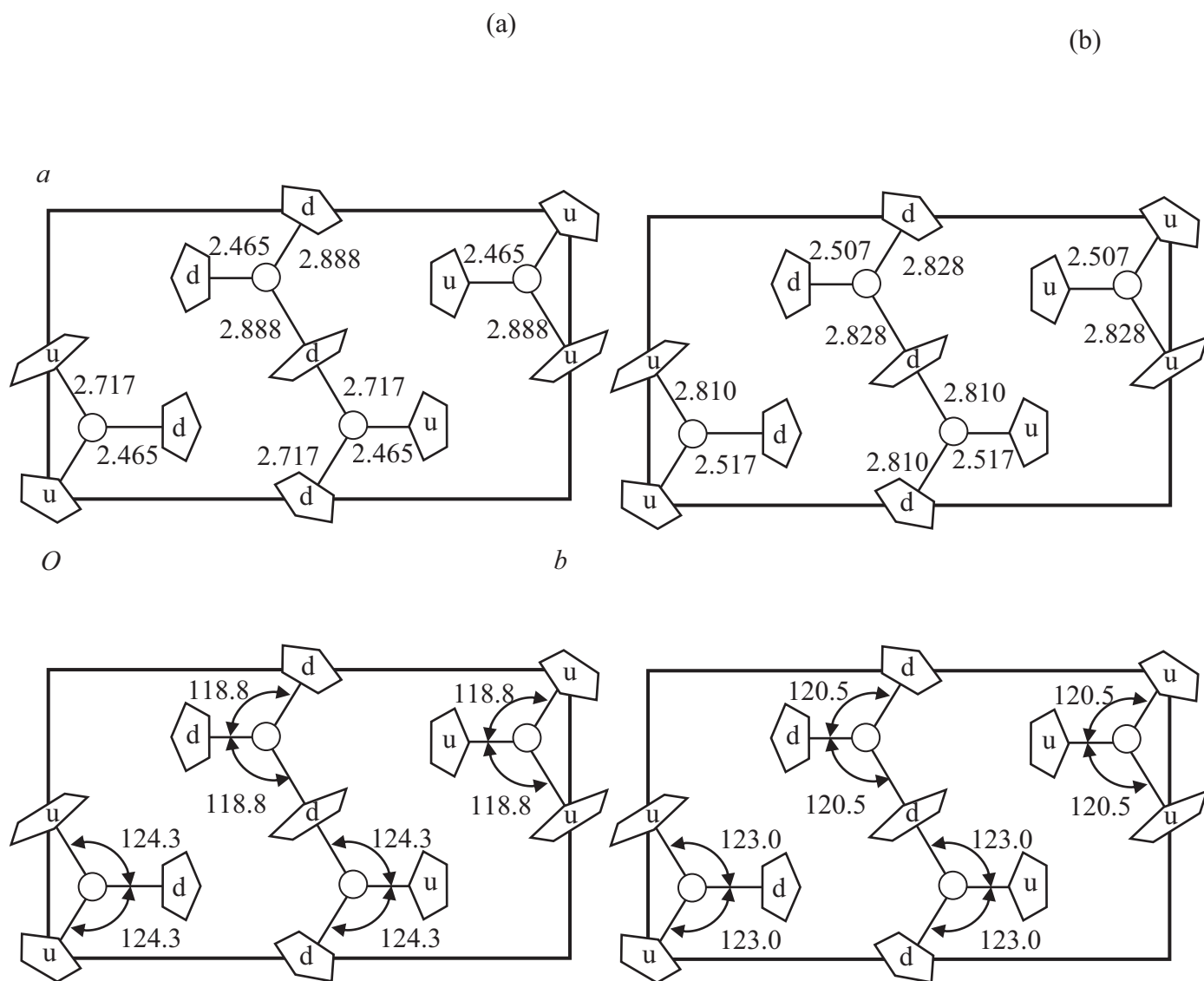
Figure 3 Figure Caption: Schematic diagram for the eclipsed lattice showing (a) experimental and (b) calculated geometric parameters [distances (Å) and angles (º)], and relative C_5H_5 ring orientation in each [Pb(C_5H_5)$_3$] unit (d = 'down', i.e. C-H pointing directly away, u = 'up' C-H pointing directly upwards).
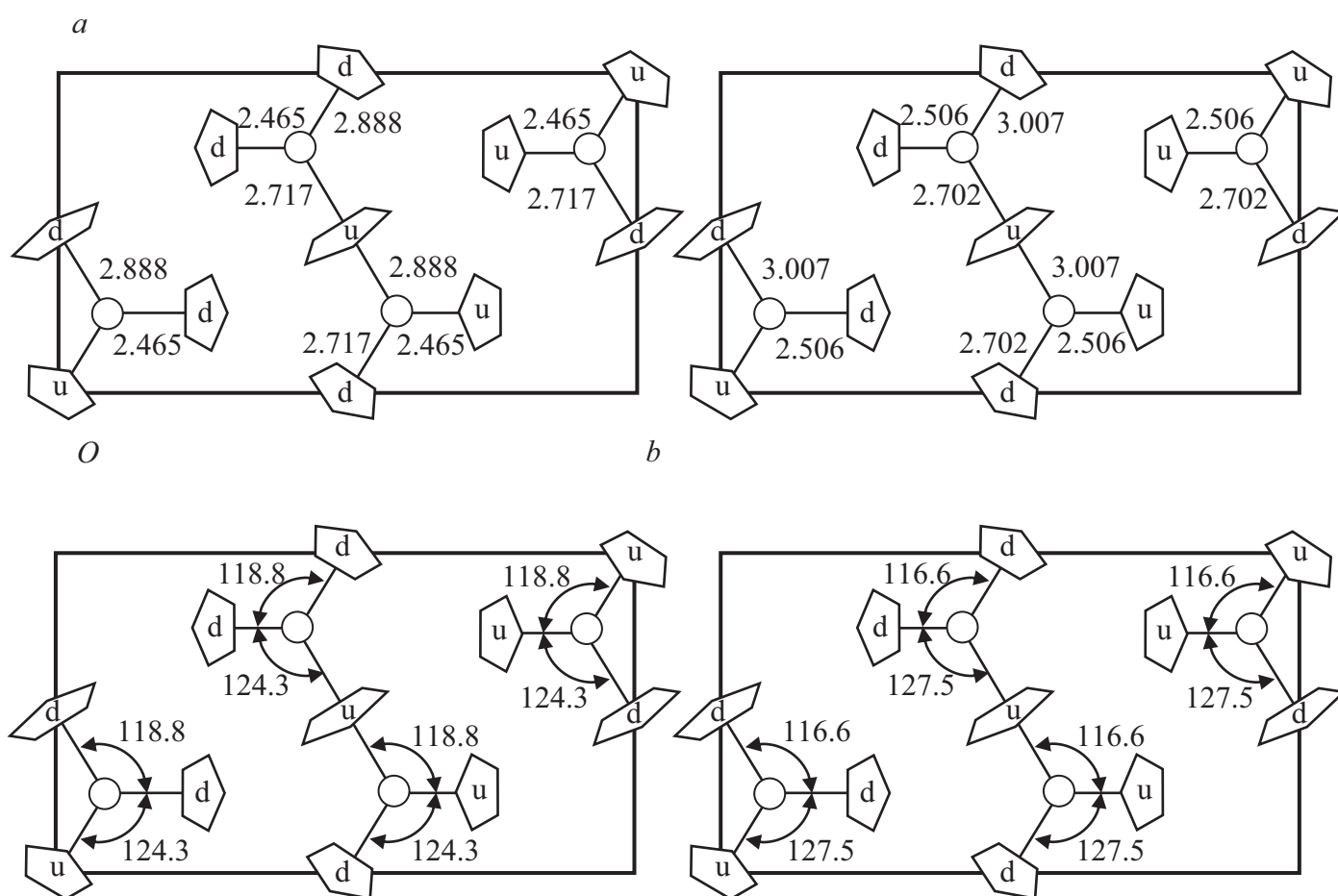
15

Figure 4 Figure Caption: Schematic diagram for the staggered lattice showing (a) experimental and (b) calculated geometric parameters [distances (Å) and angles (º)], and relative C_5H_5 ring orientation in each [Pb(C_5H_5)$_3$] unit (d = 'down', i.e. C-H pointing directly away, u = 'up' C-H pointing directly upwards).

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Conclusion

In this paper we have described the application of plane-wave density functional theory to shed light on the nature of the molecular crystal structure disorder observed in the orthorhombic zigzag polymorph of plumbocene, $Pb(C_5H_5)_2$. The energies obtained from the optimisation of the idealised crystal lattice arrangements derived from the disordered cell have allowed crystallographic occupancy factors to be calculated by a quantum mechanical technique for the first time. This has revealed a very close agreement between experiment and theory at room temperature, but that at lower temperatures one well-defined packing arrangement is increasingly favoured. Furthermore, a potential basis for constructing geometric parameter constraints, data often crucial to refinement of X-ray diffraction data, has been identified. Finally, single-point energy calculations performed on $Pb(C_5H_5)_2$ chains taken from the two different crystal lattices have highlighted the importance of chain-chain interactions in determining the greater stability of the staggered conformation.

Combined with conventional crystallographic packages, this approach could provide an important tool for determinations in a wealth of future studies where disorder in periodic structures is observed. In addition to the pragmatic nature of this work we have demonstrated, using $Pb(C_5H_5)_2$ as the illustrative example, firstly how energy differences between the disordered lattices may be determined and, secondly, how the origins of the discrepancies may be elucidated. Despite the application of this new technique to a simplified $1 \times 1 \times 1$ unit of the structure of plumbocene, with access to bigger computational resources other packing arrangements based on a bigger superlattice (*e.g.* $2 \times 2 \times 2$) could also be envisaged, providing a potentially greater level of accuracy in the calculated occupancy factors.

Table of Contents graphic
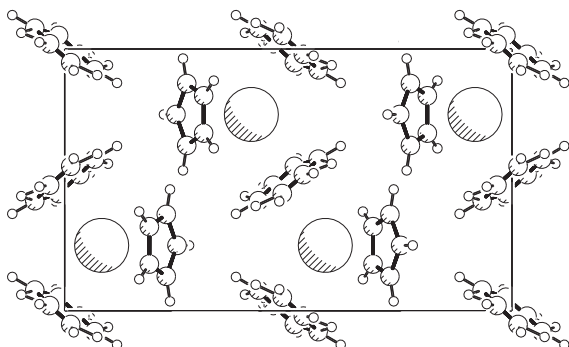
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