Do Computed Crystal Structures of Nonpolar Molecules Depend on the Electrostatic Interactions? The Case of Tetracene

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We present a strategy for comparing the global properties of competing potential models. By systematically sampling the potential energy surface of crystalline tetracene, we assess how the number, energy and structure of its minima are modified by switching on (or off) the Coulombic interactions. The increased complexity of the Coulombic potential leads to a more "rugged" potential energy surface with a larger number of minima, but the effect is not large. In fact, we find a subset of minima stable only in presence of the Coulombic interactions, a smaller subset stable only in their absence, and a large majority stable in both cases. Among these, there is a very good, but not perfect, correlation between the energies and the structures computed with and without the electrostatic interactions. Although electrostatic interactions play a role even in a rigid nonpolar molecule such as tetracene, they are not as crucial as often believed, because altering the electrostatic model (or switching it off completely) leads, in most cases, to equivalent results.

1. Introduction

The prediction of the crystal structure of an organic compound given its chemical formula is a very challenging problem, as shown by the surprisingly few successful predictions identified in a survey by Price and co-workers[1] or listed in the on-line database maintained by the same group.[2] Because failed calculations are likely to go unreported, actual successes might be even less common than suggested by these surveys. A more objective assessment of the current state of the art is given by the blind tests conducted by the Cambridge Crystallographic Data Centre in 1999, 2001, 2004 and 2007.[3−6] Each test involved several research groups, which were invited to submit predictions for a handful of given compounds. The success rate using classical potential models was quite low and, disappointingly, improved only slightly in the later tests.[7]

In the basic prediction strategy, adopted by most researchers, one starts from a molecular model, generates several thousands of different crystalline arrangements, and selects structures according to their lattice energy, calculated with one of the many available potential models. Although entropic and kinetic factors, besides the potential energy, may also play a role during the crystallization process, it is widely believed that the choice of an accurate and reliable potential model remains the most important unsolved issue[3,7−10] in structure predictions. The electrostatic part of the potential model, in particular, has received much attention. Many different representations have been proposed, including point charges, located on the atoms[11−13] or on additional sites,[14,15] and multipoles, located on the molecular center of mass[16] or distributed on the atoms.[17] Atomic multipoles and charges are most often obtained by least-squares fits to the *ab initio* electrostatic potentials. When additional charged sites are used, the least-squares problem presents multiple solutions, requiring stochastic methods[14,15] to find acceptable positions and charges of the sites.

Because of their perceived importance, we have decided to assess the actual effect of the electrostatic interactions by investigating whether switching them on (or off) alters the potential minima. Some hints on the possible role of the electrostatic interactions come from investigations on known crystalline polymorphs. A well studied case[1,9,10,18−20] is that of benzene, which presents orthorhombic and monoclinic polymorphs, the former of which, being experimentally stable at lower temperatures and pressures, is the most bound one. An analysis[19] of published potential models indicated that only a few models,[21−23] all including electrostatic interactions, yield the correct energy order for the two polymorphs. All successful calculations for benzene reported in the previously mentioned review[1] or in the more recent literature[9,10,20] also include electrostatic interactions. The energy order is apparently affected only by the presence (or absence) of the electrostatic interactions and not by their representation, which covers atomic charges,[9,10,20,21] a single quadrupole at the molecular center[22] and distributed quadrupoles.[23] The dependence on the electrostatic model appears to be quite weak, because changes in the potential affect mainly the energy of the minima, with minor influences on their structures. In fact, the example of benzene suggests that crystallographic structures are remarkably resilient to changes in the electrostatic model, even when these have significant effects on the energies.[9,10,18] These indications are reinforced by the observation that we could not readily find other compounds for which including (or excluding) the electrostatic

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interactions reshuffle the energy order of the experimental polymorphs. In a previous investigation[24] on tetrathiafulvalene (TTF), for example, we found no energy reshuffling of the α and β polymorphs when including the charges.

The information provided by these calculations, although quite intriguing, is limited to the structures of a few experimental polymorphs. More information may be obtained by sampling the overall distribution of potential energy minima, as we have recently done to identify the possible polymorphs of pentacene and tetracene, which both experimentally present at least two forms (high- and low-temperature polymorphs, respectively).[25,26] A surprisingly large number of distinct minima, with a variety of structural arrangements, was identified. For each compound the two deepest minima identified by sampling were found to correspond to the two experimental polymorphs, which were reproduced very satisfactorily. Of course, these results depend on the potential model chosen for the calculations, which for tetracene[26] was an atom−atom potential plus Coulombic interactions represented by atomic charges. We have now repeated the calculations for tetracene after removing the charges, to investigate the resulting changes in the distribution, identity and order of the energy minima. In fact, we have thus partially assessed the reliability of our published results for tetracene. Besides the interest for this specific molecule, we aim to investigate the role of the electrostatic interactions for a typical molecular crystal. Our conclusion that electrostatic interactions in crystalline tetracene are not as crucial as often believed (section 4) is probably valid also for other nonpolar, rigid molecules.

To provide a broader context for our investigation, we wish to emphasize that tetracene, like benzene, pentacene, TTF and many other molecular crystals,[19,24−26] presents several crystalline polymorphs, stable in different temperature and pressure ranges. Because of this, although most energy minimization calculations focus only on discovering the global minimum (which corresponds to the stable polymorph at low temperatures and pressures), we also seek the next few minima, which ought to correspond to further polymorphs. In fact, the properties and stability range of the various competing polymorphs, although outside the scope of the present work, can be accurately predicted[19] by computing the Gibbs free energy as a function of pressure and temperature, with quasi harmonic lattice dynamics (QHLD) methods.

2. Calculations

The calculation of the possible structures of minimum energy for crystalline tetracene has been discussed in the previous paper.[26] The tetracene molecules were treated as rigid units, with the *ab initio* geometry computed with a 6-31G(d) basis set in combination with an exchange-correlation functional B3LYP,[27,28] interacting through an intermolecular potential Φ'. This was represented by an atom−atom Buckingham model[29] with Williams parameter set IV,[30] combined with Coulombic interactions described by atomic charges derived from the *ab initio* electrostatic potential (ESP charges).[27] ESP charges and *ab initio* geometry are shown in the inset of Figure 1. An optimally uniform quasi-random sampling method, known as a low-discrepancy Sobol' sequence,[31] was used to generate 2500 initial structures. Starting from each of these structures, we minimized the total potential energy Φ' by adjusting cell axes, cell angles, positions and orientations of the molecules. We then checked the vibrational frequencies of the lattice, which must be real and positive at the local minima of the energy. The structures at the minima were finally analyzed[32,33] to identify their space group, a step which occasionally involved cell halving or doubling to obtain a conventional cell.

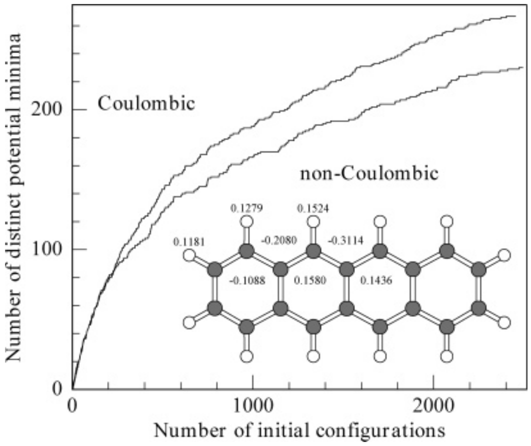

Figure 1. Number of distinct potential minima as a function of the number of initial configurations for the Coulombic and non-Coulombic potentials, as indicated in the figure. Inset: molecular geometry of tetracene ($C_{18}H_{12}$, planar with D_{2h} symmetry) and ESP charges (*e* units, drawn near the atoms). Chemically equivalent atoms have identical charges. Molecular graphics by MOLSCRIPT.[34]

As a first quick test of the importance of the Coulombic model, we re-ranked the potential minima of tetracene after replacing the ESP charges with the Mulliken charges[27] (without structural optimization). We found a very high correlation between the energies computed with the two charge models and, furthermore, there were no changes in the order of the deepest minima. Because Mulliken charges provide a poor representation of the electrostatic interactions (especially in comparison with the ESP charges), these results confirm that the details of the electrostatic model may be unimportant. In a second phase we have altogether eliminated the electrostatic interactions and repeated the complete calculations for tetracene, starting from exactly the same initial configurations[26] and using the identical methods, with a potential Φ'' identical to Φ', but with zero charges. Once identified all minima, we have compared them using a mapping procedure which allow us to discover the relationships between the minima of the Coulombic and non-Coulombic potentials Φ' and Φ'' (Section 3).

3. Results

3.1. Mapping between Minima. As just discussed, we have sampled 2500 different configurations, each used as the starting point of two independent steepest descent energy minimizations, one with the Coulombic interactions and another without them. The configurations which failed to converge to compact and stable bound states (≈30% in both cases) were discarded, and all structures encountered more than once were identified. The efficiency of the search process is analyzed in Figure 1, where we show the number of *distinct* minima encountered during the search as a function of the number of initial configurations, separately for the Coulombic and the non-Coulombic potentials. It can be seen that by increasing the coverage of the search space we approach a saturation plateau where new configurations tend to fall more and more frequently into previously encountered minima. This behavior indicates that a large part of the accessible minima has already been encountered, because to find new *distinct* minima becomes progressively more difficult. Although the *total* number of minima (either distinct or not) is essentially the same in the two cases, the saturation is slower for the Coulombic case, where we encounter a larger number of distinct minima. The Coulombic potential surface appears more rugged, with a larger number of “attraction basins”.

This suggestion, which implies a comparison between the minima computed with and without the Coulombic interactions, assumes a very clear meaning if we follow the procedure mentioned in Section 2 to obtain a mapping between Coulombic and non-Coulombic minima. To simplify the discussion, we label the Coulombic minima as $N' = 1', 2', 3', ...$, in order of increasing energy, and indicate as $\{N'\}$ the set of all such minima. Analogously, we use the labels $N'' = 1'', 2'', 3'', ...$ and the set $\{N''\}$ for the non-Coulombic minima. Starting from the structures of all distinct Coulombic minima $\{N'\}$, we minimize the energy after removing the charges. Structures usually converge to previously encountered non-Coulombic minima in $\{N''\}$, thus confirming that most of the accessible minima have already been identified. We also find some new non-Coulombic minima, which are added to $\{N''\}$. Starting from this newly extended set $\{N''\}$, we repeat the minimization in the opposite direction, after including the charges, and add any new Coulombic minima to $\{N'\}$. No new minimum appears after a second iteration of the process, leaving us with 342 Coulombic and 298 non-Coulombic minima.

This procedure yields a mapping in which each minimum in $\{N'\}$ converges to a minimum in $\{N''\}$, and a second mapping in the opposite direction. Both mappings are “many-to-one”; *i.e.*, several minima in a set may converge to a single minimum in the opposite set. Subsets for which the mapping is “one-to-one” also exist. In these subsets each minimum N' of Φ' falls onto a minimum N'' of Φ'' and *vice versa*. In these cases we consider N' and N'' as a matched couple of minima. On the contrary, no matching partner exists for N' when N' falls onto a minimum N'' that does not fall back to N'.

As an example of the information thus obtained, we represent in Figure 2 part of the mappings involving some of the deepest minima. It can be noticed that the Coulombic minimum 1′ converges to the non-Coulombic minimum 1″ and *vice versa*; *i.e.*, each of the two partners falls in the attraction basin of the other one. Thus, 1′ and 1″ effectively represent matched partners which, as discussed in section 3.3 below, exhibit small structural differences due to the different potentials. The non-Coulombic minimum 10″, instead, has no matching Coulombic partner in $\{N'\}$, because it converges to 4′, whereas 4′ does not go back to 10″. In the opposite direction, the same happens for 22′, which has no matching partner in $\{N''\}$.

This analysis allows us to identify all matched couples of Coulombic and non-Coulombic minima, plus the remaining Coulombic or non-Coulombic minima without a matching partner in the opposite set. If the Coulombic interactions are switched off or on, respectively, these minima without a partner loose their stability and disappear by falling toward distant attraction basins. By completing the analysis, we find 96 minima stable only in the presence of the Coulombic interactions, 52 minima stable only in their absence, and a majority of 246 minima stable in both cases. Thus, adding the Coulombic interactions not only increases the complexity of the potential, leading to the expected larger number of minima, but also destabilizes several non-Coulombic structures. For the majority of minima, nevertheless, switching on (or off) the Coulombic interactions does not affect the stability, although it may well modify the energy rank or the structure.

3.2. Energy of the Minima. To further investigate the effects of the Coulombic interactions, we have compared energies and crystallographic structures of the partners in all the $N = 246$ matched couples of Coulombic and non-Coulombic minima. In Figure 3 we show directly the energy Φ' of one partner as a function of the energy Φ'' of the matching partner. Although the energies Φ' and Φ'' are generally correlated, with a linear correlation coefficient[31] $r = 0.888$, their energy ranks have been reshuffled, because the data points (Φ', Φ'') do not follow a strictly monotonous curve. Minima without a matched partner, in comparison, exhibit no energy correlation with the minima on which they fall ($r = 0.317$).

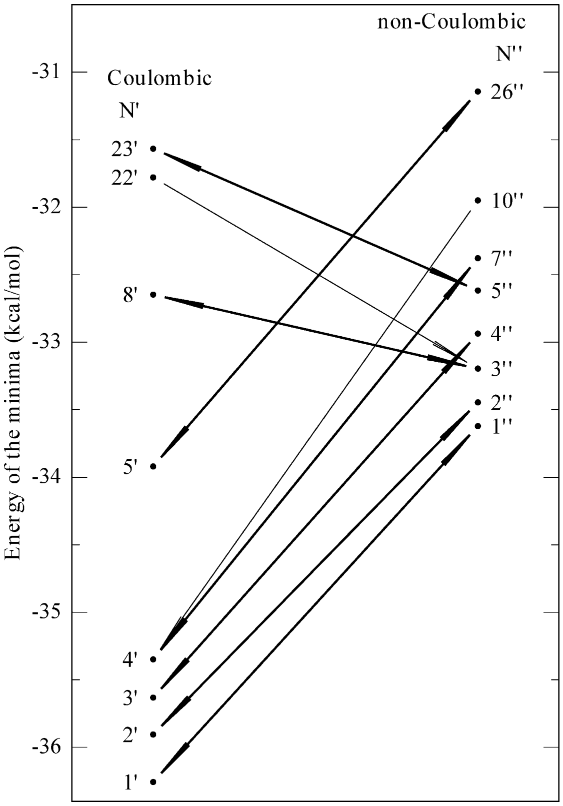

Figure 2. Mapping between Coulombic and non-Coulombic minima N' and N'' (involving the five deepest minima). Minima are represented by points, labeled by the energy rank N' or N'' and drawn at an ordinate that corresponds to the energy (with small shifts to avoid overlaps). The arrow $N' \rightarrow N''$ indicates that N' converges to N'', whereas $N' \leftrightarrow N''$ indicates that N' converges to N'' and *vice versa*.

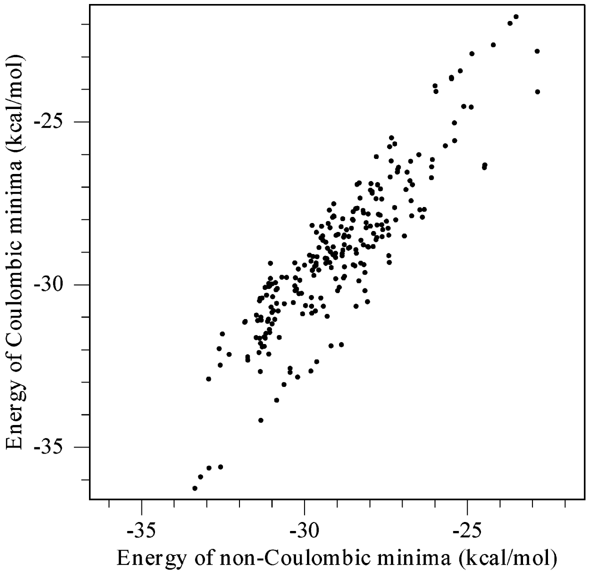

Figure 3. Energy of the Coulombic minima as a function of the energy of the matching non-Coulombic minima.

The linear correlation r is a ratio between statistical moments and, for the purposes of predicting the relative stability of different structures, does not really represent an appropriate measure of the importance of the rank reshuffling. What actually matters is the agreement (or not) between the relative order of the energies of any two couples of matched minima with or without the Coulombic interactions. For example, going back to Figure 2, the two deepest matched couples (1′, 1″) and (2′, 2″) have the same order (*i.e.*, $\Phi_{1'} < \Phi_{2'}$ and $\Phi_{1''} < \Phi_{2''}$), whereas the two matched couples (3′, 4″) and (8′, 3″) have opposite order (*i.e.*, $\Phi_{3'} < \Phi_{8'}$ and $\Phi_{4''} > \Phi_{3''}$). Judging from Figure 2, this seems to be the exception, rather than the rule. In fact, by considering all $N(N - 1)/2 = 30\,135$ pairs of matched couples, we find that Φ' and Φ'' have the same order in 25638 cases, *i.e.*, with a rather high probability $p = 0.851$. Other possible statistical measures of the correlation between the ranks of two variables are discussed in the literature on the Kendall's τ.[31] For readers who prefer τ to a probability p, it suffices to say that because we encounter no energy ties, $\tau = 2p - 1 = 0.702$.

In the previous investigation on the possible structures of tetracene[26] it was found that the two known tetracene polymorphs correspond to the two deepest Coulombic minima 1′ and 2′. As shown in Figure 2 and as we had already noticed,[26] 1′ and 2′ also match the two deepest non-Coulombic minima 1″ and 2″, respectively. This satisfactory finding implies that the absolute and relative stability of the two polymorphs is independent of the presence or absence of the Coulombic interactions in the potential model. The result that Φ' and Φ'' yield the same energy order, with high probability, indicates that this independence of the potential extends to most, although not all, pairs of matched couples.

3.3. Structure of the Minima. The properties of the Coulombic minima have been discussed in the previous paper,[26] which describes the crystallographic structures of several deep minima and presents an analysis of the statistical distribution among the various space groups. Because the analogous information for the non-Coulombic minima is almost identical, we will not report it here. This similarity is not due to chance, because we have found that the crystallographic structures of all the $N = 246$ couples of matched Coulombic and non-Coulombic minima are closely related. In fact, the two matching partners always belong to the same space group and have the same number Z of molecules in the unit cell, and the same site symmetry; *i.e.*, they belong to the same structural class as defined by Belsky.[35,36] Furthermore, the correlation between their densities, like that between the unit cell axes, is extremely high ($r = 0.997$, in both cases). For the deepest minima, we also find that matching Coulombic and non-Coulombic structures have essentially the same unit cell angles. However, this correspondence does not extend to all couples of matching minima, because the overall correlation between the cell angles is poor ($r = 0.642$). This apparent discrepancy is not significant, because the cell angles can be chosen in many different ways and are notoriously unreliable[37] when comparing structures. To overcome this problem, we have adopted the distance comparison method[38] used in the blind tests[3,5] to compare experimental and computed structures. For each structure of interest, one considers a spherical coordination shell, containing a reference molecule and at least 14 neighboring molecules, and then lists all interatomic distances between the reference molecule and its neighbors. Structures are finally compared by computing a root-mean-square deviation (RMSD) between their lists of distances. In the blind tests it has been found that correct predictions have distances whose RMSD from the experimental distances is typically below 1.0 Å, which may be considered as the "standard" accuracy of this kind of calculations.[5] In our computations for tetracene we find that the RMSD between Coulombic and non-Coulombic partners is always very small (0.11 ± 0.08 Å on the average, with a maximum RMSD of 0.5 Å). All pairs of matching partners thus would be considered identical structures in a blind test.

4. Discussion and Conclusions

We have assessed how the number, energy and structure of the potential minima of crystalline tetracene are modified by switching on, or off, the electrostatic interactions. In both cases, the nonelectrostatic part of the intermolecular potential is represented by an atom−atom Buckingham model,[29] with Williams parameter set IV.[30] The electrostatic interactions, when present, are described by atomic charges derived from the *ab initio* electrostatic potential.[27] Adding or subtracting the Coulombic interactions, while leaving unchanged the remaining atom−atom interactions, clearly is a very crude procedure. In fact, potential parameters are usually derived from the outset with a specific electrostatic model (including the "null" model),[39] and may thus partially compensate for the presence or absence of explicit electrostatic interactions.[7,39] Our procedure, in which no compensation is possible, deteriorates the starting model and thus tends to *overestimate* the computed effects of the electrostatic interactions.

By separately sampling a large number of initial configurations on the Coulombic and on the non-Coulombic potential energy surfaces, we have identified a large fraction of their minima. Starting from these, we have then investigated the natural mapping in which each Coulombic minimum converges to a non-Coulombic minimum, or *vice versa*, when the electrostatic interactions are switched off or on, respectively.

We have thus noticed a number of interesting features, probably transferable to other similar molecular crystals. (1) Crystalline minima on the Coulombic and non-Coulombic surfaces are equally "accessible"; *i.e.*, the number of initial configurations that successfully converge to compact and stable bound states is the same in the two cases. (2) The increased complexity of the Coulombic potential leads to a more "rugged" surface, with a larger number of distinct minima. As a consequence, there is subset of minima stable only in presence of Coulombic interactions. When electrostatic interactions are switched off, these purely Coulombic minima loose their stability and fall toward distant non-Coulombic minima. (3) The opposite case, with minima stable only in absence of the Coulombic interactions, also occurs, but is less frequent. (4) In the majority of cases, the stability of the minima is not affected by the presence or absence of the electrostatic interactions. Most minima form matched Coulombic and non-Coulombic couples in which each of the two partners falls in the attraction basin of the other one (with the appropriate potential). Matched partners exhibit a high degree of similarity, having identical crystallographic and site symmetries and, without exceptions, very close molecular arrangements. Furthermore, the relative energy order of Coulombic and non-Coulombic partners is, with high probability, the same.

The notion that electrostatic interactions *may* be an important ingredient in the description of molecular crystals is justified, because they play a role even in nonpolar molecules such as tetracene or benzene. However, electrostatic interactions are not as crucial as often believed, because switching them off leads, in most cases, to equivalent results. At least for rigid and highly symmetric molecules such as benzene or tetracene, all the attention given to the choice among alternative electrostatic models is probably not warranted, because just about any model would give equivalent results. This is definitely the case for TTF or tetracene, because the energy ranks of their deepest minima, and thus of the corresponding experimental polymorphs,[24,26] do not depend on the presence of the electrostatic interactions. From this point of view, benzene is an exceptional case, in which the presence (or absence) of electrostatic interactions reshuffles the predicted energy rank of the experimental polymorphs. Even for this exceptional case in which electrostatic interactions reshuffle the energy rank, the effects on the computed lattice parameters of the experimental polymorphs are not important.[9,10,18]

Our investigation is based on an analysis of the local minima of the potential energy. The local minima represent the possible configurations of *mechanical equilibrium* and thus constitute the "natural" or "inherent" structures[40] that the system can exhibit. This concept suggests a natural mapping between different potentials, in which the minima of a first potential model converge to the minima of a second model. We have found that this mapping provides a simple, yet powerful, method for comparing the *global* properties of competing potential models. The comparison includes, but is not restricted to, the standard *local* comparison between the computed properties of a few experimentally known crystalline forms.

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References and Notes

(1) Beyer, T.; Lewis, T.; Price, S. L. *Cryst. Eng. Commun.* **2001**, *44*, 1.

(2) Basic Technology Programme webpages - Control and Prediction of the Organic Solid State (CPOSS); http://www.chem.ucl.ac.uk/basictechorg/.

(3) Lommerse, J. P. M.; Motherwell, W. D. S.; Ammon, H. L.; Dunitz, J. D.; Gavezzotti, A.; Hofmann, D. W. M.; Leusen, F. J. J.; Mooij, W. T. M.; Price, S. L.; Schweizer, B.; Schmidt, M. U.; van Eijck, B. P.; Verwer, P.; Williams, D. E. *Acta Crystallogr., Sect. B* **2000**, *56*, 697.

(4) Motherwell, W. D. S.; Ammon, H. L.; Dunitz, J. D.; Dzyabchenko, A.; Erk, P.; Gavezzotti, A.; Hofmann, D. W. M.; Leusen, F. J. J.; Lommerse, J. P. M.; Mooij, W. T. M.; Price, S. L.; Scheraga, H.; Schweizer, B.; Schmidt, M. U.; van Eijck, B. P.; Verwer, P.; Williams, D. E. *Acta Crystallogr., Sect. B* **2002**, *58*, 647.

(5) Day, G. M.; Motherwell, W. D. S.; Ammon, H.; Boerrigter, S. X. M.; Della Valle, R. G.; Venuti, E.; Dzyabchenko, A.; Dunitz, J.; Schweizer, B.; van Eijck, B. P.; Erk, P.; Facelli, J. C.; Bazterra, V. E.; Ferraro, M. B.; Hofmann, D. W. M.; Leusen, F. J. J.; Liang, C.; Pantelides, C. C.; Karamertzanis, P. G.; Price, S. L.; Lewis, T. C.; Nowell, H.; Torrisi, A.; Scheraga, H. A.; Arnautova, Y. A.; Schmidt, M. U.; Verwer, P. *Acta Crystallogr., Sect. B* **2005**, *61*, 511.

(6) Day, G. M.; Cooper, T. G.; Cruz Cabeza, A. J.; Hejczyk, K. E.; Ammon, H. L.; Boerrigter, S. X. M.; Tan, J.; Della Valle, R. G.; Venuti, E.; Jose, J.; Gadre, S. R.; Desiraju, G. R.; Thakur, T. S.; van Eijck, B. P.; Facelli, J. C.; Bazterra, V. E.; Ferraro, M. B.; Hofmann, D. W. M.; Neumann, M.; Leusen, F. J. J.; Kendrick, J.; Price, S. L.; Misquitta, A. J.; Karamertzanis, P. G.; Welch, G. W. A.; Scheraga, H. A.; Arnautova, Y. A.; Schmidt, M. U.; van de Streek, J.; Wolf, A.; Schweizer, B. *Acta Crystallogr., Sect. B,* manuscript in preparation.

(7) Price, S. L.; Price, L. S. *Intermolecular Forces and Clusters I*; Structure & Bonding 115; Springer-Verlag: Berlin & Heidelberg, 2005; p 81.

(8) Schmidt, M. U.; Englert, U. *J. Chem. Soc., Dalton. Trans.* **1996**, 2077−2082.

(9) Arnautova, Y. A.; Jagielska, A.; Pillardy, J.; Scheraga, H. A. *J. Phys. Chem. B* **2003**, *107*, 7143.

(10) Day, M.; Chisholm, J.; Shan, N.; Motherwell, W. D. S.; Jones, W. *Cryst. Growth Design* **2004**, *4*, 1327.

(11) Cox, S. R.; Williams, D. E. *J. Comput. Chem.* **1981**, *2*, 304.

(12) Cornell, W. D.; Cieplak, P.; Bayly, C. I.; Kollmann, P. A. *J. Am. Chem. Soc.* **1993**, *115*, 9620.

(13) Bayly, C. I.; Cieplak, P.; Cornell, W. D.; Kollman, P. A. *J. Phys. Chem.* **1993**, *97*, 10269.

(14) Karamertzanis, P. G.; Pantelides, C. C. *Mol. Simul.* **2004**, *30*, 413.

(15) Berardi, R.; Muccioli, L.; Orlandi, S.; Ricci, M.; Zannoni, C. *Chem. Phys. Lett.* **2004**, *389*, 373.

(16) Chaka, A. M.; Zaniewski, R.; Youngs, W.; Tessier, C.; Klopman, G. *Acta Crystallogr., Sect. B* **1996**, *52*, 165.

(17) Willock, D. J.; Price, S. L.; Leslie, M.; Catlow, C. R. *Am. J. Comput. Chem.* **1995**, *16*, 628.

(18) Dzyabchenko, A. V. *J. Struct. Chem.* **1984**, *25*, 416; **1984**, *25*, 559.

(19) Della Valle, R. G.; Venuti, E.; Brillante, A. *Chem. Phys.* **1996**, *202*, 231.

(20) Raiteri, P.; Martoňák, R.; Parrinello, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 3769.

(21) Hall, D.; Williams, D. E. *Acta Crystallogr., Sect. A* **1975**, *31*, 56.

(22) Claessens, M.; Ferrario, M.; Ryckaert, J. P. *Mol. Phys.* **1983**, *50*, 217.

(23) Yashonath, S.; Price, S. L.; McDonald, I. R. *Mol. Phys.* **1988**, *64*, 361.

(24) Venuti, E.; Della Valle, R. G.; Farina, L.; Brillante, A.; Vescovi, C.; Girlando, A. *Phys. Chem. Chem. Phys.* **2001**, *3*, 4170.

(25) Della Valle, R. G.; Venuti, E.; Brillante, A.; Girlando, A. *J. Chem. Phys.* **2003**, *118*, 807.

(26) Della Valle, R. G.; Venuti, E.; Brillante, A.; Girlando, A. *J. Phys. Chem. A* **2006**, *110*, 10858.

(27) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Rega, N.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham; M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon; M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian Inc.: Pittsburgh, PA, 1998.

(28) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(29) Pertsin, A. J.; Kitaigorodsky, A. I. *The Atom-Atom Potential Method*; Springer-Verlag: Berlin, 1987.

(30) Williams, D. E. *J. Chem. Phys.* **1967**, *47*, 4680.

(31) Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes in Fortran*; Cambridge University Press: Cambridge, U.K., 1992.

(32) Le Page, Y. *J. Appl. Cryst.* **1987**, *20*, 264; **1988**, *21*, 983.

(33) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7; http://www.cryst.chem.uu.nl/platon/.

(34) Kraulis, P. J. *J. Appl. Crystallogr.* **1991**, *24*, 946; http://www.avatar.se/molscript/.

(35) Belsky, V. K.; Zorkii, P. M. *Acta Crystallogr., Sect. A* **1977**, *33*, 1004.

(36) Belsky, V. K.; Zorkaya, O. N.; Zorkii, P. M. *Acta Crystallogr., Sect. A* **1995**, *51*, 473.

(37) Andrews, L. C.; Bernstein, H. J.; Pelletier, G. A. *Acta Crystallogr., Sect. A* **1980**, *36*, 248.

(38) Chisholm, J.; Motherwell, W. D. S. *J. Appl. Crystallogr.* **2005**, *38*, 228.

(39) Filippini, G.; Gavezzotti, A. *Acta Crystallogr., Sect. B* **1993**, *49*, 868.

(40) Stillinger, F. H.; Weber, T. A. *Phys. Rev. A* **1982**, *25*, 978.