# Ab Initio Investigation of Structure and Cohesive Energy of Crystalline Urea

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The structure and cohesive energy of crystalline urea have been investigated at the ab initio level of calculation. The performance of different Hamiltonians in dealing with a hydrogen-bonded molecular crystal as crystalline urea is assessed. Detailed calculations carried out by adopting both HF and some of the most popular DFT methods in solid-state chemistry are reported. Local, gradient-corrected, and hybrid functionals have been adopted: SVWN, PW91, PBE, B3LYP, and PBE0. First, a 6-31G(d,p) basis set has been adopted, and then the basis set dependence of computed results has been investigated at the B3LYP level. All calculations were carried out by using a development version of the periodic ab initio code CRYSTAL06, which allows full optimization of lattice parameters and atomic coordinates. With the 6-31G(d,p) basis set, structural features are well reproduced by hybrid methods and GGA. LDA gives lattice parameters and hydrogen-bond distances that are too small relative to experiment, while at the HF level the opposite trend is observed. Results show that hybrid methods are more accurate than HF and both LDA and GGA functionals, with a trend in the computed properties similar to that of hydrogen-bonded molecular complexes. When BSSE and ZPE are taken into account, all methods, except LDA, give computed cohesive energies that are underestimated with respect to the experimental sublimation enthalpy. Dispersion energy, not properly taken into account by DFT methods, plays a crucial role. Such a deficiency also affects dramatically the computed crystalline structure, especially when large basis sets are adopted. We show that this is an artifact due to the BSSE. Indeed, with small basis sets the BSSE gives an extra-binding that compensates for the missing dispersion forces, thus yielding structures in fortuitous agreement with experiment.

## Introduction

Over the past decades, the scientific community has experienced the explosive growth of the density functional theory (DFT)[1,2] that has been successfully applied to deal with problems of interest in computational chemistry.[3] It has also been successful for describing H-bonded intermolecular complexes.[3] A number of papers appeared in the literature comparing different functionals and indicated that gradient-corrected DF methods are quite efficient in predicting geometry and interaction energy of hydrogen-bonded (HB) adducts. However, as far as we are aware, few attempts[4] have been made to assess the reliability of density functional methods to describe hydrogen bonding in the solid state. Thus, it is valuable to extend this kind of assessment to the class of hydrogen-bonded molecular crystals.

In the present paper, we focus on crystalline urea, as a case study, and report on a series of detailed calculations carried out by adopting some of the most popular DF methods, both local and gradient-corrected, as proposed in the literature and commonly available in solid-state codes, as well as hybrid functionals that include Hartree−Fock (HF) exact exchange. Results are also compared to those obtained at the HF level of theory.

Urea is a simple molecule that has been the subject of many papers both experimental and theoretical. From the theoretical viewpoint, more than 15 years have passed since the publication of the pioneering work performed by Dovesi et al.[5] at the HF level of theory. It was the first example of theoretical characterization of a molecular crystal by means of an ab initio periodic code (CRYSTAL[6]) that adopted atom-centered Gaussian-type basis functions to represent crystalline orbitals.[7] Other theoretical investigations of the molecular crystal of urea followed in the last years, for instance, by Rosseau et al. at the HF/6-31++G-(d,p) level of theory[8] by adopting a very large cluster model to simulate the bulk structure. The cluster approach was also adopted by Gora et al.[9] and by Ayala and Scuseria,[10] at the HF and MP2 level, to investigate the nature of intermolecular interactions in the crystal. Fully periodic DFT calculations were performed by Miao et al.[11] that studied the effect of the pressure on urea at the LDA level and more recently by Morrison and Siddick[12] to characterize the strengths of hydrogen bonds at the GGA level. Also, Sun and Kung[13] performed DFT calculations to fit parameters to refine a force field to be used in molecular modeling simulations.

In this work, we extend the study of Dovesi et al.[5] to other Hamiltonians and larger basis sets by using a development version of the CRYSTAL code[6] that allows a full optimization of the crystalline structure and the calculation of the vibrational frequencies at the Γ point. Here, we focus on the assessment of current DFT methods in predicting the crystalline structure and the cohesive energy of the molecular crystal of urea.

The paper is organized as follows. First, we discuss the structure of urea in the solid state and in the gas phase. Then

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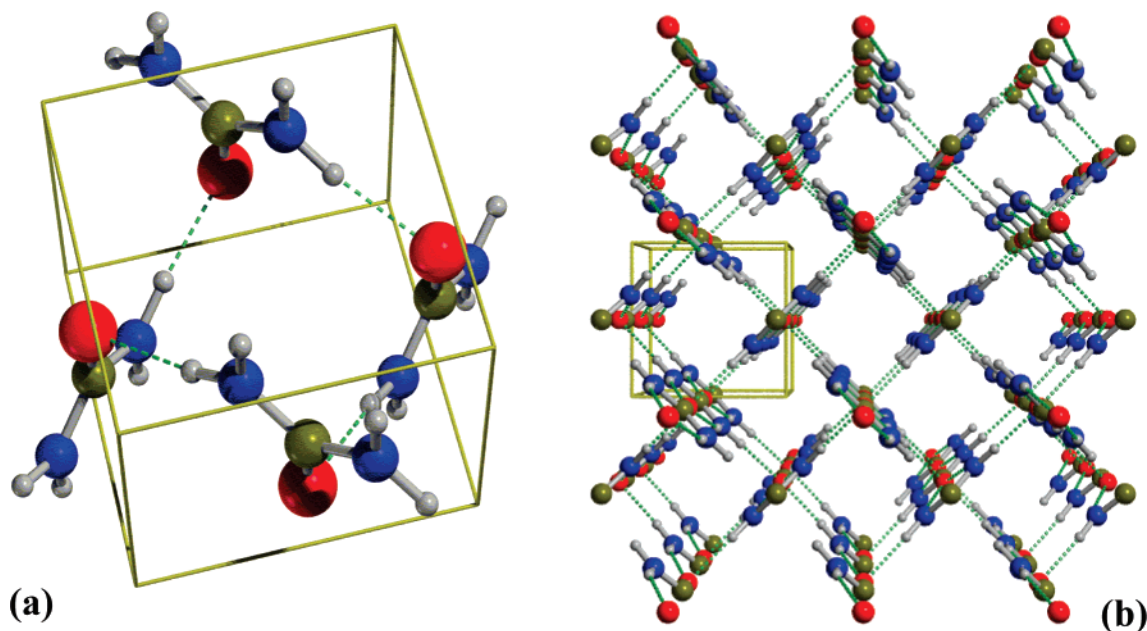


**Figure 1.** (a) Crystalline urea unit cell. (b) Arrangement of urea molecules in the crystalline structure.

results are reported on the structure and cohesive energy of the molecular crystal of urea obtained with different Hamiltonians and basis sets. Finally, we will show that current DFT methods seriously underestimate cohesive energies due to the lack of dispersion interactions, and this translates to overestimated unit cell volumes. The crucial role of the BSSE will also be addressed.

### Structure of Urea in the Solid State and in the Gas Phase

The crystal structure of urea[14] has a tetragonal cell (*P*-421) with two molecules in the unit cell, as shown in Figure 1a. Molecules are linked head−tail through a first set of hydrogen bonds to form infinite planar ribbons. Ribbons are then mutually orthogonal and oriented in opposite directions. This provides an additional stabilization through dipole−dipole forces. Molecules within ribbons are also connected to each other by a second set of hydrogen bonds. The complex network of hydrogen bonding within the crystal is shown in Figure 1b. An interesting feature of the crystal structure of urea is the peculiar hydrogen-bond pattern around the oxygen atom of the carbonyl group. Indeed, each oxygen is involved in four hydrogen bonds, two within the ribbon and two with the neighboring ribbons (Figure 2). This is a rare example of a carbonyl oxygen atom that forms four hydrogen bonds.

In the crystalline structure, each molecule adopts a planar conformation with $C_{2v}$ symmetry (Figure 3a); in contrast, in the gas phase the most stable structure has a $C_2$ symmetry with the amino group assuming a pyramidal conformation with an anti configuration, as shown in Figure 3b. This was confirmed both by microwave spectroscopic measurements[15] and through ab initio calculations. The latter indicates that the $C_{2v}$ geometry is a second-order saddle point on the potential energy surface.[16] A pyramidal conformation with a syn configuration ($C_s$ symmetry) has also been determined. Even if the determination of the relative stability of the urea conformers is still a matter of debate,[16−19] the whole set of data seem to indicate that the $C_2$-*anti* conformer is the most stable one, followed by the $C_s$-*syn* conformer, and, finally, the $C_{2v}$ planar structure. However, the differences in energy are within a few kJ/mol. In the present paper, we refer to both the $C_{2v}$ planar structure and the $C_2$-*anti* conformer.

### Computational Details

Calculations were carried out with a development version of the periodic ab initio CRYSTAL06 program.[6] Crystalline orbitals are represented as linear combinations of Bloch functions (BF) and are evaluated over a regular three-dimensional mesh in reciprocal space. Each BF is built from atom-centered atomic orbitals, which are contractions (linear combinations with constant coefficients) of Gaussian-type functions (GTF), each GTF being the product of a Gaussian times a real solid spherical harmonic.

**A. Hamiltonians and Basis Sets.** Along with the Hartree−Fock method, five different DFT methods were adopted: the simplest density functional method, LDA in its SVWN parametrization;[20,21] two gradient-corrected exachange-correlation functionals, the original GGA proposed by Perdew[22] in 1991 (PW91) and the more recent GGA functional PBE;[23] and two hybrid methods, the B3LYP functional,[24−26] probably the most widely used hybrid functional in molecular calculations, in its VWN5 formulation, and the PBE0 functional[27] (also known as PBE1PBE).

Four molecular all-electron basis sets were adopted. Two from the Pople's family of basis set,[28] 6-31G(d,p) and 6-311G(d,p); a DZP basis set as proposed by Thakkar et al.,[29] and recently used by Mitchell and Spackman and Mitchell;[30] and a TZP basis set devised by Ahlrichs and co-workers.[31] It is worth noting that, at variance with ionic systems,[6] molecular-devised basis sets of small-medium size can be reliably adopted for molecular crystals, without any reoptimization of the exponents. A recent work on organic molecular crystals has also confirmed that basis set optimization improved the quality of the calculation relatively little.[32] In the present work, comparison among HF and DFT methods was carried out by adopting the 6-31G(d,p) basis set, whereas the basis set dependence of the results was investigated at the B3LYP level.

**B. Computational Parameters.** The level of accuracy in evaluating the Coulomb and exchange series is controlled by five thresholds,[6] for which values of $10^{-7}$, $10^{-7}$, $10^{-7}$, $10^{-7}$, $10^{-16}$ were used for the Coulomb and the exchange series.

The DFT exchange-correlation contribution is evaluated by numerical integration over the cell volume.[33] Radial and angular
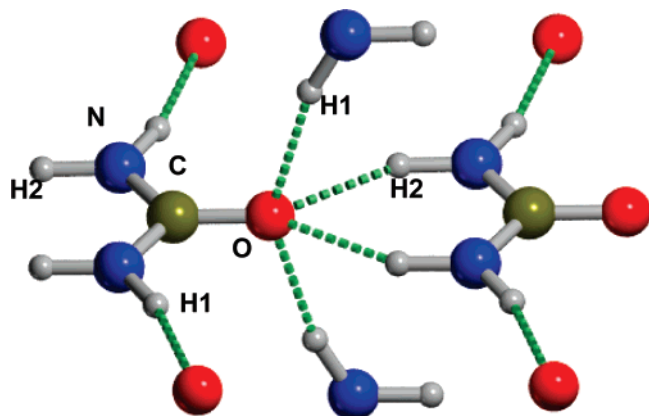
**Figure 2.** Hydrogen-bond pattern around the oxygen atom in the crystalline urea. Labeling scheme is as that adopted in the tables.
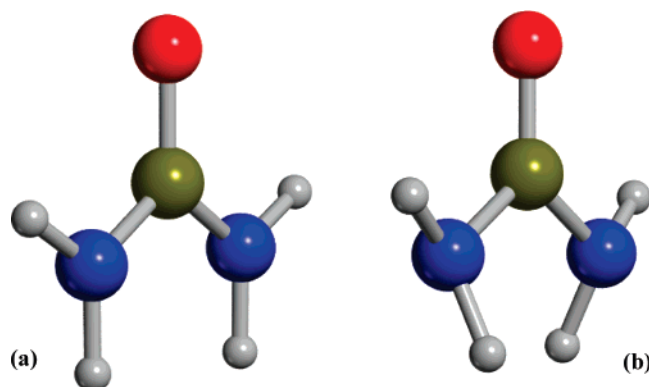


**Figure 3.** Urea molecular structures: (a) $C_{2v}$ conformation as found in the crystalline structure; (b) $C_2$-*anti* conformation as found in the gas phase.

points of the atomic grid are generated through Gauss−Legendre and Lebedev quadrature schemes. A grid pruning was adopted, as discussed in ref 33. In the present study, a (75,974)p grid has been used that contains 75 radial points and a variable number of angular points, with a maximum of 974 on the Lebedev surface in the most accurate integration region.

The condition for the SCF convergence was set to $10^{-8}$ on the root-mean-square variation of the density matrix elements between two subsequent cycles. The shrinking factor of the reciprocal space net was set to 4, corresponding to 18 reciprocal space points of the irreducible Brillouin zone at which the Hamiltonian matrix was diagonalized. The total energies obtained with this mesh are fully converged.

**C. Geometry Optimization.** Starting from the experimental crystal structure,[14] both lattice parameters and atomic coordinates have been fully relaxed by means of analytical energy gradients.[34−36] The geometry optimization is performed by means of a quasi-Newton algorithm in which the quadratic step (BFGS Hessian updating scheme) is combined with a linear one (parabolic fit) as proposed by Schlegel.[37] Convergence is tested on the rms and the absolute value of the largest component of the gradients and the estimated displacements. The threshold for the maximum force, the rms force, the maximum atomic displacement, and the rms atomic displacement on all atoms have been set to 0.00045, 0.00030, 0.00180, and 0.00120 au, respectively. The optimization is considered complete when the four conditions are simultaneously satisfied. The crystal symmetry was maintained during the whole optimization process.

**D. Cohesive Energy.** The cohesive energy of a molecular crystal is computed as:

$$\Delta E = E(\text{bulk})/Z - E(\text{mol})$$

where $E(\text{bulk})$ is the total energy of the unit cell and must be referred to the number, $Z$, of molecules in the unit cell, and $E(\text{mol})$ is the total energy of the isolated molecule in the gas phase. It corresponds to the packing energy due to the interaction among the molecules in the crystal. The computed $\Delta E$ value can be compared with experimental sublimation energies.

Sometimes $\Delta E$ is written as the sum of two contributions:[38]

$$\Delta E = \Delta E(\text{cond}) + \Delta E(\text{conf})$$

where the first term refers to the condensation of molecules that keep the conformation they have in the crystal and this term corresponds to the lattice energy; the second term is the difference between the energies of the isolated molecules in the bulk and gas phase conformation. $\Delta E(\text{conf})$ is, of course, negligible for rigid molecules, but can be significant for floppy molecules. As opposed to the $C_{2v}$ geometry of molecular urea in the bulk, the most stable structure has a $C_2$ symmetry with an anti configuration (see Figure 3). Therefore, when computing the interaction energy, $\Delta E(\text{conf})$ between the $C_2$ and the $C_{2v}$ conformers must be taken into account.

For crystalline urea, the interaction energy then becomes:

$$\Delta E = E(\text{bulk})/2 - E(\text{mol})$$

because there are two molecules in the cell.

Computed cohesive energies were corrected for the BSSE through the counterpoise method (CP).[39] The way this is accomplished in CRYSTAL06 is by supplementing the adopted basis set of the isolated molecule with the basis functions of an increasing number of neighbors (i.e., ghost atoms). The dependence of the BSSE (CP) on the number of neighboring atoms has been discussed elsewhere.[40] In the present work, the CP correction was computed by including up to 63 neighbors. A clear discussion of the problem of BSSE in molecular crystals can be also found in a recent paper by Spackman and Mitchell.[30]

Estimation of the zero-point energy (ZPE) of the crystalline urea has been obtained through the full set of vibrational frequencies computed at the Γ point.[33] Discussion of the details and results of the frequencies calculation is out the scope of the present work and will be reported in a forthcoming paper. However, here we use the ZPE to correct the computed lattice energy and arrive at an estimation of the sublimation enthalpy at 0 K, $\Delta H^0(0)$.

**Results and Discussion**

**Effect of the Hamiltonian.** *A. Crystal Structure.* Table 1 summarizes the results for the structure of crystalline urea computed at the different levels of theory with the 6-31G(d,p) basis set. The full set of fractional coordinates is reported as Supporting Information. Accurate experimental data are available for comparison. The crystal structure of urea has been determined at very low temperature (12 K) by neutron powder diffraction,[14] so that hydrogen positions are well defined and a tight comparison can be performed between experimental and computed data.

Cell parameters are largely overestimated at the HF level, underestimated at the SVWN level, and reasonably well reproduced by GGA and hybrid functionals. This trend is even more evident when the cell volume is considered as shown in Figure 4. From Table 1, we can see that for all methods the

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**TABLE 1: Effect of the Choice of the Hamiltonian on Lattice Parameters (in Å) and Relevant Geometrical Features of Crystalline Urea (in Å and deg)**[a]

| | HF | SVWN | PW91 | PBE | PBE0 | B3LYP | exp.[14] |
|---|---|---|---|---|---|---|---|
| | | | Lattice Parameters | | | | |
| $a$ | 5.949 (6.9) | 5.257 (−5.5) | 5.598 (0.6) | 5.604 (0.7) | 5.588 (0.4) | 5.675 (2.0) | 5.565 |
| $c$ | 4.750 (1.4) | 4.521 (−3.5) | 4.659 (−0.5) | 4.669 (−0.3) | 4.649 (−0.8) | 4.682 (0.0) | 4.684 |
| $c/a$ | 0.798 (−5.1) | 0.860 (2.2) | 0.832 (−1.1) | 0.833 (−1.1) | 0.825 (−1.2) | 0.825 (−2.0) | 0.842 |
| $V$ | 168.1 (15.9) | 125.0 (−13.9) | 146.0 (0.7) | 146.6 (1.1) | 145.2 (0.1) | 150.8 (3.9) | 145.1 |
| | | | Intramolecular Bond Lengths and Angles | | | | |
| C−O | 1.238 | 1.289 | 1.283 | 1.283 | 1.267 | 1.271 | 1.262 |
| C−N | 1.338 | 1.335 | 1.353 | 1.354 | 1.342 | 1.349 | 1.345 |
| N−H1 | 0.995 | 1.039 | 1.023 | 1.024 | 1.014 | 1.014 | 1.009 |
| N−H2 | 0.996 | 1.033 | 1.023 | 1.023 | 1.013 | 1.015 | 1.005 |
| O−C−N | 121.7 | 120.5 | 121.3 | 121.3 | 121.4 | 121.4 | 121.4 |
| N−C−N | 116.6 | 118.9 | 117.3 | 117.3 | 117.3 | 117.1 | 117.2 |
| C−N−H1 | 119.2 | 120.2 | 120.1 | 120.0 | 119.9 | 119.9 | 119.1 |
| C−N−H2 | 121.0 | 119.5 | 120.1 | 120.3 | 120.3 | 120.4 | 120.6 |
| H1−N−H2 | 119.7 | 120.3 | 119.7 | 119.7 | 119.9 | 119.8 | 120.3 |
| rms bonds | 0.015 | 0.025 | 0.016 | 0.016 | 0.006 | 0.007 | |
| rms angles | 0.4 | 1.1 | 0.6 | 0.5 | 0.4 | 0.4 | |
| | | | Hydrogen-Bond Distances and Angles | | | | |
| $N_{H1}\cdots O$ | 3.259 | 2.783 | 2.991 | 2.994 | 3.000 | 3.051 | 2.985 |
| $N_{H2}\cdots O$ | 3.032 | 2.798 | 2.906 | 2.921 | 2.912 | 2.936 | 2.955 |
| H1$\cdots$O | 2.284 | 1.753 | 1.977 | 1.982 | 1.994 | 2.047 | 1.992 |
| H2$\cdots$O | 2.137 | 1.896 | 2.002 | 2.012 | 2.016 | 2.037 | 2.058 |
| N−H1$\cdots$O | 166.5 | 169.3 | 167.1 | 167.2 | 167.3 | 166.9 | 167.2 |
| N−H2$\cdots$O | 148.8 | 144.4 | 146.7 | 1476.6 | 147.0 | 147.2 | 147.4 |
| rms H-bonds | 0.208 | 0.193 | 0.038 | 0.029 | 0.031 | 0.045 | |
| rms HB angles | 1.1 | 2.6 | 0.5 | 0.6 | 0.3 | 0.2 | |

[a] Basis set: 6-31G(d,p). Percentage deviation with respect to experiment is reported in parentheses.
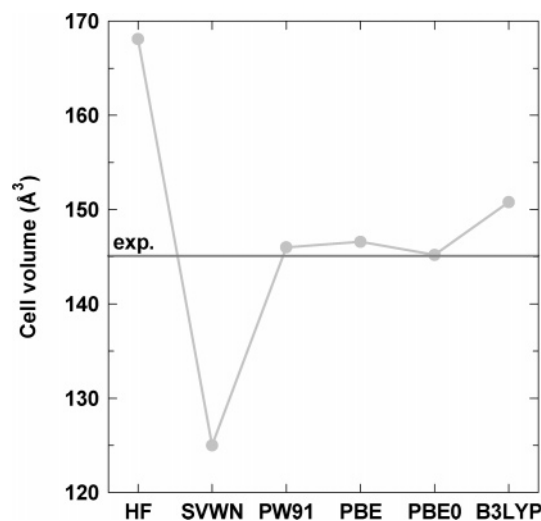


**Figure 4.** Dependence of the unit cell volume on the adopted method in combination with a 6-31G(d,p) basis set (●). Solid line represents the experimental value.[14]

agreement is better for the *c* lattice vector than for the *a* vector. This is an important aspect related to the forces that dominate the crystal packing and will be discussed later. Very satisfactory performance is observed for hybrids methods, especially PBE0, even though B3LYP tends to slightly overestimate the *a* lattice constant by a still acceptable mean deviation of 2.1%.

Relevant structural features of the urea molecular geometry in the solid and the intermolecular HB network are also reported in Table 1. For the molecular structure, the largest difference among Hamiltonians is mainly observed for the bond lengths, while angles are less affected by the adopted level of theory. With respect to experiment, as expected from experience on molecular calculations,[3] HF yields too short distances while SVWN gives too long CO and NH bonds. A better agreement is observed for GGA and hybrid methods; however, GGAs bond

lengths are slightly overestimated. PBE0 and B3LYP molecular structures agree well with experiment, with an rms deviation of only 0.006 and 0.007 Å for bond lengths and 0.4 and 0.4 for angles, respectively. Results for the intramolecular geometry parallel what was observed in calculations on molecular systems,[3] with hybrid methods being the most accurate.

Turning now to the HB network, structural results for the different methods closely follow the intramolecular ones, but a larger discrepancy with respect to experiment is observed. As before, the largest deviations are observed for distances than for angles. HF greatly overestimates HB distances, while opposite results are obtained at the SVWN level. A better description of the HB structural features is observed for the GGA and hybrids functionals, even if B3LYP tends to slightly lengthen the H1$\cdots$O distance. As a consequence, the B3LYP predicted lattice constant *a* is a bit overestimated. It is worth noting that DF methods give a description of H-bonds similar to those observed on HB molecular adducts,[41] where hybrid functionals work better than the GGA ones and much better than LDA.

The present results also agree with previously published data. Miao et al.[11] obtained at the LDA level with a plane waves basis set (cutoff energy: $E_{cut}$ = 1600 eV) and norm-conserved pseudopotentials, lattice vectors (*a* = 5.299 Å and *c* = 4.532 Å) and internal coordinates in close agreement with present calculations. Also, results by Morrison and Siddick[12] at the PBE level with ultrasoft pseudopotentials and a plane waves basis set ($E_{cut}$ = 600 eV) are similar to our PBE data, that is, *a* = 5.604 Å and *c* = 4.689 Å.

*B. Cohesive Energy.* Computed cohesive energies are reported in Table 2 for different Hamiltonians with a 6-31G(d,p) basis set. Table 2 shows that DFT methods give condensation energies higher than HF. As expected, GGA and hybrids methods are intermediate between HF and LDA (i.e., SVWN). Correlation energy, included through the DFT correlation term, is important and stabilizes the crystalline structure. Conformation energy

**TABLE 2: Computed Energy Data (in kJ/mol) for Crystalline Urea with Different Hamiltonians**[a]

|                  | HF     | SVWN    | PW91   | PBE    | PBE0   | B3LYP  |
|------------------|--------|---------|--------|--------|--------|--------|
| $\Delta E$(cond) | −83.4  | −188.3  | −124.5 | −118.5 | −113.2 | −105.6 |
| $\Delta E$(conf) | 4.8    | 4.9     | 7.5    | 7.8    | 6.1    | 6.8    |
| BSSE             | 17.0   | 44.8    | 37.7   | 36.0   | 29.4   | 32.7   |
| $\Delta E$       | −61.6  | −138.6  | −79.3  | −74.7  | −77.7  | −66.1  |
| ZPE              | 5.5    | 4.9     | 4.5    | 4.4    | 5.5    | 5.6    |
| $\Delta H^0(0)$  | −56.0  | −133.7  | −74.8  | −70.3  | −72.2  | −60.5  |

[a] Condensation energy, $\Delta E$(cond); conformation energy difference of urea molecule between $C_{2v}$ and $C_2$-anti conformers, $\Delta E$(conf); BSSE, estimated via the counterpoise correction (CPC); interaction energy, $\Delta E$; zero-point energy, ZPE; and enthalpy of formation at 0 K, $\Delta H^0(0)$.

accounts for 5−8 kJ/mol with the $C_2$ molecular structure being the most stable conformer at all levels of theory. Inclusion of the BSSE decreases considerably the computed results, with the correction being even as large as 50% of the lattice energy. The role of the BSSE is crucial and will be discussed in more detail in the next sections. From Table 2, it can be seen that the correction is not the same for the various Hamiltonians and, particularly, DFT methods suffer from a larger BSSE than HF. The BSSE correction does not change the order of the computed cohesive energies, with SVWN being the largest, followed by PW91, PBE, PBE0, B3LYP, and finally HF. The PBE value for $\Delta E$ is close to that computed by Morrison and Siddick[12] of 81.3 kJ/mol.

To compare computed results with the experimental sublimation energy of crystalline urea of 87.7 kJ/mol,[42] we also included the ZPE to arrive at an estimation of the sublimation enthalpy at 0 K. Inspection of the computed $\Delta H^0(0)$ shows that SVWN overestimates the experimental value, whereas HF largely underestimates it. Gradient-corrected functionals (PW91 and PBE) and hybrid methods give intermediate but still too small sublimation enthalpies. B3LYP works poorly with respect to PBE0. This can be explained by the different role played by the adopted exchange functional. Cybulski and Seversen[43] have recently shown through an energy decomposition scheme that, for water dimer, Becke's exchange functional[44] tends to overestimate repulsive forces with respect to HF, while the opposite is observed for the PW91 functional. As PW91 and PBE give quite similar results, we expect that the PBE exchange contribution, in the PBE0 methods, behaves in roughly the same fashion, thus reducing repulsive effects. This also explains why B3LYP gives a slightly larger value of the lattice vectors and HB distances with respect to PBE0. Overall, PBE0 gives the best performance but still a too small sublimation enthalpy. As for structural features, the computed trend in sublimation enthalpies follows closely that obtained for hydrogen-bonded molecular adducts (see refs 41, 45, and 46 for a recent study of weakly bonded molecular adducts) where LDA functionals, as SVWN, tend to greatly overestimate the interaction energy, while gradient-corrected and hybrid functionals represent definite improvements with respect to LDA. Computed lattice vectors and sublimation enthalpies are inversely correlated, indicating that the cohesive energy of the crystal is mainly dictated by the correct description of the intermolecular interactions. Apart from LDA methods that are since long recognized to poorly describe hydrogen bonds, other functionals tend to underestimate the cohesive energy. As thermal effects are expected to account for a few kJ/mol, the difference with respect to experiment must be due to something else. The role of the dispersion forces that are not properly taken into account[47] in the present exchange-correlation functionals is an important issue to be considered, but before discussing that we first need to consider another crucial aspect: the effect of the basis set on computed results.

**Basis Set Effect.** The basis set dependence of computed crystalline structure and cohesive energy has been explored at the B3LYP level. Results are gathered in Tables 3 and 4, respectively.

The four adopted basis sets are of double- and triple-$\zeta$ quality with the number of basis functions increasing from 132 to 208 atomic orbitals per unit cell. Basis sets also differ qualitatively in two respects. First, Pople's basis sets adopt the sp constraint, while DZP and TZP treat s and p shells independently, thus providing more variational freedom. Second, the exponent of the outermost Gaussian basis function, either the sp or the s and p shells, becomes more and more diffuse when passing from the Pople's basis sets to the DZP and TZP ones. For instance, in the carbon basis set it decreases from 0.1687 to 0.1009 au. Such features have a great effect in reducing the BSSE, as was previously pointed out by Spackman and Mitchell[30] and will be discussed later.

*A. Crystal Structure.* The basis set has a dramatic effect on the computed crystalline structure of urea. From Table 3, we can observe that the lattice vector $a$ becomes larger and larger when enriching the basis set, while cell parameter $c$ remains almost unchanged and close to its experimental value, as clearly shown in Figure 5. The overall effect is that the cell volume, slightly overestimated with the 6-31G(d,p) basis set, becomes largely overestimated (10.0%) when a TZP basis set is used. Such a huge increment is entirely due to the worsening in the description of the intermolecular HB distances. The molecular structure of urea in the crystal, in fact, is well reproduced and approaches experiment when passing from the 6-31G(d,p) basis set to the TZP one. Notably, the CO bond length agrees well with the experimental value when the TZP basis set is adopted, thus indicating that a TZ-quality basis set is needed to correctly describe the carbonyl group. In contrast, HB distances become increasingly overestimated, in particular the H1···O bond that rules the packing along the $a$ lattice vector.

It is worth noting that the different behavior of the lattice constant $a$ with respect to $c$ agrees with the strong anisotropic thermal expansion observed experimentally[48] that is larger for $a$ than for $c$. Indeed, the difference is related to the different balance in the intermolecular forces acting along the two directions as will be discussed below.

*B. Cohesive Energy.* The quality and size of the basis set mainly affects BSSE uncorrected condensation energy, while the BSSE-corrected values show an almost null dependence from the adopted basis set. This was already noticed by Spackman and Mitchell,[30] even if they kept the experimental crystalline structure. The enrichment of the basis set and the inclusion of more diffuse s and p functions, in particular, has a dramatic effect on the BSSE that drops from 32.7 kJ/mol (i.e., 50% of $\Delta E$) with the 6-31G(d,p) basis set to 6.8 kJ/mol (i.e., less than 10% of $\Delta E$) with the TZP basis set.

By adding the zero-point energy, the computed sublimation enthalpy at 0 K reduces, by an almost constant contribution, to

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**TABLE 3: Effect of the Basis Set on Lattice Parameters (in Å) and Relevant Geometrical Features of Crystalline Urea (in Å and deg) Computed with Different Basis Sets at the B3LYP Level[a]**

| | 6-31G(d,p) | DZP | 6-311G(d,p) | TZP | exp.[14] |
|---|---|---|---|---|---|
| | | Lattice Parameters | | | |
| $a$ | 5.675 (2.0) | 5.700 (2.4) | 5.743 (3.2) | 5.841 (5.0) | 5.565 |
| $c$ | 4.682 (0.0) | 4.678 (−0.1) | 4.707 (0.5) | 4.710 (0.5) | 4.684 |
| $c/a$ | 0.825 (−2.2) | 0.821 (−2.5) | 0.820 (−2.6) | 0.806 (−4.2) | 0.842 |
| $V$ | 150.8 (3.9) | 152.0 (4.8) | 155.2 (7.0) | 160.7 (10.7) | 145.1 |
| | | Intramolecular Bond Lengths and Angles | | | |
| C−O | 1.271 | 1.273 | 1.263 | 1.260 | 1.262 |
| C−N | 1.349 | 1.352 | 1.349 | 1.349 | 1.345 |
| N−H1 | 1.014 | 1.022 | 1.012 | 1.011 | 1.009 |
| N−H2 | 1.015 | 1.023 | 1.013 | 1.013 | 1.005 |
| O−C−N | 121.4 | 121.4 | 121.6 | 121.6 | 121.4 |
| N−C−N | 117.1 | 117.2 | 116.9 | 116.7 | 117.2 |
| C−N−H1 | 119.9 | 119.9 | 119.9 | 120.0 | 119.1 |
| C−N−H2 | 120.4 | 129.9 | 120.5 | 120.6 | 120.6 |
| H1−N−H2 | 119.9 | 120.1 | 119.6 | 119.4 | 120.3 |
| rms bonds | 0.007 | 0.013 | 0.005 | 0.005 | |
| rms angles | 0.4 | 0.5 | 0.5 | 0.6 | |
| | | Hydrogen-Bond Distances and Angles | | | |
| $N_{H1}\cdots O$ | 3.051 | 3.052 | 3.093 | 3.149 | 2.985 |
| $N_{H2}\cdots O$ | 2.936 | 2.936 | 2.969 | 2.973 | 2.955 |
| $H1\cdots O$ | 2.047 | 2.050 | 2.099 | 2.159 | 1.992 |
| $H2\cdots O$ | 2.037 | 2.021 | 2.062 | 2.065 | 2.058 |
| $N−H1\cdots O$ | 166.9 | 166.3 | 167.0 | 165.9 | 167.2 |
| $N−H2\cdots O$ | 147.2 | 147.6 | 147.8 | 147.9 | 147.4 |
| rms H-bonds | 0.045 | 0.049 | 0.076 | 0.118 | |
| rms HB angles | 0.2 | 0.7 | 0.3 | 1.0 | |

[a] Percentage deviation with respect to experiment is reported in parentheses.

**TABLE 4: Dependence of the Computed Energies (in kJ/mol) on the Adopted Basis Set at the B3LYP Level of Theory[a]**

| | 6-31G(d,p) | DZP | 6-311G(d,p) | TZP |
|---|---|---|---|---|
| $\Delta E$(cond) | −105.6 | −96.0 | −96.4 | −78.5 |
| $\Delta E$(conf) | 6.8 | 6.8 | 5.9 | 3.9 |
| BSSE | 32.7 | 22.2 | 25.1 | 6.8 |
| $\Delta E$ | −66.1 | −67.0 | −65.4 | −68.0 |
| ZPE | 5.6 | 4.8 | 4.5 | 5.5 |
| $\Delta H^0(0)$ | −60.5 | −62.2 | −60.9 | −62.5 |

[a] Condensation energy, $\Delta E$(cond); conformation energy difference of urea molecule between $C_{2v}$ and $C_2$-*anti* conformers, $\Delta E$(conf); BSSE, estimated via the counterpoise correction (CPC); interaction energy, $\Delta E$; zero-point energy, ZPE; and enthalpy of formation at 0 K, $\Delta H^0(0)$.

about −60 kJ/mol, well below the experimental sublimation enthalpy, thus confirming that the predicted cohesive energy is definitely underestimated with B3LYP. However, we expect that a similar underestimation would be obtained with the investigated GGA functionals and the PBE0 method.

**The Role of BSSE and Intermolecular Forces.** By inspecting the computed results, we arrive at three important findings. First, BSSE-corrected cohesive energies do not depend on the adopted basis sets. Although this is not unexpected, it shows that, in solid-state calculations, energetics converge more rapidly than for molecular adducts where very large basis sets are needed to reach the basis set limit (e.g., in the aug-cc-pVXZ series, X = D, T, Q, ...). Indeed, it is well established that relatively smaller basis sets perform better in periodic than in molecular calculations.[40] Second, apart from LDA that is known to poorly describe hydrogen-bonded systems with a large overestimation of the intermolecular interactions, GGA and hybrid approaches that were expected to give better results significantly underestimate the cohesive energy of urea. Finally, the reduction of the BSSE due to the enrichment of the basis

set dramatically affects the predicted crystalline structure. Even if this has been obtained at the B3LYP level, we expect it holds for other functionals as well.

Those latter findings show how the combination of DFT methods with extended basis set of TZP quality predicts too low cohesive energies and consequently too large unit cell volumes. This is of crucial importance for a correct prediction of the properties of molecular crystals and must be carefully analyzed.

The explanation for those findings must be traced back to the role played by the BSSE and in the incorrect description of the intermolecular forces acting between molecules in the crystal by current DFT methods. The most relevant contributions to bonding in hydrogen-bonded molecular crystals are long-range interactions, mainly due to electrostatic and polarization effects, and short-range contributions, as exchange repulsion and charge-transfer terms. Dispersion interactions are expected to provide a minor contribution. Present DF methods are not able to properly account for dispersive interactions,[47,49−51] but they are supposed to perform well when the interaction energy is dominated by electrostatics, as should be the case for HB molecular crystals. In this respect, crystalline urea with its extended HB network is expected to be dominated by electrostatics. However, recently, Gora et al.[9] performed MP2 calculations on cluster models of increasing size to analyze the intermolecular interactions in crystalline urea and showed that dispersion forces are not negligible. Moreover, Tsirelsov et al.[52] by means of electron-density-based calculations analyzed the interaction between urea neighboring pairs of molecules, showing that repulsive interactions rapidly become important when non-hydrogen-bonded pairs are considered. Those results highlight the delicate balance between the different types of intermolecular forces in dictating the crystalline structure and the cohesive energy. Of course, an incorrect description of the intermolecular interactions between molecules could cause the
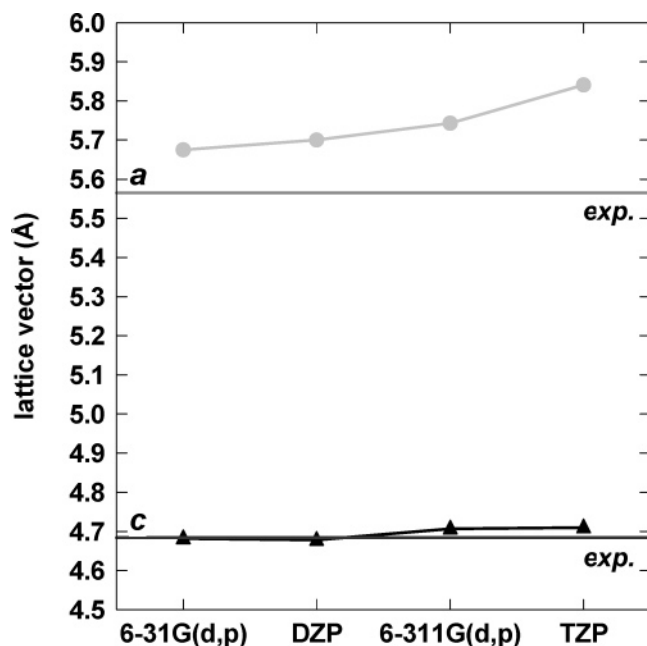
**Figure 5.** Basis set effect on the B3LYP computed lattice vectors *a* (●) and *c* (▲). Solid lines represent experimental values.[14]

large deviations with respect to experiments as observed in the computed data.

We hypothesize that: (1) with small basis sets the BSSE is large and gives an extra-binding that compensates for the missing dispersion forces, thus yielding structures in fortuitous agreement with experiment (see Tables 1 and 2); (2) when large basis sets are employed, the reduction of the BSSE removes the spurious attractive interactions between the urea molecules, leading to an improper cancellation of the repulsive interactions; the net effect is then to keep the molecules far apart from each other; and (3) previous points also explain why the largest errors in the prediction of the crystalline structure are observed for the lattice vector *a*, whereas *c* is in good agreement with experiment (see Figure 5). Indeed, by looking at the crystal packing (see Figure 1), we can see that along the *c* direction urea molecules are strongly interacting head−tail through hydrogen bonds and dipole−dipole interactions. Moreover, they form chains oriented in opposite directions that are again stabilized through dipolar forces. Therefore, interactions along *c* are dominated by electrostatics and are well reproduced at GGA and hybrid levels. On the contrary, along *a*, urea is linked through weaker hydrogen bonds,[12,52] and repulsive interactions between neighboring pairs and parallel chains do mainly act in that direction.[9,52] When BSSE decreases, the missing dispersion contribution is not compensated and repulsive forces prevail, thus causing a large overestimation of the lattice constant. As already mentioned, because Becke's exchange functional[44] tends to overestimate repulsive forces,[43] a large deviation from experiment is expected for the B3LYP methods as is indeed observed.

It is important to stress that the deficiencies of DFT methods are not dependent on the computational approach adopted in this work that employs local atomic basis functions. If we compare present results with calculations performed with the plane waves basis set that do not suffer of any BSSE, a similar trend is observed. Indeed, a recent calculation by Bucko et al.[53] on crystalline urea gives at the PW91 level, with a plane waves basis set ($E_{cut} = 800$ eV) and using the projector-augmented formalism, a quite large unit cell volume due to a marked overestimation of the lattice constant *a*. They obtained $a = 5.788$

Å and $c = 4.703$ Å. Therefore, we repeated the same PW91 calculation with the TZP basis set and found $a = 5.759$ Å and $c = 4.700$ Å in very good agreement with Bucko et al.[53] They also showed that plane waves calculations of the structure of molecular crystals can be affected by large errors on dependence of the Pulay stress (i.e., the plane waves basis set incompleteness error[54]) that can lead to a spurious underestimation of the unit cell size. Such a dependence of computed lattice vectors on plane waves kinetic energy cutoff was already pointed out by Byrd et al.[55] on studying energetic molecular crystals. They performed calculations at the PBE level of theory with a plane waves basis set ($E_{cut}$ from 280 to 800 eV) and ultrasoft pseudopotentials. Large negative errors up to −16% were obtained with small kinetic energy cutoffs, while large positive errors up to +10% were observed at the highest energy cutoffs. It is worth noticing that when accurate calculations are carried out at the same level of theory (i.e., PW91), similar results are obtained independent of the nature of the basis set employed (i.e., plane waves or Gaussian-type functions). The comparison of the two kinds of basis sets in solid-state calculations is an interesting aspect and is under investigation.[56] Agreement of our results with calculations performed with plane waves basis sets, not affected by the BSSE, then confirms that the lack of dispersion forces is a genuine feature of current DFT methods.

**Conclusions**

In the present work, crystalline urea has been chosen as a case study of the class of HB molecular crystals, and its structure and cohesive energy have been investigated to assess the performance of LDA, GGA, and hybrids DF methods. With small basis sets, GGA and hybrid functionals give structures in good agreement with experiment. However, after BSSE correction and inclusion of the ZPE, cohesive energies are underestimated with respect to the enthalpy of sublimation by about 20 kJ/mol on average. When the basis set dependence is taken into account at the B3LYP level of theory, the reduction of the BSSE leads to an overestimation of the cell parameters, especially the *a* lattice constant. The B3LYP computed $\Delta H^0(0)$ is almost independent of the basis set and definitely underestimated with respect to experiment by some 30 kJ/mol. It is worth noting that the same deviation from experiment is also observed when the cell parameters are fixed at their experimental values, thus confirming the reported underestimation of the cohesive energies.

Overall, results show that the shortcoming of DF methods in describing dispersive forces and the spurious extra binding given by the BSSE dramatically hampers a proper prediction of the structure and stability of the molecular crystal of urea. Deficiencies observed in the current DF functionals pose a general concern on the accuracy of ab initio calculations of molecular crystals. What might be considered as an acceptable error in reproducing the interaction of small molecular adducts, in extended systems, such as crystals or large molecules, is amplified and becomes of crucial importance to properly predict their structure and stability. Similar conclusions have been also drawn by Byrd et al.[55] on studying energetic molecular crystals and by van Mourik et al.[57] in the prediction of the correct conformation of a large organic molecule. This has important consequences on many applications such as crystal structure prediction, ranking of molecular crystals polymorphs, and theoretical charge density analysis, where ab initio calculations are now widely used.

Methods that properly account for dispersion need to be used in solid-state calculations. Solutions to this relevant issue have

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been proposed,[58–64] but unfortunately they are not fully available in present ab initio periodic codes. New exchange-correlation functionals[65–70] have also been recently proposed that are claimed to provide a better description of noncovalent interactions. As soon as they will be routinely available in periodic ab initio code, they deserve to be assessed in dealing with HB molecular crystals. Also, post-HF techniques would be a definite improvement, but, as opposed to molecular calculations, they are still unfeasible for crystalline systems, even though work is at an advanced stage to implement a local-MP2 scheme for insulators.[71]

**Supporting Information Available:** Lattice parameters (in Å) and atomic fractional coordinates of the optimized structures of crystalline urea computed with different Hamiltonians and a 6-31G(d,p) basis set (Table S1) and at the B3LYP level with different basis sets (Table S2). CPU time for SCF and gradients calculation on the first optimization step (in seconds) and total CPU time of the geometry optimization (Table S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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