# Theoretical Study on the Urea−Hydrogen Peroxide 1:1 Complexes

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The structures, interaction energies, vibrational analysis, and electronic properties for different urea−hydrogen peroxide (UHP) 1:1 complexes have been studied. Density functional theory (DFT) using the B3LYP hybrid exchange−correlation functional was employed to characterize five new cyclic structures in addition to the experimental one. The basis sets used were Dunning's correlation consistent cc-pVDZ and Pople's 6-31G(2d,p) ones. Ab initio MP2(full)/6-31G(2d,p)//MP2(full)/6-31G(2d,p) calculations were performed to verify the appropriateness of the DFT methods for hydrogen-bonding systems. The basis set superposition error has been eliminated by using the full counterpoise correction method. The Bader analyses were also applied to investigate the hydrogen-bonding electronic properties.

## 1. Introduction

Given the considerable usefulness of hydrogen peroxide in many fields, such as atmospheric chemistry,[1] photodissociation dynamics,[2−6] and oxidation reactions,[7] and of urea in biological processes because of potential hydrogen-bonding and acid−base properties associated with both the amine and the carbonyl groups, the urea−hydrogen peroxide (UHP) 1:1 complex has been widely used in several oxidation processes[8−12] and also as a safe source to produce hydrogen peroxide.[13] The crystal structure of UHP 1:1 complex was first experimentally investigated by X-ray[14] and later by neutron diffraction at low temperatures.[15,16] In addition, theoretical research was conducted on several urea complexes (e.g., urea−water, urea−hydrogen fluorine complexes,[17] urea dimer, and trimer,[18] and crystalline structure[19]). We recently published several studies concerning hydrogen peroxide complexes, in which we used the ab initio molecular orbital theory, paying particular attention to the basis set superposition error (BSSE), to the interaction energies of the complexes and to the vibrational spectra on the $(H_2O_2)_2$,[20] $H_2O_2\cdots H_2O$,[21] and $H_2O_2\cdots XH$ (X = F or Cl).[22]

Density functional theory (DFT),[23−25] which has emerged over the past decade as a reliable and versatile computational method, has been successfully used to study physical and chemical properties of molecules.[26−30] Moreover, its utility was pointed out elsewhere,[31,32] as in the recent study of hydrogen-bonding systems.[33−36]

In the present paper, we expand our studies on hydrogen peroxide to the UHP complexes. The goal of the present work is to characterize the different UHP complexes (to our knowledge, the first theoretical investigation) and to report on the structures, interaction energies, vibrational analysis, and electronic properties of these systems. In addition, we apply DFT methods to assess the capability of reproducing hydrogen-bonding systems, and we compare the results to the ab initio MP2(full) calculations and experimental data.

## 2. Methods of Calculation

The DFT calculations were carried out with the Gaussian 94 package of programs,[37] using Dunning's correlation consistent cc-pVDZ[38] and Pople's 6-31G(2d,p)[39−41] basis sets, together with the Becke III−Lee−Yang−Parr (B3LYP) exchange−correlation functional.[42,43] MP2(full) all electron calculations were performed with the 6-31G(2d,p) basis. The UHP complexes described were fully optimized at the three levels of theory mentioned, with constrained symmetry ($C_2$) only for the structures **1** and **3**. A vibrational analysis was made to check the nature of the stationary points, and no structure **1**−**6** presented imaginary frequencies (true minima) at the B3LYP level with both basis sets. The BSSE was estimated using the full counterpoise method,[44] as previously described.[20−22]

The Bader analyses were performed with the AIMPAC series of program[45] using the MP2 wave function as input, as described in *Atoms in Molecules Theory*.[46,47]

The topology of the electronic charge density ($\rho(r)$), as pointed out by Bader,[46] is an accurate mapping of a chemical concept of atom, bond and structure. The principal topological properties are summarized in terms of their critical points (CP).[46,47] The nuclear positions behave topologically as local maxima in $\rho(r)$, and a bond critical point (BCP) is found between each pair of nuclei, which are considered to be linked by a chemical bond, with two negative curvatures and one positive. Ring CPs are characterized by a single negative curvature. Each (3,−1) CP generates a pair of gradient paths[46] which originate at a CP and terminate at neighboring attractors; this gradient path defines a line through the charge distribution linking the neighboring nucleus and, along this line, $\rho(r)$ is a maximum with respect to any neighboring line. Such a line is referred to as an atomic interaction line.[46,47] The presence of an atomic interaction line in such equilibrium geometry satisfies both the necessary and sufficient condition that the atoms be bonded together.

The Laplacian of the electronic charge density ($\nabla^2\rho(r)$) determines two extreme situations. The first $\rho$ is locally concentrated ($\nabla^2\rho(r) < 0$) and the second is locally depleted ($\nabla^2\rho(r) > 0$). Thus, a value of $\nabla^2\rho(r) < 0$ at a BCP is unambiguously related to a covalent bond, showing that a sharing of charge has taken place. However, in a closed-shell interaction a value of $\nabla^2\rho(r) > 0$ is expected such as found in noble gas repulsive states, in ionic bonds, in hydrogen bonds, and in van der Waals molecules.

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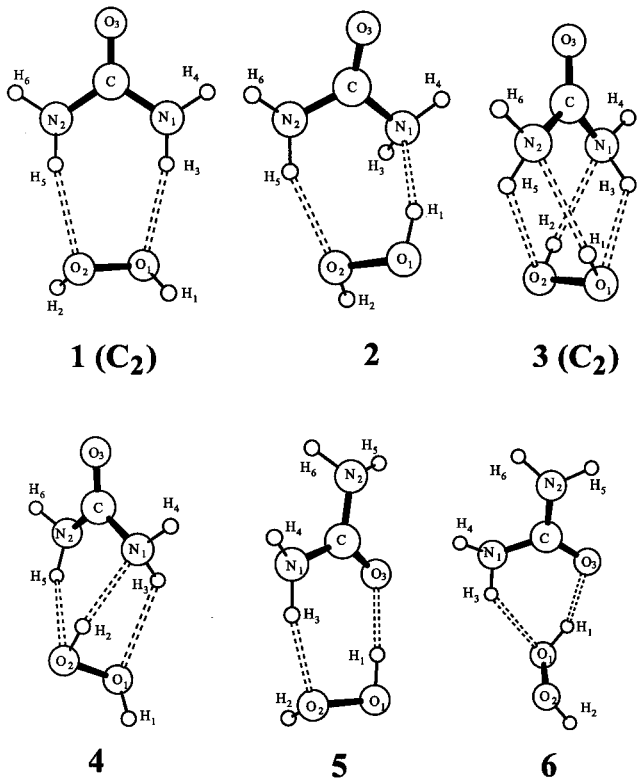


**Figure 1.** The urea−hydrogen peroxide (UHP) 1:1 complexes (structures **1**−**6**), with the corresponding atom numbering.

## 3. Results

The DFT and MP2 calculations performed predicted six stationary points on the potential energy surface (PES) of the UHP 1:1 complex (structures **1**−**6**) (see Figure 1). The energies for the different structures obtained at the different levels of theory are depicted in Table 1. Moreover, the numerical values of the optimized geometrical parameters for the monomers and structures **1**−**6** at the various levels are available in Tables 2−4. Structures **1**−**6** were obtained as true minima, all of them being cyclic with a different number of hydrogen bonds. Accordingly, structures **1** and **3** were cyclic ones, with $C_2$ symmetry, and **2**,**4**−**6**, without symmetry ($C_1$). The minimum energy structure on the UHP PES was **5**, at both the DFT and MP2 levels. Nevertheless, structure **6** was closer in energy to **5** than to the rest.

Structure **1** was very close to the X-ray experimental data; however, it was the less stable structure. Table 1 also shows the binding energies (corrected and uncorrected for the BSSE) and the dipole moments, at the three levels of theory used.

## 4. Discussion

**A. Molecular Structure and Hydrogen Bonding.** All the structures obtained were cyclic with two (structures **1**, **2**, **5**, and **6**), three (structure **4**), and four hydrogen bonds (structure **3**). The last structure also displayed a cage system.

For the different structures, hydrogen peroxide oxygen, carbonylic oxygen, and amide nitrogen behaved as electron donors, with all the possible hydrogens acting as electron acceptors (see Figure 1). The optimized geometrical parameters are listed in Tables 2−4, in which the DFT and MP2 results were compared. As reflected in the different tables, the DFT and MP2 results are very similar and in good agreement with experimental structure **1**. Furthermore, the main differences between the experimental UHP complex and structure **1** were due to the planarity of the urea moiety, possibly caused by the packing forces in the solid state. All the structures calculated showed a nonplanar urea moiety, concordant with the possible nonplanar urea structure in gas phase proposed both experimentally[48] and theoretically.[49,50]

**TABLE 1: Binding Energies (without($\Delta E$) and with BSSE Correction ($\Delta E_{corr}$)), BSSE, Relative Energy ($E_r$), and Dipole Moment (DM), for the UHP Complexes (Structures 1−6), at the Different Levels of Theory**

| structure | $\Delta E$ (kcal mol$^{-1}$) | $\Delta E_{corr}$ (kcal mol$^{-1}$) | BSSE (kcal mol$^{-1}$) | $E_r$ (kcal mol$^{-1}$) | DM (D) |
|---|---|---|---|---|---|
| B3LYP/cc-pVDZ//B3LYP/cc-pVDZ | | | | | |
| **1**($C_2$) | −8.09 | −4.38 | 3.70 | 7.75 | 6.43 |
| **2** | −11.84 | −6.96 | 4.88 | 3.99 | 3.88 |
| **3**($C_2$) | −10.07 | −2.31 | 7.76 | 5.76 | 0.55 |
| **4** | −11.48 | −5.93 | 5.55 | 4.35 | 3.26 |
| 5 | −15.83 | −10.65 | 5.19 | *a* | 4.79 |
| **6** | −14.57 | −9.12 | 5.44 | 1.26 | 3.10 |
| B3LYP/6-31G(2d,p)//B3LYP/6-31G(2d,p) | | | | | |
| **1**($C_2$) | −7.10 | −2.82 | 2.70 | 7.83 | 6.37 |
| **2** | −10.18 | −6.97 | 3.21 | 4.75 | 3.84 |
| **3**($C_2$) | −8.78 | −3.29 | 5.49 | 6.15 | 0.77 |
| **4** | −10.05 | −6.12 | 3.93 | 4.88 | 3.27 |
| **5** | −14.93 | −10.71 | 4.22 | *b* | 4.80 |
| **6** | −13.73 | −9.21 | 4.51 | 1.21 | 3.08 |
| MP2(full)/6-31G(2d,p)//MP2(full)/6-31G(2d,p) | | | | | |
| **1**($C_2$) | −8.06 | −4.99 | 3.07 | 7.16 | 6.69 |
| **2** | −12.16 | −7.54 | 4.62 | 3.06 | 4.20 |
| **3**($C_2$) | −10.97 | −4.16 | 6.81 | 4.25 | 0.78 |
| **4** | −12.02 | −7.06 | 4.96 | 3.20 | 3.75 |
| **5** | −15.22 | −10.29 | 4.94 | *c* | 4.95 |
| **6** | −14.30 | −9.01 | 5.29 | 0.92 | 3.30 |

[a] Reference energy value (−376.857 198 6 au), and the corresponding ones (−151.550 663 7 and −225.281 305 4 au) for hydrogen peroxide and urea, respectively. [b] Reference energy value (−376.854 820 9 au), and the corresponding ones (−151.551 519 2 and −225.279 508 8 au) for hydrogen peroxide and urea, respectively. [c] Reference energy value (−375.977 570 9 au), and the corresponding ones (−151.215 899 9 and −224.737 412 9 au) for hydrogen peroxide and urea, respectively.

For all the structures, the geometrical parameters for the monomers within the complex remained almost unchanged with respect to the hydrogen peroxide and urea isolated monomers values. The main difference between structures **1**−**6** was the number and type of hydrogen bonds. Consequently, the two most stable structures (**5** and **6**) both showed an O−H···O (carbonylic) hydrogen bond, this type being the most stabilizing one, in agreement with the preferred protonation position in urea.[51] The different geometrical features of the hydrogen bonds for the structures **1**−**6** are listed in Table 5. In Figure 1 and Table 5 three different types of hydrogen bonds are identifiable: Hbond1 (the hydrogen peroxide oxygen acts as an electron donor), Hbond2 (the urea nitrogen acts as an electron donor), and Hbond3 (the urea carbonylic oxygen acts as an electron donor).

The behavior of the different hydrogen bonds presented in structures **1**−**6** was submitted to a topological analysis of the electron charge density $\rho(r)$ following the Bader's method. From this analysis the different BCP were obtained and characterized with the $\rho(r)$ and $\nabla^2\rho(r)$ values (see Table 5).

Structures **5** and **6** (the most stable ones) were monocyclic systems with two hydrogen bonds of types Hbond1 and Hbond3. These systems were stabilized by the Hbond3 in each structure, yielding the largest $\rho(r)$ values for the critical points of the corresponding hydrogen bonds (0.036 and 0.038). This agrees with the shortest hydrogen-bond lengths (ca. 1.7 Å). Moreover, in both structures, the hydrogen-bond angles for the Hbond3

**TABLE 2: Geometrical Parameters (Angstroms and Degrees) for the Urea, the Hydrogen Peroxide Monomers, and UHP Complexes (Structures 1 and 3), at the Different Levels of Theory**

| | B3LYP/cc-pVDZ | B3LYP/6-31G(2d,p) | MP2(full)/6-31G(2d,p) | exptl[a−c] ($C_{2v}$) |
|---|---|---|---|---|
| | | Urea ($C_2$) | | |
| $O_3-C$ | 1.219 | 1.214 | 1.215 | 1.257 |
| $C-N_1$ | 1.392 | 1.390 | 1.389 | 1.340 |
| $N_1-H_3$ | 1.016 | 1.010 | 1.007 | 1.042 |
| $N_1-H_4$ | 1.016 | 1.010 | 1.007 | 1.064 |
| $\angle O_3-C-N_1$ | 123.3 | 123.2 | 123.6 | 121.56 |
| $\angle H_3-N_1-C$ | 116.4 | 116.5 | 115.6 | 114.70 |
| $\angle H_4-N_1-C$ | 112.0 | 111.8 | 111.5 | 118.78 |
| $\angle H_3-N_1-C-O_3$ | 147.3 | 147.8 | 130.9 | 180.0 |
| $\angle H_4-N_1-C-O_3$ | 15.1 | 15.4 | 15.5 | 0.0 |
| | | Hydrogen Peroxide ($C_2$) | | |
| $O_2-O_1$ | 1.453 | 1.450[d] | 1.462 | 1.464 |
| $H_1-O_1$ | 0.973 | 0.968[d] | 0.965 | 0.965 |
| $\angle H_1-O_1-O_2$ | 99.8 | 100.3[d] | 99.0 | 99.44 |
| $\angle H_1-O_1-O_2-H_2$ | 117.7 | 111.5[d] | 112.2 | 111.83 |

| | **1** ($C_2$) | **3** ($C_2$) | **1** ($C_2$) | **3** ($C_2$) | **1** ($C_2$) | **3** ($C_2$) | **1** ($C_2$) |
|---|---|---|---|---|---|---|---|
| $C-O_3$ | 1.223 | 1.215 | 1.216 | 1.212 | 1.219 | 1.212 | 1.261 |
| $C-N_1$ | 1.388 | 1.404 | 1.385 | 1.399 | 1.384 | 1.398 | 1.340 |
| $N_1-H_3$ | 1.018 | 1.023 | 1.010 | 1.015 | 1.008 | 1.010 | 1.009 |
| $N_1-H_4$ | 1.014 | 1.018 | 1.007 | 1.013 | 1.006 | 1.012 | 1.007 |
| $O_1-O_2$ | 1.454 | 1.454 | 1.448 | 1.448 | 1.465 | 1.464 | 1.457 |
| $O_1-H_1$ | 0.974 | 0.982 | 0.967 | 0.972 | 0.967 | 0.971 | 1.001 |
| $O_1\cdots H_3$ | 2.168 | 2.144 | 2.196 | 2.179 | 2.177 | 2.145 | 2.004 |
| $N_1\cdots H_2$ | | 2.219 | | 2.270 | | 2.214 | |
| $\angle O_3-C-N_1$ | 123.1 | 123.8 | 123.1 | 123.7 | 123.4 | 123.9 | 120.99 |
| $\angle C-N_1-H_3$ | 117.7 | 113.3 | 118.0 | 113.7 | 116.6 | 112.9 | 120.80 |
| $\angle C-N_1-H_4$ | 112.7 | 110.7 | 112.6 | 110.7 | 112.2 | 110.0 | 119.00 |
| $\angle O_2-O_1-H_1$ | 99.9 | 100.7 | 100.2 | 100.9 | 98.9 | 99.7 | 102.53 |
| $\angle O_1\cdots H_3-N_1$ | 157.1 | 133.2 | 157.8 | 134.3 | 158.2 | 133.4 | 163.78 |
| $\angle O_2-O_1\cdots H_3$ | 101.2 | 88.3 | 100.7 | 87.9 | 99.5 | 88.1 | 100.26 |
| $\angle N_1\cdots H_2-O_2$ | | 129.3 | | 128.9 | | 129.8 | |
| $\angle H_1-O_1-O_2-H_2$ | −124.9 | 99.8 | −120.0 | 100.9 | −118.6 | 100.5 | 111.87 |
| $\angle O_3-C-N_1-H_3$ | −156.3 | 135.1 | −156.5 | 136.1 | −155.5 | 134.8 | 180.0 |
| $\angle O_3-C-N_1-H_4$ | −18.5 | 8.2 | −18.4 | 8.2 | −19.2 | 8.5 | 0.0 |
| $\angle O_2-O_1\cdots N_1\cdots N_2$ | 28.1 | 83.7 | 31.5 | 83.9 | 36.6 | 83.6 | 18.2 |

[a] Urea X-ray values from ref 58. [b] Hydrogen peroxide experimental values from ref 59. [c] UHP X-ray values from ref 16. [d] Values from ref 31.

type were compatible with reasonable standard hydrogen bond angles. The main differences between **5** and **6** concerned the geometry of the two Hbond1 also presented. Whereas, for structure **5** the Hbond1 presented a bond length and angle compatible with a medium-strength hydrogen bond (1.9 Å and 180°), the bond lengths in turn increased as the angles decreased (2.1 Å and 140°), due to the rigidity of the six-membered ring of structure **6** (in which the hydrogen peroxide oxygen acts as electron and proton donor). The $\rho(r)$ values at the Hbond1 critical points of structure **5**, were larger than in **6** (0.024 and 0.019).

Structures **2** and **4** had similar stability at the DFT and MP2 levels, increasing in descending order. Both structures displayed Hbond1 and Hbond2 types. Furthermore, the Hbond2 were second in strength, and their respective bond lengths and angles were ca. 1.9 Å and 145°. On the other hand, the $\rho(r)$ for the Hbond2 critical points remained within Hbond1 and Hbond3, with values closer to Hbond3.

Structure **3** with two Hbond1 and two Hbond2 was less stable than **2** and **4**, due to the large strain of the hydrogen bonds, as observed for the hydrogen bond angles (ca. 130°), producing smaller values of $\rho(r)$ for the bond critical points.

Structure **1**, with only two Hbond1, was the most unstable one and presented standard hydrogen bond geometrical parameters. However, the $\rho(r)$ for the hydrogen bond critical points became smaller.

Finally, the values for the $\nabla^2\rho(r)$ in the different hydrogen bond critical points invariably remained positive, compatible with a closed-shell interaction, and generally consistent with an electrostatic interaction. In addition, the $\nabla^2\rho(r)$ values increased with greater hydrogen bond strength, indicating a stronger electrostatic interaction. The cyclic nature of all the structures **1**−**6** was verified by the existence of only one ring critical point for the structures **1**, **2**, **5**, and **6**; two ring critical points for structure **4**; and one cage critical point in addition to the corresponding ring critical points for structure **3** (all of these obtained by the topological study of $\rho(r)$, see Table 5). The geometry of the different structures **1**−**6** (see Tables 2−4), indicated that the HP dihedral angle ($\angle H_1-O_1-O_2-H_2$) in the structures differed substantially, compared to the HP monomer. This can be seen in structure **3**, in which both hydrogens from the HP were involved in the hydrogen bond formation, giving extremely small values ca. 100°. However, structure **1**, in which both hydrogens from the HP moiety were not involved in hydrogen-bond formation, gave large dihedral angle values ca. 120°. For structures **2** and **4**−**6**, only one hydrogen from the HP moiety was involved in hydrogen-bond formation, giving the HP dihedral a value

**TABLE 3: Geometrical Parameters (Angstroms and Degrees) for the UHP Complexes (Structures 2 and 4), at the Different Levels of Theory**

| | B3LYP/cc-pVDZ | | B3LYP/6-31G(2d,p) | | MP2(full)/6-31G(2d,p) | |
|---|---|---|---|---|---|---|
| | **2** | **4** | **2** | **4** | **2** | **4** |
| $C-O_3$ | 1.216 | 1.216 | 1.212 | 1.216 | 1.214 | 1.213 |
| $C-N_1$ | 1.424 | 1.415 | 1.420 | 1.407 | 1.412 | 1.411 |
| $C-N_2$ | 1.373 | 1.376 | 1.372 | 1.376 | 1.327 | 1.374 |
| $N_1-H_3$ | 1.021 | 1.025 | 1.014 | 1.018 | 1.011 | 1.012 |
| $N_1-H_4$ | 1.019 | 1.018 | 1.013 | 1.012 | 1.009 | 1.007 |
| $N_2-H_5$ | 1.020 | 1.016 | 1.015 | 1.012 | 1.009 | 1.008 |
| $N_2-H_6$ | 1.014 | 1.011 | 1.009 | 1.009 | 1.006 | 1.005 |
| $O_1-O_2$ | 1.454 | 1.449 | 1.451 | 1.451 | 1.466 | 1.465 |
| $O_1-H_1$ | 0.991 | 0.973 | 0.984 | 0.964 | 0.980 | 0.963 |
| $O_2-H_2$ | 0.972 | 0.991 | 0.967 | 0.981 | 0.964 | 0.981 |
| $O_2\cdots H_5$ | 2.035 | 2.262 | 2.081 | 2.297 | 2.085 | 2.257 |
| $H_1\cdots N_1$ | 1.901 | | 1.941 | | 1.922 | |
| $N_1\cdots H_2$ | | 1.920 | | 1.982 | | 1.954 |
| $O_1\cdots H_3$ | | 2.336 | | 2.363 | | 2.324 |
| $\angle O_3-C-N_1$ | 121.9 | 122.3 | 121.9 | 122.5 | 122.2 | 122.5 |
| $\angle O_3-C-N_2$ | 125.3 | 124.8 | 125.2 | 124.3 | 125.0 | 125.0 |
| $\angle C-N_1-H_3$ | 113.1 | 114.0 | 113.5 | 114.8 | 113.9 | 113.7 |
| $\angle C-N_1-H_4$ | 109.6 | 110.1 | 109.6 | 110.1 | 110.1 | 109.8 |
| $\angle C-N_2-H_5$ | 117.4 | 117.2 | 117.6 | 117.2 | 117.6 | 116.6 |
| $\angle C-N_2-H_6$ | 113.7 | 113.7 | 113.4 | 113.3 | 113.0 | 112.6 |
| $\angle O_2\cdots H_5-N_2$ | 152.9 | 139.8 | 160.0 | 139.7 | 149.9 | 139.6 |
| $\angle N_1\cdots H_1-O_1$ | 157.8 | | 159.9 | | 151.6 | |
| $\angle N_1\cdots H_2-O_2$ | | 144.5 | | 142.5 | | 142.9 |
| $\angle O_1\cdots H_3-N_1$ | | 120.1 | | 120.7 | | 119.1 |
| $\angle O_2-O_1-H_1$ | 99.1 | 100.6 | 99.9 | 101.0 | 97.8 | 99.2 |
| $\angle O_1-O_2-H_2$ | 100.8 | 99.5 | 101.1 | 100.0 | 99.5 | 98.5 |
| $\angle H_1-O_1-O_2-H_2$ | 117.9 | 110.2 | 108.6 | 104.4 | 117.6 | 108.0 |
| $\angle O_3-C-N_1-H_3$ | −153.4 | −138.3 | −139.4 | −140.5 | −145.0 | −141.5 |
| $\angle O_3-C-N_1-H_4$ | −15.3 | −12.2 | −14.0 | −12.8 | −17.8 | −14.3 |
| $\angle O_3-C-N_2-H_5$ | −139.7 | −151.8 | −151.9 | −151.2 | −153.3 | −149.8 |
| $\angle O_3-C-N_2-H_6$ | −13.7 | −12.8 | −13.2 | −13.5 | −14.9 | −13.8 |

**TABLE 4: Geometrical Parameters (Angstroms and Degrees) for the UHP Complexes (Structures 5 and 6), at the Different Levels of Theory**

| | B3LYP/cc-pVDZ | | B3LYP/6-31G(2d,p) | | MP2(full)/6-31G(2d,p) | |
|---|---|---|---|---|---|---|
| | **5** | **6** | **5** | **6** | **5** | **6** |
| $C-O_3$ | 1.232 | 1.236 | 1.228 | 1.228 | 1.232 | 1.228 |
| $C-N_1$ | 1.366 | 1.370 | 1.363 | 1.369 | 1.366 | 1.370 |
| $C-N_2$ | 1.384 | 1.380 | 1.382 | 1.380 | 1.384 | 1.378 |
| $N_1-H_3$ | 1.016 | 1.024 | 1.015 | 1.017 | 1.026 | 1.009 |
| $N_1-H_4$ | 1.011 | 1.011 | 1.010 | 1.008 | 1.011 | 1.008 |
| $N_2-H_5$ | 1.015 | 1.017 | 1.007 | 1.007 | 1.015 | 1.006 |
| $N_2-H_6$ | 1.013 | 1.013 | 1.011 | 1.013 | 1.013 | 1.006 |
| $O_1-O_2$ | 1.455 | 1.454 | 1.449 | 1.451 | 1.455 | 1.464 |
| $O_1-H_1$ | 0.997 | 1.000 | 0.993 | 0.994 | 0.997 | 0.985 |
| $O_2-H_2$ | 0.969 | 0.973 | 0.966 | 0.970 | 0.969 | 0.966 |
| $O_3\cdots H_1$ | 1.718 | 1.720 | 1.736 | 1.744 | 1.718 | 1.752 |
| $O_2\cdots H_3$ | 1.936 | | 1.967 | | 1.936 | |
| $O_1\cdots H_3$ | | 2.054 | | 2.091 | | 2.103 |
| $\angle O_3-C-N_1$ | 123.4 | 123.1 | 123.3 | 123.3 | 123.4 | 123.7 |
| $\angle O_3-C-N_2$ | 121.2 | 121.2 | 121.0 | 121.2 | 121.2 | 121.7 |
| $\angle C-N_1-H_3$ | 114.3 | 113.1 | 114.2 | 113.4 | 114.3 | 113.3 |
| $\angle C-N_1-H_4$ | 118.3 | 117.9 | 118.0 | 118.0 | 118.3 | 116.5 |
| $\angle C-N_2-H_5$ | 112.9 | 113.2 | 112.9 | 112.9 | 112.9 | 112.3 |
| $\angle C-N_2-H_6$ | 117.6 | 117.5 | 117.3 | 117.2 | 117.6 | 116.6 |
| $\angle O_3\cdots H_1-O_1$ | 172.8 | 159.1 | 173.3 | 158.3 | 172.8 | 159.6 |
| $\angle O_2\cdots H_3-N_1$ | 159.9 | | 160.4 | | 159.9 | |
| $\angle O_1\cdots H_3-N_1$ | | 140.7 | | 140.2 | | 139.9 |
| $\angle O_2-O_1-H_1$ | 100.3 | 100.9 | 100.7 | 101.0 | 100.3 | 99.0 |
| $\angle O_1-O_2-H_2$ | 100.9 | 100.1 | 101.1 | 100.4 | 100.9 | 99.2 |
| $\angle H_1-O_1-O_2-H_2$ | 105.7 | −108.8 | 101.4 | −104.7 | 105.7 | −103.9 |
| $\angle O_3-C-N_1-H_3$ | 11.8 | 13.5 | 12.5 | 13.6 | 11.8 | 15.0 |
| $\angle O_3-C-N_1-H_4$ | 154.7 | 153.4 | 155.1 | 153.9 | 154.7 | 152.0 |
| $\angle O_3-C-N_2-H_5$ | 13.9 | 13.9 | 14.2 | 14.9 | 13.9 | 15.0 |
| $\angle O_3-C-N_2-H_6$ | 150.0 | 150.7 | 150.3 | 150.8 | 150.0 | 148.9 |

intermediate from those presented in the structures **1** and **3** and closer to that of the dihedral angle for the HP monomer. This deviation of the dihedral angle with the monomer was related with the stability of the different structures. Thus, structures **1** and **3**, which gave the largest deviations were the least stable ones.

**TABLE 5: Hydrogen-Bond Geometrical Parameters, Charge Density ($\rho(r)$) and the Laplacian of the Charge Density ($\nabla^2\rho(r)$) for the UHP Complexes (Structures 1−6), at the MP2(full)/6-31G(2d,p)//MP2(full)/6-31G(2d,p) Level of Theory**

| critical points | definition[a] | $\rho(r)$ (e/$a_0^3$) | $\nabla^2\rho(r)$ (e/$a_0^5$) | bond length (Å) | angle (degrees) |
|---|---|---|---|---|---|
| | | **1** ($C_2$) | | | |
| (3,−1) | Hbond1 ($O_1\cdots H_3-N_1$) | 0.015 | 0.050 | 2.177 | 158.2 |
| (3,1) | ring ($O_2-O_1\cdots H_3-N_1-C-N_2-H_5$) | 0.004 | 0.025 | | |
| | | **2** | | | |
| (3,−1) | Hbond1 ($O_2\cdots H_5-N_2$) | 0.016 | 0.063 | 2.085 | 149.9 |
| (3,−1) | Hbond2 ($N_1\cdots H_1-O_1$) | 0.031 | 0.090 | 1.922 | 151.6 |
| (3,1) | ring ($O_1-O_2\cdots H_5-N_2-C-N_1\cdots H_1$) | 0.007 | 0.037 | | |
| | | **3** ($C_2$) | | | |
| (3,−1) | Hbond1 ($O_1\cdots H_3-N_1$) | 0.019 | 0.064 | 2.145 | 133.4 |
| (3,−1) | Hbond2 ($N_2\cdots H_1-O_1$) | 0.017 | 0.060 | 2.214 | 129.8 |
| (3,3) | cage | 0.008 | 0.043 | | |
| (3,1) | ring ($O_1-H_1\cdots N_2-C-N_1-H_3$) | 0.008 | 0.043 | | |
| (3,1) | ring ($O_2-O_1\cdots H_3-N_1\cdots H_2$) | 0.013 | 0.070 | | |
| | | **4** | | | |
| (3,−1) | Hbond1 ($O_2\cdots H_5-N_2$) | 0.014 | 0.049 | 2.257 | 139.6 |
| (3,−1) | Hbond1 ($O_1\cdots H_3-N_1$) | 0.013 | 0.054 | 2.324 | 119.1 |
| (3,−1) | Hbond2 ($N_1\cdots H_2-O_2$) | 0.028 | 0.085 | 1.954 | 142.9 |
| (3,1) | ring ($O_2\cdots H_5-N_2-C-N_1\cdots H_2$) | 0.009 | 0.046 | | |
| (3,1) | ring ($O_1-O_2-H_2\cdots N_1-H_3$) | 0.012 | 0.060 | | |
| | | **5** | | | |
| (3,−1) | Hbond1 ($O_2\cdots H_3-N_1$) | 0.024 | 0.078 | 1.936 | 159.9 |
| (3,−1) | Hbond3 ($O_3\cdots H_1-O_1$) | 0.036 | 0.128 | 1.718 | 172.8 |
| (3,1) | ring ($O_1-O_2\cdots H_3-N_1-C-N_3\cdots H_1$) | 0.007 | 0.040 | | |
| | | **6** | | | |
| (3,−1) | Hbond1 ($O_1\cdots H_3-N_1$) | 0.019 | 0.065 | 2.103 | 139.9 |
| (3,−1) | Hbond3 ($O_3\cdots H_1-O_1$) | 0.038 | 0.132 | 1.752 | 159.6 |
| (3,1) | ring ($O_1\cdots H_3-N_1-C-O_3\cdots H_1-O_1$) | 0.011 | 0.066 | | |

[a] Atom numbering is depicted in Figure 1.

### B. Binding Energy and BSSE

Table 1 shows the binding energy (corrected and uncorrected for the BSSE), the BSSE, the relative energy and the dipole moment, at the three levels of theory used.

The III-parameter hybrid density functional was chosen as a suitable method to describe different molecular properties,[42,43] including hydrogen bonding.[33−36] The basis set chosen was the 6-31G(2d,p), which provided an appropriate description of the hydrogen peroxide geometry, together with the B3LYP functional.[31] Additional calculations with the Dunning's correlation consistent cc-pDVZ basis set were carried out for comparison. To test the quality of the results, we also performed the MP2-(full) calculations with the former basis.

As shown in Table 1, the results obtained at the three levels of theory all agree with the resulting structure **5** as the global minimum. Moreover, the stability order for the structures remained exactly equivalent at the three levels used. On the other hand, the least stable structure was **1**, related to the experimentally observed one. The difference in energy between the most and least stable structures was about 7.5 kcal $mol^{-1}$ at the three levels. This energy was easily released from the packing forces, considering the high symmetry, large dipolar moment, and the possibility of two additional strong hydrogen bonds: one from the urea carbonylic oxygen with the hydrogen of the hydrogen peroxide and the other from the neighboring complexes.[16]

The study of the binding energy in the intermolecular complexes was affected by the so-called BSSE. This error increased in importance as the quality of the basis set decreased. From our previous studies of the hydrogen peroxide complexes,[20−22] we concluded that the binding energy using the 6-31G(2d,p) basis has to be corrected for the BSSE, and specially for the electron correlation methods.

The BSSE, for structures **1**−**6**, was estimated with the full counterpoise procedure defined as

$$\mathrm{BSSE} = E(\mathrm{X})_{\mathrm{X}} - E(\mathrm{X})_{\mathrm{XY}} + E(\mathrm{Y})_{\mathrm{Y}} - E(\mathrm{Y})_{\mathrm{XY}}$$

where $E(X)_{XY}$ and $E(X)_X$ represent the energy of X calculated using its geometry within the dimer and the basis functions of X plus Y in the former and those of X alone in the latter. The full counterpoise correction can be taken as an upper bound estimate of the BSSE, and is known to work generally well at the SCF level, except when minimal basis sets were used.[20,52,53] We have taken into account that the correction of the BSSE for the interaction energy should be performed at the BSSE corrected equilibrium geometry. This can be easily achieved in systems where only one intermolecular parameter was needed for the definition of the system.[54] However, when there are two or more parameters, and when the relaxation of the monomer was pronounced, it was difficult and expensive to perform that correction. Therefore, only an energy correction at the uncorrected equilibrium geometry has been performed with the calculations presented.

There are conflicting views[55,56] on whether one should implement BSSE correction at the correlated level. The use of the full counterpoise correction method for correlated methods is questionable, since in the calculation of the $E(X)_{XY}$, and analogously $E(Y)_{XY}$, excitations from occupied orbitals of X to the *occupied* orbitals of Y are allowed and may lead to a spurious overcorrection. The *occupied* orbitals of Y are not accessible for electrons of X in the supermolecule calculation. Attempts to utilize only the virtual spaces of X and Y have led to discouraging results.[57] However, recently the BSSE correction at the correlated level has been performed to study the hydrogen bonding.[34] The resulting values are presented in Table

**TABLE 6: Vibrational Frequencies[a] and ZPE[b] for the UHP Complexes (Structures 1−6) and Monomers (the Hydrogen Peroxide and the Urea), at the B3LYP/6-31(2d,p)//B3LYP/6-31(2d,p) Level of Theory**

| no. | **1** ($C_2$) | **2** | **3** ($C_2$) | **4** | **5** | **6** | Hydrogen Peroxide ($C_2$) | | urea ($C_2$) | |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 3765(**A**) | 3770 | 3666(**A**) | 3760 | 3764 | 3767 | 3762(**B**) | 3608[c] | 3680(**A**) | 3545[d] |
| 2 | 3764(**B**) | 3676 | 3651(**B**) | 3680 | 3695 | 3694 | 3762(**A**) | 3599[c] | 3679(**B**) | 3535[d] |
| 3 | 3685(**A**) | 3638 | 3631(**B**) | 3639 | 3661 | 3666 | 1448(**A**) | 1402[c] | 3568(**A**) | 3440[d] |
| 4 | 3683(**B**) | 3533 | 3630(**A**) | 3548 | 3580 | 3579 | 1348(**B**) | 1266[c] | 3564(**B**) | 3440[d] |
| 5 | 3554(**A**) | 3523 | 3493(**A**) | 3520 | 3457 | 3502 | 946(**A**) | 877[c] | 1831(**A**) | 1740[d] |
| 6 | 3544(**B**) | 3462 | 3488(**B**) | 3490 | 3353 | 3349 | 383(**A**) | 371[c] | 1639(**B**) | 1590[d] |
| 7 | 1819(**A**) | 1842 | 1840(**A**) | 1836 | 1778 | 1778 | | | 1637(**A**) | 1590[d] |
| 8 | 1656(**A**) | 1651 | 1641(**B**) | 1654 | 1655 | 1652 | | | 1415(**B**) | 1393[d] |
| 9 | 1653(**B**) | 1626 | 1635(**A**) | 1639 | 1638 | 1636 | | | 1195(**A**) | 1145[d] |
| 10 | 1469(**A**) | 1555 | 1496(**A**) | 1522 | 1588 | 1521 | | | 1062(**B**) | 1004[d] |
| 11 | 1420(**B**) | 1399 | 1444(**B**) | 1401 | 1467 | 1467 | | | 949(**A**) | 940[d] |
| 12 | 1335(**B**) | 1356 | 1380(**B**) | 1375 | 1356 | 1387 | | | 794(**B**) | 785[d] |
| 13 | 1213(**A**) | 1213 | 1221(**A**) | 1210 | 1205 | 1202 | | | 635(**A**) | 580[d] |
| 14 | 1081(**B**) | 1094 | 1129(**B**) | 1092 | 1087 | 1085 | | | 588(**B**) | 543[d] |
| 15 | 958(**A**) | 946 | 939(**A**) | 942 | 986 | 981 | | | 553(**B**) | 500[d] |
| 16 | 949(**A**) | 934 | 932(**A**) | 937 | 939 | 958 | | | 472(**A**) | 479[d] |
| 17 | 786(**B**) | 859 | 842(**B**) | 836 | 809 | 910 | | | 452(**B**) | |
| 18 | 595(**B**) | 774 | 833(**A**) | 778 | 751 | 791 | | | 393(**A**) | 273[d] |
| 19 | 593(**A**) | 639 | 689(**B**) | 713 | 692 | 686 | | | | |
| 20 | 553(**B**) | 628 | 653(**A**) | 593 | 598 | 602 | | | | |
| 21 | 526(**B**) | 583 | 591(**B**) | 571 | 563 | 563 | | | | |
| 22 | 501(**A**) | 541 | 555(**B**) | 534 | 502 | 499 | | | | |
| 23 | 471(**A**) | 489 | 521(**A**) | 495 | 451 | 454 | | | | |
| 24 | 378(**A**) | 441 | 496(**A**) | 489 | 404 | 399 | | | | |
| 25 | 195(**B**) | 285 | 420(**B**) | 293 | 357 | 252 | | | | |
| 26 | 135(**B**) | 224 | 189(**B**) | 213 | 239 | 238 | | | | |
| 27 | 121(**A**) | 160 | 179(**A**) | 138 | 181 | 158 | | | | |
| 28 | 87(**B**) | 130 | 143(**A**) | 118 | 155 | 128 | | | | |
| 29 | 59(**A**) | 68 | 126(**B**) | 83 | 82 | 91 | | | | |
| 30 | 44(**B**) | 51 | 72(**B**) | 69 | 56 | 47 | | | | |
| ZPE[b] | 58.03 | 58.74 | 59.36 | 58.86 | 58.62 | 58.67 | 16.15 | | 40.18 | |

[a] Frequency in $cm^{-1}$ with the symmetry in parentheses. [b] Zero point vibrational energy in kcal $mol^{-1}$. [c] Experimental frequencies from ref 60. [d] Experimental frequencies from ref 61.

1, remaining in the same magnitude order of the binding energy, corroborating the necessity of this correction. All the complexes investigated yielded attractive corrected binding energies, with values of around −10.5 kcal $mol^{-1}$ for the most stable structures (i.e., structure **5**). This result was compatible with a medium-to-strong strength contribution for a hydrogen bond. As pointed out above, the nature of the stationary points was tested with the frequency calculations, giving real frequencies for all the structures. The numerical results obtained at the B3LYP/6-31G(2d,p)//B3LYP/6-31G(2d,p) level are presented in Table 6, also including the corresponding monomers (urea and hydrogen peroxide) for comparison.

## 5. Conclusions

Five new UHP cyclic complexes were characterized in addition to the experimental complex (structure **1**) by the ab initio MP2 and DFT methods, and the results indicated that all the structures corresponded to the true minima stationary points. The DFT methods showed good agreement in reproducing the geometrical parameters and the energetics compared to the MP2 and the experimental results. Moreover, the BSSE obtained with the DFT methods (ca. 5 kcal $mol^{-1}$) was similar to the MP2 values; hence, the BSSE correction was required to obtain accurate binding energies. All the theoretical results designated the structures **5** and **6** (bonded to the carbonylic oxygen of urea) as the most stable ones. The existence of the structure **1** in the solid state was explained by means of the packing forces, the larger dipolar moment, and the presence of additional hydrogen bonds.

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