

# The molecular properties of heterocyclic and homocyclic hydrogen-bonded complexes evaluated by DFT calculations and AIM densities

Boaz G. Oliveira · Regiane C. M. U. Araújo ·  
Antônio B. Carvalho · Mozart N. Ramos

Received: 14 January 2008 / Accepted: 31 October 2008 / Published online: 27 November 2008  
© Springer-Verlag 2008

**Abstract** This theoretical study presents a comparative analysis of the molecular properties of heterocyclic ( $C_2H_4O \cdots HF$  and  $C_2H_5N \cdots HF$ ) and homocyclic ( $C_3H_6 \cdots HF$ ) hydrogen-bonded complexes. Initially, the equilibrium geometries of these complexes were analyzed in detail at the B3LYP/6-311++G(d,p) level of theory. Subsequently, the interaction energies and polarizabilities were also evaluated, as well as the infrared stretch frequencies and absorption intensities. In addition, by combining intermolecular criteria and charge density concepts, calculations of Bader's theory of atoms in molecules were used to determine the maxima and minima for electron density in order to measure the strength of the  $n \cdots H$  and  $p\pi \cdots H$  hydrogen bonds. Finally, the possibility of an  $F \cdots H_\alpha$  secondary interaction between the fluoride (F) of hydrogen fluoride and the axial hydrogen atoms ( $H_\alpha$ ) of the  $C_2H_4O$  and  $C_2H_5N$  heterocyclic rings was explored.

**Keywords** AIM · B3LYP · Heterocyclic · Homocyclic · Hydrogen bonds

## Introduction

It has long been known that hydrogen bonds belongs to a non-covalent interaction category often investigated by experimentalists and theoreticians [1]. Nowadays, the hydrogen bond plays a fundamental role in important scientific research, e.g., the study of solvation in the biological medium [2], characterization of the building blocks of protein chains, amino acids and enzymes [3], as well as in the development of new pharmacological drugs [4]. A historical survey reveals a large number of reports of new insights into the molecular parameters of hydrogen-bonded complexes [5–6].

A commonly used experimental technique is Fourier Transform Microwave Spectroscopy (FTMS) [7], which estimates the equilibrium geometry of intermolecular systems by analyzing their inertial moments and rotational constants [8–10]. On the other hand, the study of hydrogen-bonded complexes has also been carried out using theoretical calculations [11–14], mainly in special cases where some of the classic parameters of weakly bound systems, such as attraction energies, infrared stretch frequencies, absorption intensities, and obviously the charge transfer [15], are difficult to explore experimentally. For this reason, Rozas et al. [16] and Tang et al. [17] have shown that the  $C_3H_6 \cdots HF$  homocyclic hydrogen-bonded complex is formed and stabilized by means of a pseudo (p)

**Electronic supplementary material** The online version of this article (doi:10.1007/s00894-008-0380-2) contains supplementary material, which is available to authorized users.

B. G. Oliveira (✉) · R. C. M. U. Araújo · A. B. Carvalho  
Departamento de Química, Universidade Federal da Paraíba,  
58036–300 João Pessoa, PB, Brazil  
e-mail: boazgaldino@gmail.com

M. N. Ramos  
Departamento de Química Fundamental,  
Universidade Federal de Pernambuco,  
50739–901 Recife, PE, Brazil

$\pi \cdots \text{H}$  hydrogen bond, which is manifested by an interaction of proton donors aligned exactly at the middle of the C–C bond of the cyclopropane ( $\text{C}_3\text{H}_6$ ) moiety. In our recent studies [18–20], however, the chemical nature of  $\text{C}_2\text{H}_4\text{O} \cdots \text{HF}$  and  $\text{C}_2\text{H}_5\text{N} \cdots \text{HF}$  heterocyclic hydrogen-bonded complexes was discussed in terms of their  $n \cdots \text{H}$  hydrogen bonds, which originate from the interaction of hydrogen fluoride (HF) with the  $n$ -lone pairs of oxygen and nitrogen of the three-membered rings ( $\text{C}_2\text{H}_4\text{O}$  and  $\text{C}_2\text{H}_5\text{N}$ ) [21–22]. In fact, intermolecular cyclic systems (heterocyclic and homocyclic) have been widely studied by many research groups all over the world [23–24], although it has to be said that some questions about these systems, such as those of an electronic or vibrational nature [25], still require further investigation.

Nevertheless, an interesting conclusion of our studies on hydrogen-bonded complexes is that the charge transfer mechanism may be useful in the interpretation of observable parameters, e.g., polarizability and infrared stretching modes [15]. Not surprisingly, however, it has been widely reported that charge transfer also plays an essential role in explaining some effects inherent to molecular energy [26–31], although it should be noted that the charge transfer phenomenon is essentially non-observable because the quantification of atomic charges is not based on physical arguments [32]. In other words, atomic charges are not computed directly from *ab initio* wave functions, which usually leads to some divergence in interpretation if atomic charge partitions derived from distinct approaches are used [15]. To avoid this, it is recommended to use a method that has been implemented by means of purely physical parameters, for example electron density. Such an objective can thus be effectively associated with the quantum theory of atoms in molecules (QTAIM) [33–35], whose efficiency is well-known in the scientific community, particularly in studies that characterize intermolecular interactions by measuring electron density, as well as in the interpretation of surface operators [26–41].

In this work, we have performed a theoretical study of the molecular properties of the  $\text{C}_3\text{H}_6 \cdots \text{HF}$ ,  $\text{C}_2\text{H}_4\text{O} \cdots \text{HF}$  and  $\text{C}_2\text{H}_5\text{N} \cdots \text{HF}$  hydrogen-bonded complexes using density functional theory (DFT) [42–43], as well as by analysis of molecular descriptors embodied in QTAIM topological integrations. Besides structural, electron and vibrational parameters, by taking into account QTAIM descriptors such as electronic density ( $\rho$ ), Laplacian ( $\nabla^2\rho$ ) and charge transfer ( $\delta Q_{(i)}$ ), our main goal is that of examining charge density maxima and minima, thereby predicting the strength of  $\pi \cdots \text{H}$  and  $n \cdots \text{H}$  hydrogen bonds. We have also investigated the existence of a secondary  $\text{F} \cdots \text{H}_\alpha$  interaction between the fluoride (F) of the hydrogen fluoride and the axial hydrogen atoms ( $\text{H}_\alpha$ ) of the  $\text{C}_2\text{H}_4\text{O}$  and  $\text{C}_2\text{H}_5\text{N}$  heterocyclic

rings. Thereby, we expect to demonstrate the reactivity of the  $\text{C}_2\text{H}_4\text{O}$  and  $\text{C}_2\text{H}_5\text{N}$  heterocyclic compounds in comparison with the  $\text{C}_3\text{H}_6$  homocyclic system.

## Computational methods

The optimized geometries of the  $\text{C}_2\text{H}_4\text{O} \cdots \text{HF}$ ,  $\text{C}_2\text{H}_5\text{N} \cdots \text{HF}$  and  $\text{C}_3\text{H}_6 \cdots \text{HF}$  hydrogen-bonded complexes were obtained at the B3LYP/6–311++G(d,p) level of theory [44–46] with calculations performed using the GAUSSIAN 98W program [47]. To obtain the QTAIM data, all topological calculations were executed using GAUSSIAN software [48–50], although some integrations were also processed using the program AIM 2000 1.0 [51]. The values of interaction energies ( $\Delta E$ ) of the hydrogen-bonded complexes ( $\text{A} \cdots \text{B}$ ) were determined as follows [52]:

$$\Delta E = E(\text{A} \cdots \text{B}) - [E(\text{A}) + E(\text{B})] \quad (1)$$

According to Eq. 2, the  $\Delta E$  results were corrected by zero point vibrational energy (ZPE) [53] and basis sets superposition error (BSSE) [54].

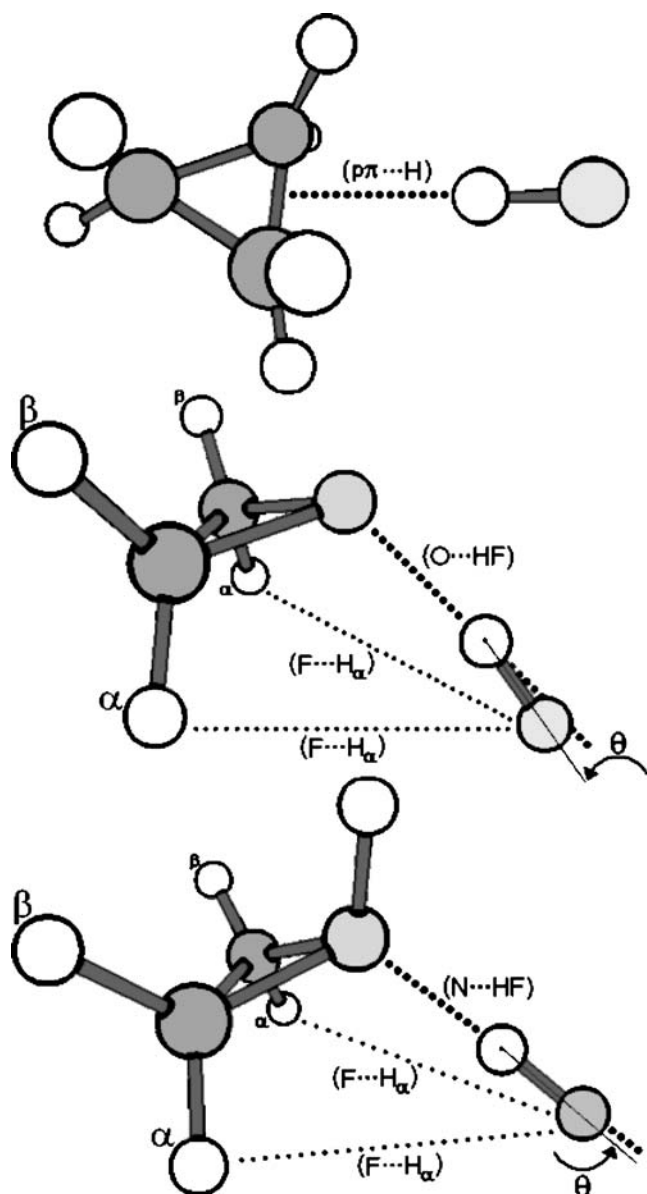
$$\Delta E^{\text{C}} = \Delta E - \Delta \text{ZPE} - \text{BSSE} \quad (2)$$

## Results and discussion

### Geometry

#### Hydrogen bond distance

Taking the B3LYP/6–311++G(d,p) calculations as a basis, the optimized geometries of the  $\text{C}_2\text{H}_4\text{O} \cdots \text{HF}$ ,  $\text{C}_2\text{H}_5\text{N} \cdots \text{HF}$  and  $\text{C}_3\text{H}_6 \cdots \text{HF}$  hydrogen-bonded complexes are illustrated in Fig. 1. Some time ago, Legon et al. [55] reported FTMS data on the experimental structure of the  $\text{C}_2\text{H}_4\text{O} \cdots \text{HF}$  complex, and determined a value for the  $R_{(n \cdots \text{H})}$  hydrogen bond distance of 1.700 Å. In view of the data collected in Table 1, it can be seen that our  $R_{(n \cdots \text{H})}$  theoretical result of 1.662 Å is in satisfactory agreement with the experimental value mentioned above [55]. In the  $\text{C}_3\text{H}_6 \cdots \text{HF}$  homocyclic complex, the  $R_{(\pi \cdots \text{H})}$  hydrogen bond distance presents a result of 2.080 Å [8], which is longer than the values of 1.662 Å and 1.623 Å for the corresponding  $\text{C}_2\text{H}_4\text{O} \cdots \text{HF}$  and  $\text{C}_2\text{H}_5\text{N} \cdots \text{HF}$  systems. One explanation for this is that the low charge density on the C–C bond of the cyclopropane results in a low quantity of intermolecular charge being transferred to the HF molecule. Thereby,  $\text{C}_3\text{H}_6 \cdots \text{HF}$  is thus considered to be a weakly bound complex. So, the large  $R_{(\pi \cdots \text{H})}$  hydrogen bond distance provides some structural justification of the lower reactivity of the



**Fig. 1** Optimized geometries of  $C_3H_6 \cdots HF$ ,  $C_2H_4O \cdots HF$  and  $C_2H_5N \cdots HF$  hydrogen-bonded complexes using the B3LYP/6-311++G(d,p) calculations

homocyclic system in comparison with the heterocyclic complexes.

#### Non-linearity in the hydrogen bonds

The electronic structure of  $C_2H_4O$  and  $C_2H_5N$  is composed of oxygen and nitrogen atoms that have  $n$ -lone pairs of electrons orthogonally aligned to the trigonal surface of these heterorings. Besides the formation of  $n \cdots H$  hydrogen bonds, another interesting structural aspect can be seen regarding the  $F \cdots H_\alpha$  secondary interaction between the fluoride and axial

**Table 1** Main structural parameters of heterocyclic and homocyclic  $C_3H_6 \cdots HF$ ,  $C_2H_4O \cdots HF$  and  $C_2H_5N \cdots HF$  hydrogen-bonded complexes using the B3LYP/6-311++G(d,p) calculations. CY is the “hetero” bond, where Y represents the oxygen and nitrogen atoms in the  $C_2H_4O$  and  $C_2H_5N$  rings, respectively; values of  $R$  and  $\delta r$  are in Angstroms (Å); values of  $\theta$  are in degrees

Parameter	Hydrogen-bonded complexes		
	$C_2H_4O \cdots HF$	$C_2H_5N \cdots HF$	$C_3H_6 \cdots HF$
$R_{(n \cdots H)}$	1.662 (1.700) <sup>a</sup>	1.623	—
$R_{(p\pi \cdots H)}$	—	—	2.080 Å
$R_{(F \cdots H_\alpha)}$	3.273	3.394	—
$\theta$	9.2	4.0	—
$\delta r_{HF}$	0.025	0.045	0.010
$\delta r_{CY}$	0.012	0.032	—
$\delta r_{CC}$	-0.001	-0.002	—

<sup>a</sup> Reference [55]

hydrogen atoms ( $H_\alpha$ ) of the three-membered rings [56]. It can be hypothesized that the  $F \cdots H_\alpha$  secondary interaction shows some structural distortions in the  $C_2H_4O \cdots HF$  and  $C_2H_5N \cdots HF$  hydrogen-bonded complexes, such as the linearity deviation ( $\theta$ ) on the  $n \cdots H$  hydrogen bonds. From the B3LYP/6-311++G(d,p) results listed in Table 1, the respective  $\theta$  values of 9.2° and 4.0° for  $C_2H_4O \cdots HF$  and  $C_2H_5N \cdots HF$  suggest the existence of linearity deviation in their hydrogen bonds. However, the  $R_{(F \cdots H_\alpha)}$  theoretical distances of 3.273 Å and 3.394 Å for the  $C_2H_4O \cdots HF$  and  $C_2H_5N \cdots HF$  hydrogen complexes are longer than the van der Waals radii for hydrogen ( $H=1.2$  Å) and fluoride ( $F=1.35$  Å) atoms, which add up to a combined length of 2.55 Å [57]. Thus, although FTMS [55] analysis suggests the existence of  $F \cdots H_\alpha$ , the  $R_{(F \cdots H_\alpha)}$  results indicate that this secondary interaction is unlikely to form.

#### Important structural changes

By further comparing the cyclic structures, an elongation of the  $r_{HF}$  bond length can be detected (see Table 1), whose  $\delta r_{HF}$  variations are 0.025 Å, 0.045 Å and 0.010 Å for the  $C_2H_4O \cdots HF$ ,  $C_2H_5N \cdots HF$  and  $C_3H_6 \cdots HF$  complexes, respectively. It should be noted that  $\delta r_{HF}$  cannot be considered the only evidence of cyclic complexation, because significant variations are observed on the  $r_{CY}$  “heterobond” (notation for CO and CN bonds of  $C_2H_4O$  and  $C_2H_5N$ , respectively), whose values for the  $C_2H_4O \cdots HF$  and  $C_2H_5N \cdots HF$  hydrogen-bonded complexes are 0.012 Å and 0.032 Å, respectively. These “heterobond” enhancements are an indication of the relaxation of the  $C_2H_4O$  and  $C_2H_5N$  strained molecules. On the other hand, it should be noted that  $\delta r_{CC}$  does not deform significantly in view of the results of -0.001 Å and -0.002 Å.

## Infrared harmonic spectrum

## Vibrational modes of three-member rings

In the context of the structural results presented in this study, we have already discussed the fact that variations of rCY “heterobonds” constitute important evidence regarding the formation of heterocyclic hydrogen-bonded complexes. Hence, for the sake of accuracy, it is very important to identify the  $\nu_{\text{CY-i}}$  stretch modes of the CO and CN bonds of the  $\text{C}_2\text{H}_4\text{O}$  and  $\text{C}_2\text{H}_5\text{N}$  monomers prior to the formation of the heterocyclic hydrogen-bonded complexes. Thus, according to the B3LYP/6–311++G(d,p) results listed in Table 2, the values of  $1,298\text{ cm}^{-1}$  and  $1,266\text{ cm}^{-1}$  correspond to the  $\nu_{\text{CO-i}}$  and  $\nu_{\text{CN-i}}$  stretch frequencies. Moreover, these values are in satisfactory agreement with the available experimental data of  $1,250\text{ cm}^{-1}$  and  $1,200\text{ cm}^{-1}$  for the  $\text{C}_2\text{H}_4\text{O}$  [58] and  $\text{C}_2\text{H}_5\text{N}$  [59] monomers, respectively. In fact, a knowledge of the variations in the stretch modes for CO and CN bonds is essential to explain the strain relaxation phenomenon on the  $\text{C}_2\text{H}_4\text{O}$  and  $\text{C}_2\text{H}_5\text{N}$  rings [60]. This trend is confirmed by the  $\Delta\nu_{\text{CY}}$  frequency shifts, whose values are  $-3.7\text{ cm}^{-1}$  and  $-20.6\text{ cm}^{-1}$  (Table 3). Of course, the infrared variations on the CO and CN bonds can also be described by an increase in their absorption intensities, whose  $(A_{\text{CY,c}}/A_{\text{CY-i}})$  ratios are 1.4 and 2.4 for the  $\text{C}_2\text{H}_4\text{O}\cdots\text{HF}$  and  $\text{C}_2\text{H}_4\text{N}\cdots\text{HF}$  hydrogen-bonded complexes, respectively.

## Shift modes on the HF acid

Of the many changes observed in the infrared spectrum of hydrogen-bonded complexes, the most pronounced effect is related to the stretch frequencies of the proton donors, which are shifted downwards, while their absorption intensities are increased drastically. According to the

**Table 2** Values of the main stretch modes and absorption intensities of the HF,  $\text{C}_2\text{H}_4\text{O}$  and  $\text{C}_2\text{H}_5\text{N}$  isolated molecules using B3LYP/6–311++G(d,p) calculations. CY is the “heterobond”, where Y represents the oxygen and nitrogen atoms in the  $\text{C}_2\text{H}_4\text{O}$  and  $\text{C}_2\text{H}_5\text{N}$  rings, respectively; values of  $\nu$  and A are given in  $\text{cm}^{-1}$  and  $\text{km mol}^{-1}$ , respectively

Parameter	Isolated molecule		
	HF	$\text{C}_2\text{H}_4\text{O}$	$\text{C}_2\text{H}_5\text{N}$
$\nu_{\text{CY-i}}$	—	1,298 (1,250) <sup>a</sup>	1,266 (1,200) <sup>b</sup>
$A_{\text{CY-i}}$	—	15.2	10.7
$\nu_{\text{HF-i}}$	4,096 (3,962) <sup>c</sup>	—	—
$A_{\text{HF-i}}$	130 (77) <sup>d</sup>	—	—

<sup>a</sup> Reference [58]

<sup>b</sup> Reference [59]

<sup>c</sup> Reference [61]

<sup>d</sup> Reference [62]

**Table 3** Values of the main stretch modes and absorption intensities of the heterocyclic and homocyclic hydrogen-bonded complexes using B3LYP/6–311++G(d,p) calculations. CY is the “heterobond”, where Y represents the oxygen and nitrogen atoms in the  $\text{C}_2\text{H}_4\text{O}$  and  $\text{C}_2\text{H}_5\text{N}$  rings, respectively; values of  $\nu$  and A are given in  $\text{cm}^{-1}$  and  $\text{km mol}^{-1}$ , respectively

Parameter	Hydrogen-bonded complex		
	$\text{C}_2\text{H}_4\text{O}\cdots\text{HF}$	$\text{C}_2\text{H}_5\text{N}\cdots\text{HF}$	$\text{C}_3\text{H}_6\cdots\text{HF}$
$\Delta\nu_{\text{CY}}$	-3.7	-20.6	—
$(A_{\text{CY,c}}/A_{\text{CY-i}})$	1.4	2.4	—
$\Delta\nu_{\text{HF}}$	-538.2	-960.2	-222
$(A_{\text{HF,c}}/A_{\text{HF-i}})$	9.7	8.3	5.6
$\nu_{(\text{n}\cdots\text{H})}$	254.3	281.1	—
$A_{(\text{n}\cdots\text{H})}$	23.3	15.0	—
$\nu_{(\text{p}\pi\cdots\text{H})}$	—	—	127.2
$A_{(\text{p}\pi\cdots\text{H})}$	—	—	1.62

B3LYP/6–311++G(d,p) results presented in Table 3, the  $\Delta\nu_{\text{HF}}$  shifts of the  $\text{C}_2\text{H}_4\text{O}\cdots\text{HF}$ ,  $\text{C}_2\text{H}_5\text{N}\cdots\text{HF}$  and  $\text{C}_3\text{H}_6\cdots\text{HF}$  complexes are  $-538.2\text{ cm}^{-1}$ ,  $-960.2\text{ cm}^{-1}$  and  $-222\text{ cm}^{-1}$ , and the  $(A_{\text{HF,c}}/A_{\text{HF-i}})$  absorption intensity ratios are 9.7, 8.3 and 5.6, respectively. In short, it can be seen that the strongest  $\text{n}\cdots\text{H}$  hydrogen bonds cause large shifts in the stretch modes of HF. However, the formation of hydrogen bond complexes is one phenomenon responsible for manifestation of the hydrogen bond stretch frequencies, whose modes are characterized at low values of spectrum with weak absorption intensities. Table 2 therefore also lists the  $\nu_{(\text{n}\cdots\text{H})}$  hydrogen bond stretch frequencies of the  $\text{C}_2\text{H}_4\text{O}\cdots\text{HF}$  and  $\text{C}_2\text{H}_5\text{N}\cdots\text{HF}$  heterocyclic complexes, whose values are  $254.3\text{ cm}^{-1}$  and  $281.1\text{ cm}^{-1}$ , respectively. In terms of absorption intensities, the  $A_{(\text{n}\cdots\text{H})}$  values of  $23.3\text{ km mol}^{-1}$  and  $15.0\text{ km mol}^{-1}$  are lower than those observed for hydrogen fluoride, although by analyzing the new stretch mode  $\nu_{(\text{p}\pi\cdots\text{H})}$  of  $127.2\text{ cm}^{-1}$  and its absorption intensity  $A_{(\text{p}\pi\cdots\text{H})}$  of  $1.62\text{ km mol}^{-1}$ , it can be seen that these modest values are in fact indications of how weakly bound the  $\text{C}_3\text{H}_6\cdots\text{HF}$  homocyclic complex actually is.

## Electronic structure

## Charge transfer and polarizability

Electrostatic interaction and charge transfer [1] are the principal factors used to determine molecular energy and hence predict intermolecular interactions, in particular hydrogen bonds. The values of the charge transfers ( $\delta Q_{(\Omega)}^{\text{HF}}$ ) and variations in dipole moments ( $\delta\mu$ ) for the  $\text{C}_2\text{H}_4\text{O}\cdots\text{HF}$  and  $\text{C}_2\text{H}_5\text{N}\cdots\text{HF}$  heterocyclic hydrogen-bonded complexes are listed in Table 4. First, it can be seen that  $\text{C}_2\text{H}_5\text{N}\cdots\text{HF}$  is the strongest hydrogen-bound system because of the higher calculated charge transfer



**Table 4** Values of charge transfer ( $\delta Q_{(\Omega)}^{\text{HF}}$ ), dipole moment ( $\delta\mu$ ), uncorrected interaction energies ( $\Delta E$ ), basis sets superposition error (BSSE), changes in zero point vibrational energy ( $\Delta ZPE$ ) and corrected interaction energies ( $\Delta E^{\text{C}}$ ) of the heterocyclic and homocyclic hydrogen-bonded complexes using B3LYP/6–311++G(d,p) calculations. Values of  $\Delta E$ ,  $\Delta E^{\text{C}}$ , BSSE, and  $\Delta ZPE$  are in  $\text{kJ mol}^{-1}$ ; values of  $\delta Q_{(\Omega)}$  are in electronic units (e.u.); values of  $\delta\mu$  are in Debye (D)

Parameter	Hydrogen-bonded complex		
	$\text{C}_2\text{H}_4\text{O}\cdots\text{HF}$	$\text{C}_2\text{H}_5\text{N}\cdots\text{HF}$	$\text{C}_3\text{H}_6\cdots\text{HF}$
$\delta Q_{(\Omega)}^{\text{HF}}$	–0.049	–0.087	–0.030
$\delta\mu$	0.45	1.43	0.85
$\Delta E$	43.00	63.24	16.43
BSSE	1.90	0.64	0.46
$\Delta ZPE$	9.90	10.70	6.42
$\Delta E^{\text{C}}$	31.20	51.90	9.55

$\delta Q_{(\Omega)}^{\text{HF}}$  of –0.087 e.u.. By way of comparison, the charge transfer value of –0.030 is one more indication that  $\text{C}_3\text{H}_6\cdots\text{HF}$  is a weakly bound complex. For notation purposes only, the results of atomic charges (Q) and consequently charge transfers ( $\delta Q_{(\Omega)}$ ) were obtained through the QTAIM calculations as follows:

$$q_{(\Omega)} = Z - \int_{\Omega} \rho(\vec{r}, x) d\tau \quad (3)$$

Note that all  $\delta Q_{(\Omega)}^{\text{HF}}$  values are negative, which indicates a dominant charge donation from the highest occupied molecular orbital (HOMO) represented by n-lone electron pairs of oxygen and nitrogen to the hydrogen  $\sigma^*$  lowest unoccupied molecular orbital (LUMO) of the HF molecule. This leads to an electrical rearrangement of the molecular structure, which can be interpreted as an increase in the dipole moment,  $\delta\mu$ . The positive values for  $\delta\mu$  indicate that the polarizability of the heterocyclic hydrogen-bonded complexes is larger than the vector sum of the respective isolated molecules, especially in the case of the  $\text{C}_2\text{H}_5\text{N}\cdots\text{HF}$  complex, whose value of 1.43 D lead us to affirm that  $\text{C}_2\text{H}_5\text{N}$  is more reactive with HF than  $\text{C}_2\text{H}_4\text{O}$  or  $\text{C}_3\text{H}_6$ .

### Interaction energy

Table 4 also presents results for corrected interaction energies ( $\Delta E^{\text{C}}$ ), uncorrected interaction energies ( $\Delta E$ ), BSSE quantities and ZPE thermodynamic corrections. Initially, however, it is worth stressing that the values of  $31.20 \text{ kJ mol}^{-1}$  and  $51.90 \text{ kJ mol}^{-1}$  of the  $\text{C}_2\text{H}_4\text{O}\cdots\text{HF}$  and  $\text{C}_2\text{H}_5\text{N}\cdots\text{HF}$  complexes are higher than those of van der Waals contacts ( $\sim 8 \text{ kJ mol}^{-1}$ ) [63] or biological interactions ( $\sim 35 \text{ kJ mol}^{-1}$ ) [64]. The  $\text{C}_3\text{H}_6\cdots\text{HF}$  complex presents the

lowest interaction energy, whose value of  $9.55 \text{ kJ mol}^{-1}$  shows that cyclopropane yields a less stable intermolecular system. In determining  $\Delta E^{\text{C}}$  values, ZPE contributed the most and BSSE the least. Note that BSSE values range from  $0.46 \text{ kJ mol}^{-1}$  to  $1.90 \text{ kJ mol}^{-1}$  for  $\text{C}_3\text{H}_6\cdots\text{HF}$  homocyclic and  $\text{C}_2\text{H}_4\text{O}\cdots\text{HF}$  heterocyclic complexes, respectively. By taking into account the conclusions reported by Rozas et al. [16], the B3LYP/6–311++G(d,p) level of theory is in fact sufficient to determine minima for BSSE contributions.

### QTAIM molecular topology

#### Characterization of $n\cdots H$ and $p\pi\cdots H$ hydrogen bonds

It is evident that specific features of hydrogen bonding cannot be interpreted only in terms of intermolecular energy, but may also be adequately defined quantum mechanically and computed by using QTAIM theory. The QTAIM methodology performs a numerical integration of electron density, whereby a number of topological parameters, such as electron density ( $\rho$ ) and the Laplacian ( $\nabla^2\rho$ ) descriptor are calculated. Tables 5 and 6 present the values of electron density and Laplacian descriptors for the isolated molecules, as well as for the  $\text{C}_2\text{H}_4\text{O}\cdots\text{HF}$ ,  $\text{C}_2\text{H}_5\text{N}\cdots\text{HF}$ , and  $\text{C}_3\text{H}_6\cdots\text{HF}$  hydrogen-bonded complexes.

According to the scheme elaborated by Koch and Popelier [65], the characterization of intra- and/or intermolecular interactions is based on bond critical points (BCP) [33] located between neighboring atoms, according to which two essential criteria must be obeyed: (1) besides the proton donor, the acceptor center for positive charge must contain a minimum level of electron density, and (2) typical values for the Laplacian descriptor of charge density must be carefully interpreted. The Laplacian descriptors computed lead us to consider that  $\nabla^2\rho < 0$  and  $\nabla^2\rho > 0$  when covalent bonds (shared) or intermolecular/intramolecular

**Table 5** Values of electron densities ( $\rho$ ) and Laplacian field ( $\nabla^2\rho$ ) of the HF,  $\text{C}_2\text{H}_4\text{O}$  and  $\text{C}_2\text{H}_5\text{N}$  isolated molecules. CY is the “hetero-bond”, where Y represents the oxygen and nitrogen atoms in the  $\text{C}_2\text{H}_4\text{O}$  and  $\text{C}_2\text{H}_5\text{N}$  rings, respectively; values of  $\rho$  and  $\nabla^2\rho$  are given in  $\text{e}/a_0^3$  and  $\text{e}/a_0^5$ , respectively

Parameter	Isolated molecule		
	HF	$\text{C}_2\text{H}_4\text{O}$	$\text{C}_2\text{H}_5\text{N}$
$\rho_{\text{HF-i}}$	0.369	—	—
$\rho_{\text{CC}}$	—	0.255	0.245
$\rho_{\text{CY}}$	—	0.248	0.251
$\nabla^2\rho_{\text{HF-i}}$	–2.890	—	—
$\nabla^2\rho_{\text{CC}}$	—	–0.558	–0.486
$\nabla^2\rho_{\text{CY}}$	—	–0.358	–0.467

**Table 6** Values of electron densities ( $\rho$ ) and Laplacian fields ( $\nabla^2\rho$ ) of the heterocyclic and homocyclic hydrogen-bonded complexes. CY is the “heterobond”, where Y represents the oxygen and nitrogen atoms in the  $C_2H_4O$  and  $C_2H_5N$  rings, respectively; values of  $\rho$  and  $\nabla^2\rho$  are given in  $e/a_0^3$  and  $e/a_0^5$ , respectively

Parameter	Hydrogen-bonded complex		
	$C_2H_4O\cdots HF$	$C_2H_5N\cdots HF$	$C_3H_6\cdots HF$
$\rho_{(n\cdots H)}$	0.046	0.062	—
$\rho_{HF-(n\cdots H)}$	0.335	0.311	—
$\rho_{(p\pi\cdots H)}$	—	—	0.017
$\rho_{HF-(p\pi\cdots H)}$	—	—	0.355
$\rho_{(F\cdots H\alpha)}$	nd <sup>a</sup>	nd	—
$\rho_{CC}$	0.258	0.247	—
$\rho_{CY}$	0.239	0.245	—
$\nabla^2\rho_{(n\cdots H)}$	0.149	0.116	—
$\nabla^2\rho_{HF-(n\cdots H)}$	-2.432	-2.110	—
$\nabla^2\rho_{(p\pi\cdots H)}$	—	—	0.058
$\nabla^2\rho_{HF-(p\pi\cdots H)}$	—	—	-2.266
$\nabla^2\rho_{CC}$	-0.581	-0.504	—
$\nabla^2\rho_{CY}$	-0.294	-0.456	—
$\nabla^2\rho_{(F\cdots H\alpha)}$	nd	nd	—

<sup>a</sup> Not determined

(closed-shell) contacts are examined [66–70], respectively. Undoubtedly, these conditions are satisfied for the  $C_2H_4O\cdots HF$  and  $C_2H_5N\cdots HF$  heterocyclic complexes, where their BCP (see Fig. 2) describes the proton donor as being HF, whereas the proton acceptors are the oxygen and nitrogen atoms of the  $C_2H_4O$  and  $C_2H_5N$  rings, respectively.

For  $n\cdots H$  hydrogen bonds, the electron density values are  $0.046 e/a_0^3$  and  $0.062 e/a_0^3$  for the  $C_2H_4O\cdots HF$  and  $C_2H_5N\cdots HF$  complexes ( $\rho=10^{-3} e/a_0^3$  is typical for van der Waals complexes) [16], respectively. Moreover, the  $\nabla^2\rho_{(n\cdots H)}$  positive values of  $0.149 e/a_0^5$  and  $0.116 e/a_0^5$  indicate that the  $n\cdots H$  hydrogen bonds possess the typical characteristic of closed-shell interactions. In other words, the charge density is concentrated on separated nuclei, i.e., in the  $O\cdots H$  and  $N\cdots H$  hydrogen bonds. In fact, the  $n\cdots H$

hydrogen bond of the  $C_2H_5N\cdots HF$  complex shows a higher concentration of electron density, which demonstrates the greater susceptibility of the  $C_2H_5N$  heterocyclic to bind with HF. For the  $C_3H_6\cdots HF$  homocyclic complex, the hydrogen bond presents the lowest values of  $\rho_{(p\pi\cdots H)}$  and  $\nabla^2\rho_{(p\pi\cdots H)}$ , of  $0.017 e/a_0^3$  and  $0.058 e/a_0^5$ , respectively.

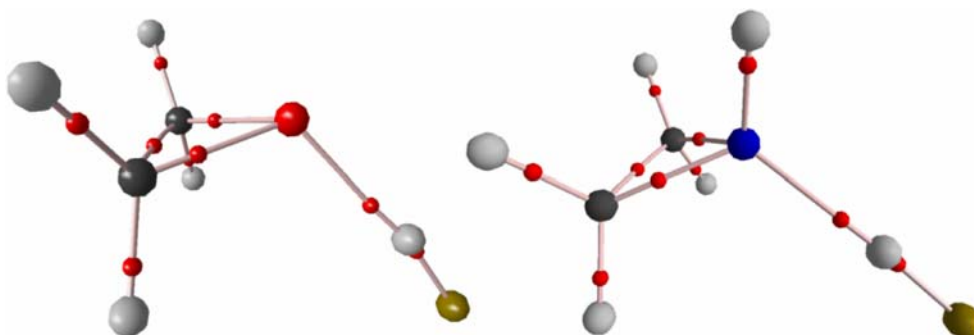
#### $F\cdots H_\alpha$ secondary interaction versus QTAIM parameters

One of the most important objectives of this study was the identification of the  $F\cdots H_\alpha$  secondary interaction between fluoride (F) of the HF acid and the axial hydrogen atoms ( $H_\alpha$ ) of the  $C_2H_4O$  and  $C_2H_5N$  rings. In light of the QTAIM results, the secondary interaction was not characterized because neither BCP was found between the F and  $H_\alpha$  atoms [71–74]. There is a debate in the field of structural analysis where it is admitted that the  $R_{(F\cdots H_\alpha)}$  distance must be either longer than or equal to the van der Waals radii. Our QTAIM results suggest that formation of this interaction is unlikely as there are no other interactions in the  $C_2H_4O\cdots HF$  and  $C_2H_5N\cdots HF$  heterocyclic hydrogen-bonded complexes besides the  $n\cdots H$  hydrogen bonds.

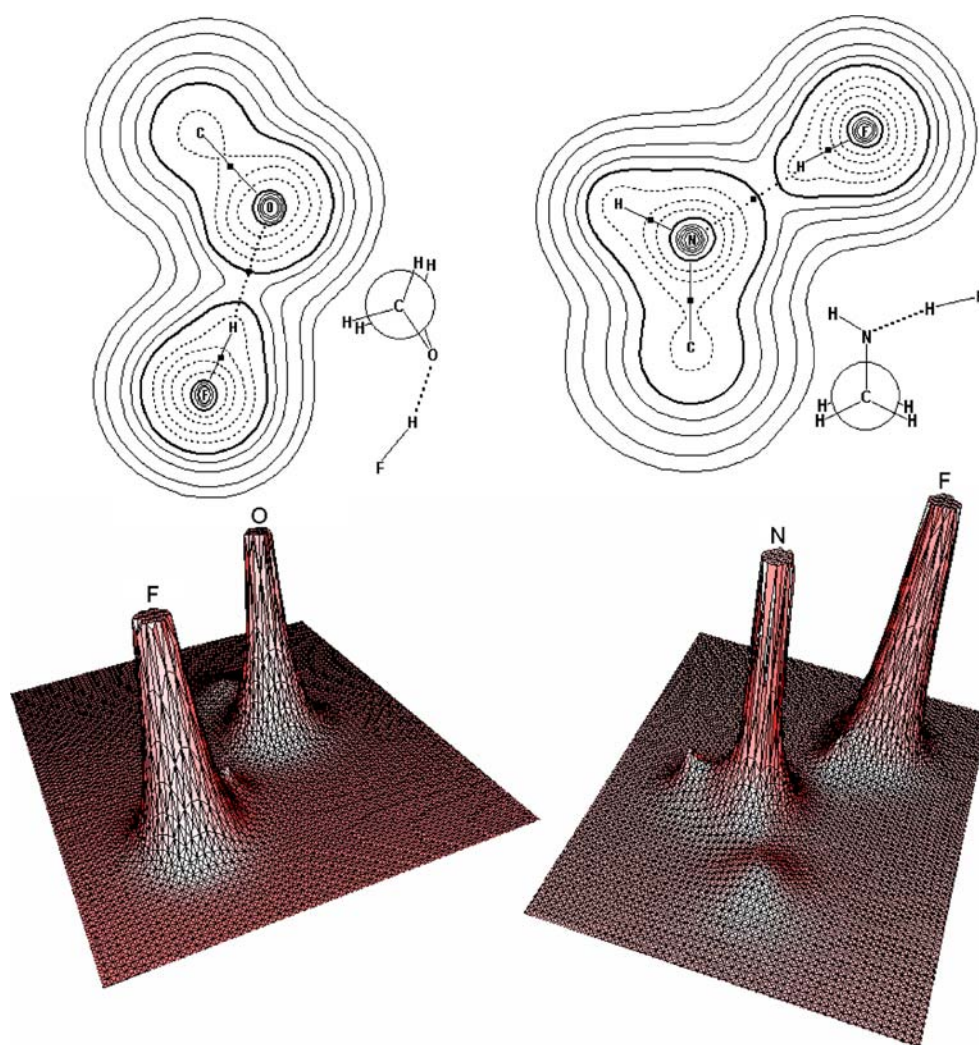
#### Concentration of charge density on heterocyclic hydrogen-bonded complexes

Table 4 also shows the topological parameters of HF. As can be clearly seen in the relief maps (3-D) and contour line plots (2-D) graphically illustrated in Fig. 3, the electron density in HF is higher than that of the  $n\cdots H$  hydrogen bonds. Due the accumulated concentration of electron density, the HF covalent bond was characterized by AIM postulates as a shared interaction by means of the Laplacian values of  $-2.432 e/a_0^5$  and  $-2.110 e/a_0^5$  on the  $C_2H_4O\cdots HF$  and  $C_2H_5N\cdots HF$  heterocyclic hydrogen-bonded complexes, respectively. As observed in the analysis of structural parameters and vibrational modes, the formation of the  $C_2H_4O\cdots HF$  and  $C_2H_5N\cdots HF$  heterocyclic hydrogen-bonded complexes causes a significant deformation of the molecular properties of the isolated molecules, principally

**Fig. 2** Bond paths and bond critical points (BCP) of the  $C_2H_4O\cdots HF$  and  $C_2H_5N\cdots HF$  heterocyclic hydrogen-bonded complexes obtained through quantum theory of atoms in molecules (QTAIM) integrations. BCP are represented by the *smallest spheres*



**Fig. 3** Representation of relief maps (3-D) and contour line plots (2-D) of the electron density of the  $C_2H_4O \cdots HF$  and  $C_2H_5N \cdots HF$  heterocyclic hydrogen-bonded complexes using the QTAIM calculations. The charge concentration indicated by  $\nabla^2\rho < 0$  identifies the fluorine atoms of the HF acid. In contrast,  $\nabla^2\rho > 0$  indicates a depletion of electron density, which is represented by  $n \cdots H$  hydrogen bonds



the CY “heterobonds” of the three-membered rings. Indeed, analysis of the AIM results presented in Tables 5 and 6 shows that the electron density on the CY bond is diminished, which confirms the tendency towards strain relaxation on the  $C_2H_4O$  and  $C_2H_5N$  rings upon the formation of the heterocyclic hydrogen-bonded complexes. Moreover, an increase in the Laplacian values for the CO and CN bonds can be observed, which is similar to the electron density results discussed above. For instance, the  $\nabla^2\rho_{CY}$  values of  $-0.358 e/a_0^5$  and  $-0.467 e/a_0^5$  for isolated three-membered rings ( $C_2H_4O$  and  $C_2H_5N$ ) are more negative compared with  $-0.294 e/a_0^5$  and  $-0.456 e/a_0^5$  when the respective  $C_2H_4O \cdots HF$  and  $C_2H_5N \cdots HF$  heterocyclic hydrogen-bonded complexes are formed.

## Conclusions

Based on B3LYP/6-311++G(d,p) calculations, it has been demonstrated that  $C_2H_4O \cdots HF$  and  $C_2H_5N \cdots HF$  heterocyclic

complexes are more strongly bound than the  $C_3H_6 \cdots HF$  homocyclic complex. The chemistry of the  $C_2H_4O$  and  $C_2H_5N$  monomers was discussed by focusing on the relaxation of these strained rings, which was described using rupture trends on the CY “heterobonds”. Furthermore, a detailed investigation on HF was carried out, from which some interesting results were obtained, such as the increase in the length of the rHF bond, variation in  $\rho_{HF}$  electron density quantified using QTAIM calculations, and vibrational red-shift effects. In addition, an exploratory investigation based on QTAIM topology was performed for the purpose of identifying the maximum and minimum electron density and Laplacian shapes. It was demonstrated that heterocyclic complexes have a greater concentration of intermolecular charge density, which is in accord with the higher values of interaction energies. Although formation of an  $F \cdots H_\alpha$  secondary interaction between the fluoride of HF acid and the  $H_\alpha$  atoms of the  $C_2H_4O$  and  $C_2H_5N$  rings was previously indicated by FTMS analysis, our results did not confirm the existence of  $F \cdots H_\alpha$  because no connection between the F



and  $H_{\alpha}$  atoms was identified using QTAIM calculations. To corroborate this result, it is very important to point out that this secondary interaction was not possible because the R ( $F \cdots H_{\alpha}$ ) distances are longer than the van der Waals radii. Finally, the main conclusion of this study is that  $C_2H_4O \cdots HF$  and  $C_2H_5N \cdots HF$  heterocyclic complexes are stabilized by only one hydrogen bond,  $n \cdots H$ , which is formed by the interaction between the n-lone pairs of oxygen and nitrogen atoms and the HF molecule.

**Acknowledgments** Thanks to Brazilian funding agencies CAPES and CNPq.

## References

- Larsen RW, Suhm MA (2006) *J Chem Phys* 125:154314–154319 doi:10.1063/1.2358349
- Smallwood CJ, McAllister MA (1997) *J Am Chem Soc* 119:11277–11281 doi:10.1021/ja972517p
- Grabowski SJ (2001) *J Mol Struct* 562:137–143 doi:10.1016/S0022-2860(00)00863-2
- Oliveira BG, Araújo RCMU, Carvalho AB, Ramos MN, Hernandez MZ, Cavalcante KR (2007) *J Mol Struct THEOCHEM* 802:91–97 doi:10.1016/j.theochem.2006.09.002
- Hobza P, Sponer J (1999) *Chem Rev* 99:3247–3276 doi:10.1021/cr9800255
- Delanoye SN, Herrebout WA, van der Veken B (2002) *J Am Chem Soc* 124:11854–11855 doi:10.1021/ja027610e
- Suenram RD, Grabow JU, Zuban A, Leonov I (1999) *Rev Sci Instrum* 70:2127–2135 doi:10.1063/1.1149725
- Legon AC, Aldrich PD, Flygare WH (1981) *J Chem Phys* 75:625–630 doi:10.1063/1.442079
- Legon AC, Aldrich PD, Flygare WH (1982) *J Am Chem Soc* 104:1486–1490 doi:10.1021/ja00370a007
- Cole GC, Legon AC (2004) *Chem Phys Lett* 400:419–424 doi:10.1016/j.cplett.2004.10.138
- Araújo RCMU, da Silva JBP, Ramos MN (1995) *Spectrochim Acta [A]* 51:821–830 doi:10.1016/0584-8539(94)00194-G
- Araújo RCMU, Ramos MN (1996) *J Mol Struct THEOCHEM* 366:233–240 doi:10.1016/0166-1280(96)04536-8
- Araújo RCMU, Ramos MN (1998) *J Braz Chem Soc* 9:499–505
- Silva JBP, Silva MR Jr, Ramos MN (2005) *J Braz Chem Soc* 16:844–850
- Oliveira BG, Araújo RCMU (2007) *Quim Nova* 30:791–796
- Rozas I, Alkorta I, Elguero J (1997) *J Phys Chem A* 101:9457–9463 doi:10.1021/jp971893t
- Zhang Y-H, Hao J-K, Wang X, Zhou W, Tang T-H (1998) *J Mol Struct THEOCHEM* 455:85–99 doi:10.1016/S0166-1280(98)00247-4
- Oliveira BG, Santos ECS, Duarte EM, Araújo RCMU, Ramos MN, Carvalho AB (2004) *Spectrochim Acta [A]* 60:1883–1887 doi:10.1016/j.saa.2003.10.006
- Oliveira BG, Duarte EM, Araújo RCMU, Ramos MN, Carvalho AB (2005) *Spectrochim Acta [A]* 61:491–494 doi:10.1016/j.saa.2004.04.023
- Oliveira BG, Araújo RCMU, Carvalho AB, Ramos MN (2007) *Spectrochim Acta [A]* 68:626–631 doi:10.1016/j.saa.2006.12.038
- Cremer D, Kraka E (1985) *J Am Chem Soc* 107:3800–3810 doi:10.1021/ja00299a009
- Greenberg A, Liebman JF (1978) *Strained organic compounds*. Academic, New York
- Castaneda JP, Denisov GS, Kucherov SY, Schreiber VM, Shurukhina AV (2003) *J Mol Struct* 660:25–40 doi:10.1016/j.molstruc.2003.07.010
- Chandra AK, Minh TN, Uchimaru T, Zeegers-Huyskens T (2000) *J Mol Struct* 555:61–66 doi:10.1016/S0022-2860(00)00587-1
- Dimitrova Y (1999) *Rec Res Dev Phys Chem* 3:133–148
- Tretiak S, Mukamel S (2002) *Chem Rev* 102:3171–3212 doi:10.1021/cr0101252
- Bredas JL, Beljonne D, Coropceanu V, Cornil J (2004) *Chem Rev* 104:4971–5004 doi:10.1021/cr040084k
- Rubtsov IV, Redmore NP, Hochstrasser RM, Therien MJ (2004) *J Am Chem Soc* 126:2684–2685 doi:10.1021/ja0305499
- Bredenbeck J, Helbing J, Hamm P (2004) *J Am Chem Soc* 126:990–991 doi:10.1021/ja0380190
- Sun MT, Chen YH, Song P, Ma FC (2005) *Chem Phys Lett* 413:110–117 doi:10.1016/j.cplett.2005.07.070
- Sun D, Fang J, Yu G, Ma F (2007) *J Mol Struct THEOCHEM* 806:105–112 doi:10.1016/j.theochem.2006.11.015
- Reed AE, Curtiss LA, Weinhold F (1988) *Chem Rev* 88:899–926 doi:10.1021/cr00088a005
- Bader RFW (1991) *Chem Rev* 91:893–928 doi:10.1021/cr00005a013
- Bader RFW (1990) *Atoms in molecules. A quantum theory*. Clarendon, Oxford, UK
- Popelier PLA (2000) *Coord Chem Rev* 197:169–189 doi:10.1016/S0010-8545(99)00189-7
- Oliveira BG, Pereira FS, Araújo RCMU, Ramos MN (2006) *Chem Phys Lett* 427:181–184 doi:10.1016/j.cplett.2006.06.019
- Oliveira BG, Vasconcelos MLAA (2006) *J Mol Struct THEOCHEM* 774:83–88 doi:10.1016/j.theochem.2006.06.018
- Oliveira BG, Araújo RCMU, Carvalho AB, Lima EF, Silva WL, Ramos MN, Tavares AM (2006) *J Mol Struct THEOCHEM* 775:39–45 doi:10.1016/j.theochem.2006.06.028
- Bader RFW, MacDougall PJ, Lau CD (1984) *J Am Chem Soc* 106:1594–1605 doi:10.1021/ja00318a009
- Bader RFW (1980) *J Chem Phys* 73:2871–2883 doi:10.1063/1.440457
- Bone RGA, Bader RFW (1996) *J Phys Chem* 100:10892–10911 doi:10.1021/jp953512m
- Hohenberg P, Kohn W (1964) *Phys Rev B* 136:864–871 doi:10.1103/PhysRev.136.B864
- Kohn W, Sham LJ (1965) *Phys Rev A* 140:1133–1138 doi:10.1103/PhysRev.140.A1133
- Becke AD (1997) *J Chem Phys* 107:8554–8560 doi:10.1063/1.475007
- Becke AD (1993) *J Chem Phys* 98:5648–5652 doi:10.1063/1.464913
- Lee C, Yang W, Parr RG (1988) *Phys Rev B* 37:785–789 doi:10.1103/PhysRevB.37.785
- Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA Jr, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Rega N, Salvador P, Dannenberg JJ, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA (1998) *GAUSSIAN 98W (Revision A.1)*. Gaussian, Pittsburgh PA



48. Cioslowski J (1992) Chem Phys Lett 194:73–78 doi:10.1016/0009-2614(92)85745-V
49. Cioslowski J (1992) Chem Phys Lett 219:151–154 doi:10.1016/S0009-2614(94)87001-2
50. Cioslowski J, Nanayakkara A, Challacombe M (1993) Chem Phys Lett 203:137–142 doi:10.1016/0009-2614(93)85377-Z
51. AIM (2000) 1.0 program designed by Biegler-König F, University of Applied Sciences. Bielefeld, Germany
52. van Duijneveldt FB, Murrell JN (1967) J Chem Phys 46:1759–1767 doi:10.1063/1.1840932
53. McQuarrie DA (1973) Statistical thermodynamics. Harper and Row, New York
54. Boys SB, Bernardi F (1970) Mol Phys 19:553–566 doi:10.1080/00268977000101561
55. Legon AC, Kisiel Z, Georgiou AS, Millen DJ (1989) Chem Phys Lett 155:447–454 doi:10.1016/0009-2614(89)87184-2
56. Oliveira BG, Araújo RCMU, Carvalho AB, Ramos MN (2007) J Theor Comp Chem 6:647–660
57. Pauling L (1960) The nature of the chemical bond, 3rd edn. Cornell University, New York
58. Lord RC, Nolin B (1956) J Chem Phys 24:656–658 doi:10.1063/1.1742592
59. Shagidullin RR, Grechkin NP (1969) Chem Heter Comp 3:232–235 doi:10.1007/BF01172558
60. Dudev T, Lim C (1998) J Am Chem Soc 120:4450–4458 doi:10.1021/ja973895x
61. Prichard DG, Nandi RN, Muentzer JS (1988) J Chem Phys 89:115–123 doi:10.1063/1.455513
62. Bishop DM, Cheung LM (1982) J Phys Chem Ref Data 11:119–133
63. Carbó R, Klobukowski M (1990) Self consistent field: theory and applications. Elsevier, Amsterdam
64. Stryer L (1995) Biochemistry. Freeman, New York
65. Koch U, Popelier PLA (1995) J Phys Chem 99:9747–9754 doi:10.1021/j100024a016
66. Grabowski SJ (2004) J Phys Chem A 108:1806–1812 doi:10.1021/jp036770p
67. Grabowski SJ, Sokalski WA, Leszczynski J (2006) Chem Phys Lett 432:33–39 doi:10.1016/j.cplett.2006.10.069
68. Grabowski SJ (2007) Chem Phys Lett 436:63–67 doi:10.1016/j.cplett.2007.01.041
69. Grabowski SJ (2007) J Phys Chem A 111:13537–13543 doi:10.1021/jp076990t
70. Grabowski SJ (2007) J Phys Chem A 111:3387–3393 doi:10.1021/jp070530i
71. Oliveira BG, Araújo RCMU, Chagas FC, Carvalho AB, Ramos MN (2008) J Mol Model 14:949–955 doi:10.1007/s00894-008-0337-5
72. Oliveira BG (2007) J Arg Chem Soc 95:59–69
73. Oliveira BG, Araújo RCMU, Pereira FS, Lima EF, Silva WL, Carvalho AB, Ramos MN (2008) Quim Nova (in press)
74. Oliveira BG, Araújo RCMU, Carvalho AB, Ramos MN (2007) Quim Nova 30:1167–1170