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Inter- and intramolecular hydrogen bonds – Structures of 1-methylpyrrole-2-carboxamide and 1-hydroxypyrrole-2-carboxamide

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This paper is dedicated to Professor Lucjan Sobczyk on the occasion of his 80th birthday

Abstract

The structures of 1-methylpyrrole-2-carboxamide (MPCA) and 1-hydroxypyrrole-2-carboxamide (HPCA) are analyzed, for both structures B3LYP/6-311++G(d,p) calculations were performed on *s-cis* and *s-trans* conformations and on monomeric and dimeric forms of these conformers. N–H···O hydrogen bonds exist for dimers. The X-ray crystal structure of MPCA is also analyzed; centrosymmetric dimers of *syn* conformers connected through N–H···O hydrogen bonds exist in crystal structure as well as C–H···O intramolecular interactions possessing some of characteristics typical for hydrogen bond.

Keywords: Hydrogen bonding; AIM theory; Critical points; Carbonyl group; Pyrrole derivatives; Binding energy

1. Introduction

It is well known that hydrogen bonds are among interactions which are mostly responsible for the arrangement of molecules in crystals [1–4]. Different H-bonded motifs are known, they were systemized and classified; the classification of Etter [5,6] is very well known but also the other classifications are often applied, as for example that one with a synthon term as a type of the motif with H-bond interaction included [7].

Etter also classified the importance of different hydrogen bonds [5] and she stated that in crystal structures the existence of intramolecular six-membered ring H-bonds is preferred and that after the creation of such rings in crystals the other intermolecular hydrogen bonds are formed, mostly between ''good proton donors'' and ''good proton acceptors''. The latter terms were introduced by Donohue [8] and briefly speaking they correspond to the most acidic and basic groups, respectively; since H-bond may be treated as the Bronsted acid–Bronsted base interaction [9,10].

It is also worth mentioning that hydrogen bonds may strongly influence on geometries of molecules, mainly on the terminal groups of atoms participating in these interactions [3,4]. The elongation of the proton donating bond as an effect of complexation is mostly observed [11] (so-called blue shifting hydrogen bonds are an exception [12]), but also the influence on the proton acceptor is detected [11]. In the latter case one can mention the elongation of C=O carbonyl group [13] as well as the changes of methoxy groups if H-bonds are formed [14].

Numerous studies on the structures for which the mentioned above effects are observed were performed very recently. One can mention investigations on pyrrole derivatives' structures. Pyrrole 2-carboxylic acid (PCA) [15] possesses the proton donating and proton accepting COOH

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carboxylic group as well as the N–H proton donating bond. And really, all of them are involved in hydrogen bond interactions in the crystal structure of PCA where the centrosymmetric dimers are formed with two equivalent O–H···O bonds between carboxylic groups as well as N–H···O bonds between N–H pyrrole ring and C=O carboxyl group, the C–H···O interactions also exist [16]. Hence, according to the Etter grafs' designations [5], following H-bond motifs were detected for the crystal structure of PCA: $R_2^2(8)$ and $R_2^2(10)$. Similarly, for the crystal structure of pyrrole-2-carboxamide (PyCa) [17] the same H-bond motifs exist. For both crystal structures mentioned here (PCA and PyCa) H-bonds attributed to $R_2^2(8)$ motifs may be classified as intermolecular resonance assisted hydrogen bonds [18] since the strength of these interactions is enhanced owing to the π-electron delocalization [19]. Very recently the crystal structure of 1-methylpyrrol-2-yl trichloromethyl ketone (PTK) was reported [20] for which only one typical proton accepting carbonyl group exists and there are not typical proton donors. As an effect of that only one type of hydrogen bond exists – C–H···O. One can see that because of the lack of typical proton donating bonds the C–H bond of pyrrole ring acts as the proton donor. Additionally for the latter crystal structure of PTK the C–Cl···O halogen bonds are formed. For these interactions C–Cl bonds act as Lewis acids [21–23]. One can see that for all of the mentioned above crystal structures being the pyrrole derivatives there is the crucial role of the carbonyl group influencing the arrangement of molecules in crystals.

The aim of this study is to analyze the crystal structure of 1-methylpyrrole-2-carboxamide (MPCA) since it belongs the series of structures mentioned above possessing the C=O proton acceptor centre. Additionally DFT calculations for the monomers and dimers of MPCA were performed as well as for analogous systems of 1-hydroxypyrrole-2-carboxamide (HPCA). The QTAIM (Quantum Theory of "Atoms in Molecules") [24,25] was applied for these systems to deepen the characteristics of H-bond interactions.

2. Experimental

2.1. General methods

Melting point was measured on Büchi B-540 apparatus. NMR spectra were recorded with the Bruker AC 200F (200 MHz) spectrometer using DMSO solution with TMS as an internal standard. Infrared spectra were recorded on Nicolet Magna-IR 550 Series II as a KBr pellets. All solvents were dried and freshly distilled prior to use.

2.2. Synthesis of the 1-methylpyrrole-2-carboxamide

Synthesis of MPCA proceeding according to the description given by Israel [26]. One gram (0.007 mol) methyl 1-methylpyrrole-2-carboxylate was dissolved in 50 ml of concentrated NH_4OH. The reaction mixture was stirred 48 h at room temperature and the product was extracted twice with ether. The extract was dried over $MgSO_4$ and solvent was evaporated in vacuo. Crude product was purified by crystallization from hexane to give 0.4 g (0.003 mol) of crystal 1-methylpyrrole-2-carboxamide (MPCA).

Mp 95 °C (decomposition).

IR (KBr, $\bar{\nu}$ cm^{-1}): 3378, 3183, 2951, 1639, 1605, 1529, 1285, 729, 606, 512.

^{1}H NMR (DMSO) δ ppm: 6.86 (1H, m, Ar-H); 6.78 (1H, m, Ar-H); 5.98 (1H, m, Ar-H); 3.82 (3H, s, NCH_3).

^{13}C NMR (DMSO) δ ppm: 163.2 (C=O); 127.85 (CH); 125.28 (C); 113.06 (CH); 106.53 (CH); 36.25 (CH_3).

2.3. X-ray measurements

Colorless, needle crystal of 1-methylpyrrole-2-carboxamide (MPCA), mounted on glass fiber, was used for diffraction measurement. The data were collected on a STOE IPDS imaging plate single crystal diffractometer [27] with low temperature device, using MoK_α source and a graphite monochromator. Data reduction was performed with the STOE IPDS-software package [27]. The Lorentz and polarization corrections were applied. Cell parameters were determined by indexing of 8000 reflections with $I/\sigma(I) > 6.0$.

The structure was solved by direct methods using SIR-97 [28] and refined by full-matrix least-squares methods on F^2 using SHELXL97 [29]. All nonhydrogen atoms were refined with anisotropic thermal displacement parameters. Hydrogen atoms were located geometrically using AFIX in SHELXL97 [29]. At the final stage of structure refinement H atoms attached to non-carbon atoms (H211 and H212) were fully refined with isotropic thermal displacements. Molecular geometries were calculated by PARST [30]. Graphical presentation of molecules was performed using PLATON [31]. The crystal data and details of the X-ray analysis are given in Table 1. Table 2 presents the selected geometrical parameters of MPCA. Fig. 1 shows the molecular structure of MPCA with the designations of atoms used in further tables and discussions, Fig. 2 shows the part of the crystal lattice of MPCA where H-bonds are visible. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre (Deposition No.: CCDC 637873).

2.4. Computational details

The calculations have been carried out using the Gaussian03 set of codes [32]. The B3LYP method is applied; this method is a hybrid density functional theory approach which combines Becke's three-parameter nonlocal exchange potential with the nonlocal correlation functional of Lee, Yang and Parr [33]. The inclusion of diffuse components in the basis set is desired to describe properly the hydrogen

Table 1
Crystallographic data and structure refinement

Formula	$C_6H_8N_2O$
M_w	124.14
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	9.791(8)
b (Å)	4.858(3)
c (Å)	14.004(13)
β (deg)	107.96(10)
V (Å^3)	633.6(9)
Z	4
D_x (g cm^{-3})	1.301
μ (mm^{-1})	0.092
T (K)	173(1)
λ (Å)	0.71073
Index ranges	$-11 \leqslant h \leqslant 11$ $-5 \leqslant k \leqslant 5$ $-17 \leqslant l \leqslant 17$
No. of data collected	5375
No. of unique data	1199
R_{int}	0.0365
No. of $I > 2\sigma(I)$ data	980
No. of parameters	90
R_1 (all data)	0.0493
wR_2 (all data)	0.1075
R_1 [$I > 2\sigma(I)$]	0.0402
wR_2 [$I > 2\sigma(I)$]	0.1034
$\Delta\rho_{min}$ (eÅ^{-3})	−0.164
$\Delta\rho_{max}$ (eÅ^{-3})	0.218

Table 2
Selected geometric parameters for 1-methylpyrrole-2-carboxamide (MPCA) [Å, °]

N1–C2	1.384(2)
N1–C5	1.364(2)
N1–C11	1.459(2)
N21–C21	1.345(2)
O21–C21	1.242(2)
C2–C21–O21	122.7(2)
C2–C21–N21	115.4(2)
N21–C21–O21	121.9(2)
C2–N1–C5	108.2(2)
N1–C2–C21	123.3(2)
C4–C5–N1–C11	176.2(2)
C3–C2–C21–O21	152.9(2)
C3–C2–C21–N21	−25.9(2)
C2–C3–C4–C5	−0.5(2)
C3–C4–C5–N1	1.0(2)

bonding interaction thus the 6-311++G** basis set [34] was applied for calculations since H-bonded systems were considered here. In other words the B3LYP/6-311++G** level of theory was applied for all calculations performed here. The wave functions obtained within this level of approximation were further applied for the calculations performed with the use of AIM2000 program [35]. This program allows to determine topological parameters based on the Bader theory. Hence critical points (CPs) were localized and their properties such as electron densities at CPs and their Laplacians were analysed.

In this study two conformations of 1-methylpyrrole-2-carboxamide are analyzed, *s-cis* conformer where C=O

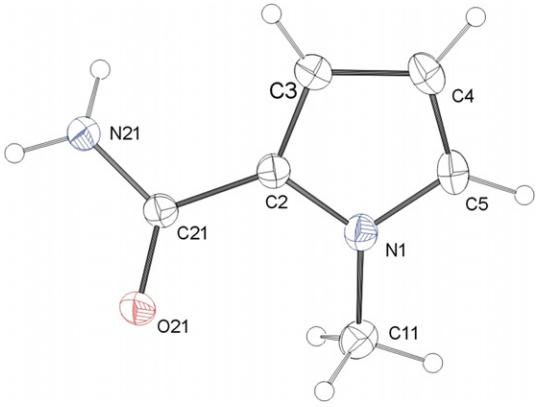

Fig. 1. Drawing of MPCA molecule with atom labeling scheme. Displacement ellipsoids of non-hydrogen atoms are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.

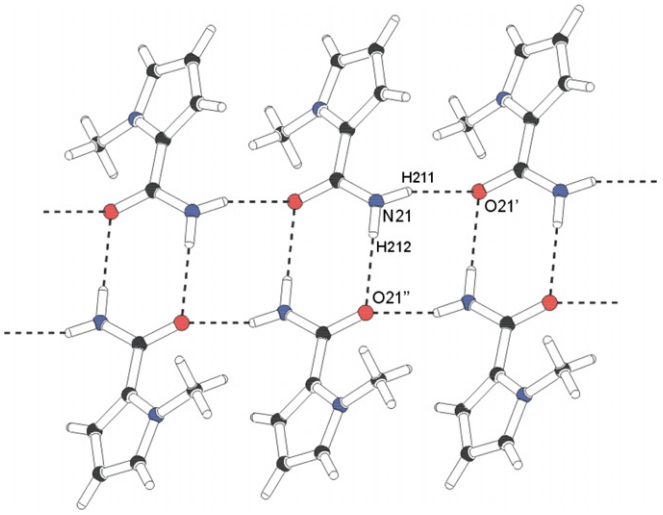

Fig. 2. Network of intermolecular contacts in the crystal structure of MPCA. N–H···O interactions are shown with dotted lines. Non-hydrogen atoms are drawn as spheres of arbitrary radii: black corresponds to carbon, red – to oxygen, blue – to nitrogen. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

carbonyl group lies at the same side of N–CH_3 of pyrrole ring and *s-trans* where these groups are at the opposite sides of molecule. It is worth to mention that for the crystal structure of pyrrole-2-carboxylic acid (PCA) [16] analyzed previously the *s-cis* conformation exists, the same *s-cis* conformer is observed for pyrrole-2-carboxamide crystal structure [17]. The crystal structure results presented here for 1-methylpyrrole-2-carboxamide (MPCA) also show the existence of that conformation.

The B3LYP/6-311++G** calculations on dimers of both conformers of MPCA were carried out here. These are centrosymmetric dimers connected through equivalent N–H···O hydrogen bonds. Fig. 3 presents the molecular graphs for both kinds of dimers of MPCA. Since for monomeric and dimeric forms of *s-cis* conformation of MPCA a weak C–H···O intramolecular hydrogen bond may exist

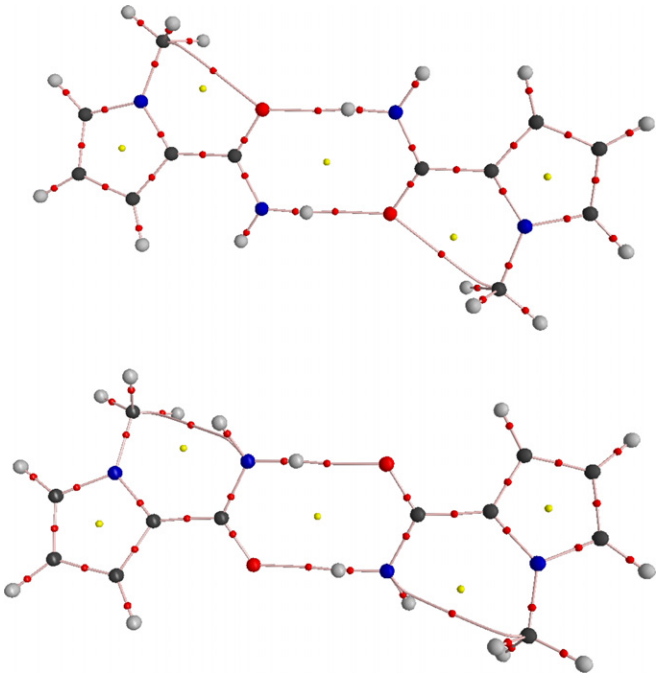

Fig. 3. Molecular graphs of dimers of *s-syn* and *s-trans* conformers of MPCA, big circles designate attractors attributed to the positions of nuclei while small circles designate critical points, bond paths are also shown.

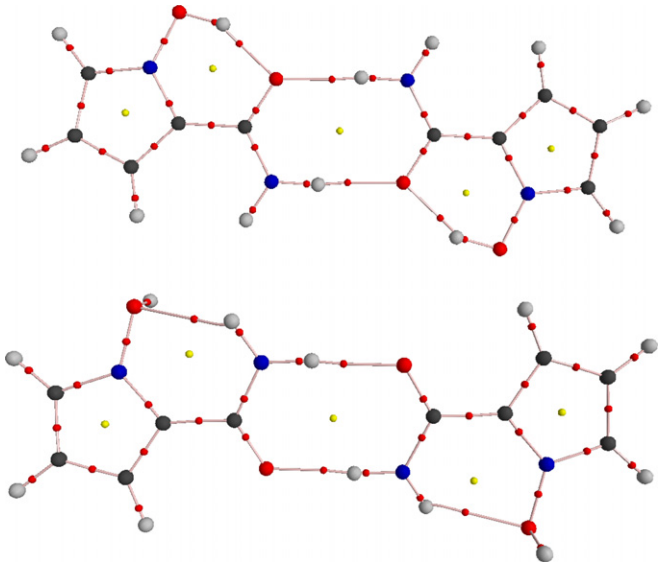

Fig. 4. Molecular graphs of dimers of *s-syn* and *s-trans* conformers of HPCA, big circles designate attractors attributed to the positions of nuclei while small circles designate critical points, bond paths are also shown.

thus analogeous calculations were carried out on 1-hydroxypyrrole-2-carboxamide (HPCA). The latter system was chosen since in such a case the stronger than C–H···O interactions may exist, these are O–H···O bonds. For HPCA the analogous calculations as for MPCA were performed here. These are calculations on *s-cis* and *s-trans* conformers, in the former case the OH hydroxyl group is placed at the same side as C=O group, the calculations on the corresponding centrosymmetric dimers of HPCA were also carried out here. Fig. 4 shows the molecular graphs for both dimers of HPCA.

It is worth mentioning that all systems considered here correspond to energy minima since no imaginary frequencies were observed. That is observed even for dimers where symmetry constraints were applied connected with the existence of the inversion centre between interacting MPCA and HPCA molecules. The calculations of binding energies were performed to take into account the deformation of molecules as a result of complexation [36] as well as to include the BSSE correction according to Boys and Bernardi [37].

3. Results and discussion

3.1. Crystal structure

Fig. 2 shows the arrangement of molecules in crystals of MPCA, there are $R_2^2(8)$ H-bonded motifs with two N–H···O hydrogen bonds equivalent owing to the symmetry constraints. Such motifs are also observed for PCA and PyCa crystal structures and are very common for the crystal structures of carboxylic acids as well as of amides. The geometrical parameters of that N–H···O hydrogen bond (N21-H212···O21″) are given in Table 3, the N···O distance is equal to 2.982 Å and the system is close to the linearity since the N–H···O angle is equal to 168.0°. The analogous distance for the PyCa crystal structure is equal to 2.987 Å and the N–H···O angle amounts to 145.8°; for the crystal structure of PCA the O–H···O H-bonds exist with O···O distance of 2.647 Å, less than N···O distances mentioned above. Additionally, O–H···O angle amounts to 176.3°, this is closer to the linearity than N–H···O bridges are. It is well known that generally homonuclear O–H···O hydrogen bonds are stronger than heteronuclear N–H···O ones, and as a consequence the former ones have shorter H···O distances. For example, this is observed for O–H···O and N–H···O hydrogen bonds of carboxylic acids and amides, respectively. It was stated that these H-bonds in carboxylic acids and amides may be classified as intermolecular resonance assisted hydrogen bonds [18]. The detailed analysis of these interactions was performed [38] and it was found that for carboxylic acids the electrostatic interaction energy term is the most important attractive one. This is in line with the postulate of Pauling who stated that H-bonds are mostly electrostatic interactions [39]. However the other attractive term, delocalization interaction energy, is more important for carboxylic acids than for amides [38]. It is worth mentioning that delocalization seems to be attributed to stronger, covalent or partially covalent in nature, hydrogen bonds [40] and that the ratio of electrostatic to delocalization energies decreases if the strength of H-bond increases [41].

For the MPCA structure analyzed here the C=O carbonyl group takes part in the other N–H···O interaction (N21-H211···O21′, Fig. 2 and Table 3) with the N···O distance equal to 2.944 Å and an angle of 157.0° (Table

Table 3
The possible hydrogen bonds (distances in Å, angles in degrees)

X–H···Y	X–H	H···Y	X···Y	∠X–H···Y	Symmetry
N21–H211···O21′	0.88(2)	2.11(2)	2.944(3)	157(2)	$x, -1+y, z$
N21–H212···O21″	0.89(2)	2.11(2)	2.982(3)	168(2)	$-x, 1-y, -z$
C11–H112···O21[a]	0.98	2.56	2.959(3)	104.0	–

[a] Intramolecular contact.

3). The similar extra N–H···O interactions exist in the crystal structure of PyCa. Hence one may say that in both crystal structures, MPCA and PyCa, the carbonyl group participates at least in two hydrogen bonds – this is so-called acceptor bifurcated hydrogen bond according to the terminology introduced by Desiraju and Steiner [3]. Thus there is an additional $R_4^2(8)$ motif for MPCA and PyCa crystal structures where subscript designates the number of the proton donating bonds while superscript the number of acceptors. One can see that for MPCA there is an extra intramolecular C–H···O interaction within the H112–C11–N1–C2–C21–O21 ring (Fig. 1) designated in terms of the graphs' nomenclature as S(6). The parameters of C–H···O system are presented in Table 3, this interaction may be hardly classified as hydrogen bond since C–H···O angle is far from linearity and H···O distance close to the sum of the corresponding van der Waals radii.

3.2. The role of C=O group in intra- and intermolecular interactions

It is well known that H-bond formation influences on geometrical parameters of interacting molecules. Terminal groups forming H-bridge are mainly changed, however hydrogen bond also influences distant geometrical parameters [10]. The key role of carbonyl group in formation of hydrogen bonds was discussed in the previous section. Table 4 presents geometrical and topological parameters of C=O group of systems analyzed here, these systems were calculated with the use of B3LYP/6-311++G(d,p) level of approximation. Monomers and dimers of two conformations (*s-cis* and *s-trans*) of 1-methylpyrrole-2-carboxamide (MPCA) and 1-hydroxypyrrole-2-carboxamide (HPCA) are considered. It is worth mentioning, that the crystal structure of MPCA analyzed in the previous section contains dimers of *syn* conformer.

Analyzing B3LYP/6-311++G** results, if one compares the monomeric forms with the corresponding dimeric ones thus regularly for the latter the C=O bond is longer. The range of C=O bond length is within 1.221–1.259 Å. The longest C=O bond exists for the dimeric form of *syn* conformation of HPCA, for that system the carbonyl group is involved in intermolecular N–H···O interaction as well as in intramolecular O–H···O bond, two relatively strong interactions. The shortest C=O bond length of 1.221 Å is detected for monomer of *s-trans* conformer of MPCA. In the latter case carbonyl group is not involved in any type of interaction which may be classified as hydrogen bonding, C=O bond is at the same side as C–H bond of pyrrole ring, the (C–)H···O(=C) distance amounts to 2.765 Å, this means that C–H···O does not fulfil the geometrical criteria of the existence of hydrogen bonding. For the *s-cis* MPCA monomer the C=O bond length is equal to 1.227 Å. The elongation of C=O bond in comparison with *s-trans* conformer may be an effect of the existence of the intramolecular C–H···O interaction. However the geometrical parameters presented in the previous section for the crystal structure of MPCA indicate the C–H···O intramolecular contact being hardly classified as hydrogen bonding.

Fig. 3 presents molecular graphs of dimers of MPCA, for *syn* conformation there is the $CH_3\cdots O{=}C$ bond path between the C-atom of methyl group and O-atom of carbonyl group. The similar N···C bond path exists between NH_2 and CH_3 groups for *s-trans* conformer. Analogous paths are observed for the corresponding monomeric forms of both conformers. For HPCA species there are stronger

Table 4
The bond lengths (in Å) of C=O group as well as the characteristics of the corresponding BCP (in a.u.); electron density at BCP – ρ_C, its Laplacian – $\nabla^2\rho_C$, kinetic electron energy density at BCP – G_C, potential electron energy density at BCP – V_C

System	C=O	ρ_C	$\nabla^2\rho_C$	G_C	V_C
MPCA-mon. *s-syn*	1.227	0.4015	−0.3558	0.5823	−1.2536
MPCA-mon. *s-trans*	1.221	0.4062	−0.3165	0.6040	−1.2870
HPCA-mon. *s-syn*	1.244	0.3874	−0.4420	0.5261	−1.1627
HPCA-mon. *s-trans*	1.222	0.4064	−0.3381	0.5992	−1.2830
MPCA-dim. *s-syn*	1.241	0.3877	−0.4183	0.5323	−1.1691
MPCA-dim. *s-trans*	1.238	0.3911	−0.3975	0.5463	−1.1920
HPCA-dim. *s-syn*	1.259	0.3728	−0.4799	0.4807	−1.0814
HPCA-dim. *s-trans*	1.237	0.3920	−0.4081	0.5457	−1.1935

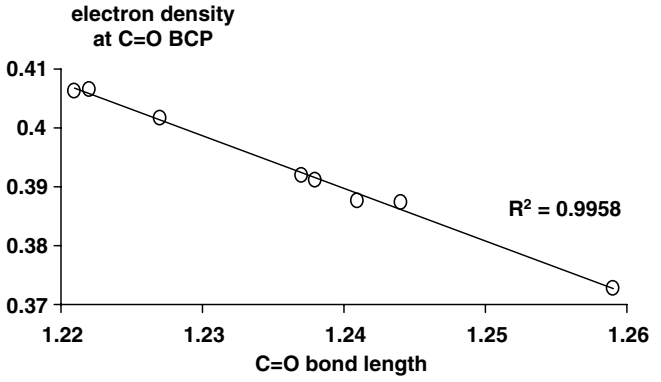

Fig. 5. The relationship between C=O bond length (in Å) and the electron density at corresponding bond critical point (in a.u.).

N–H···O and O–H···O interactions and the H···O bond paths exist in these cases (Fig. 4).

Table 4 shows changes of C=O bond length being in line with the changes of topological parameters. Fig. 5 presents the linear relationship between C=O bond length and the electron density at the corresponding bond critical point (ρ_C), the greater ρ_C corresponds to the shorter and stronger C=O bond. The other topological parameters also correlate with the C=O bond length (Fig. 6), these are: Laplacian of the electron density at C=O BCP – $\nabla^2\rho_C$, the total, kinetic and potential electron energy densities at this BCP (H_C, G_C and V_C, respectively).

3.3. The H···O contact

Table 4 shows lengths and topological characteristics of H···O contacts in intramolecular N–H···O and O–H···O H-bonds as well as such contacts of intermolecular N–H···O bonds. The parameters of intramolecular C–H···O and C–H···N interactions (Fig. 3) are not presented since these are weaker interactions which are hardly classified as hydrogen bonds if they are at all. The topological parameters of C–H···O and C–H···N interactions do not directly correspond to H···O and H···N contacts since C···O and C···N bond paths exist. The results concerning H···O contacts of all monomers and dimers are included in Table 5. One can see that the intramolecular interactions are stronger than intermolecular ones since the appropriate contacts of the former are shorter and the electron densities of corresponding BCPs are greater. Fig. 7 presents the relationship between H···O distance and the electron density at the corresponding BCP; this is not linear correlation. The correlation between bond length of C=O and the electron density at BCP analyzed in the previous section is linear (Fig. 5); however the range of C=O bond lengths is of about 0.04 Å. The range of H···O contacts presented in Fig. 7 amounts to 0.49 Å, 10 times more. It is well known that the relationship between the atom-atom distance and the electron density at corresponding BCP is generally exponential and it may be approximated as the linear relation for narrower ranges of distances. In the case of the relationship presented in Fig. 7 the power function correlation is indicated and the correlation coefficient is high ($R^2 = 0.984$), the latter value is slightly lower but still close to unity if exponential relationship is considered.

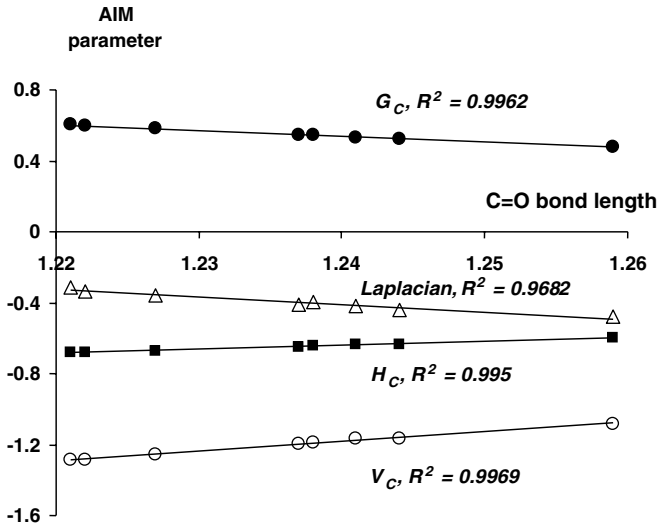

Fig. 6. The relationship between C=O bond length (in Å) and the characteristics of the corresponding bond critical point such as, Laplacian, G_C, V_C and H_C (all in a.u.).

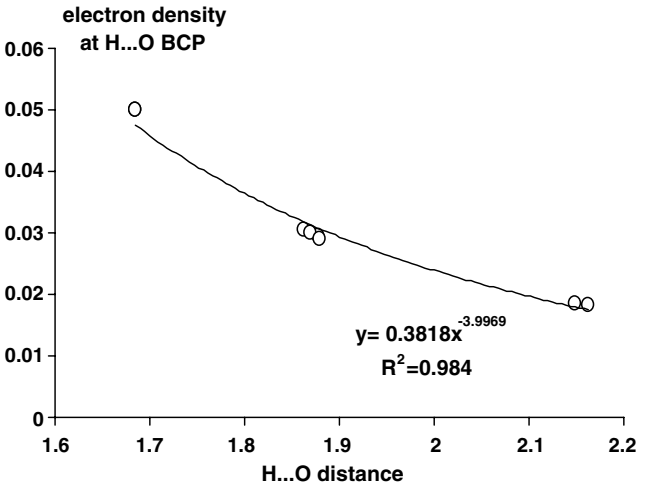

Fig. 7. The relationship between H···O distance (in Å) and the electron density at corresponding bond critical point (in a.u.).

Table 5
The H···O distance (in Å) as well as the characteristics of the corresponding BCP (in a.u.); electron density at BCP – ρ_C, its Laplacian – $\nabla^2\rho_C$, kinetic electron energy density at BCP – G_C, potential electron energy density at BCP – V_C, for bolded V_C and G_C values $|V_C| > |G_C|$, thus $H_C < 0$

System	H-bond type	O···H	ρ_C	$\nabla^2\rho_C$	G_C	V_C
HPCA-mon. *s-syn*	O–H···O intra	1.685	0.0499	0.1378	**0.0411**	**−0.0477**
HPCA-mon. *s-trans*	N-H···O intra	2.163	0.0182	0.068	0.0149	−0.0128
MPCA-dim. *s-syn*	N–H···O inter	1.878	0.0295	0.1011	0.0240	−0.0227
MPCA-dim. *s-trans*	N–H···O inter	1.863	0.0306	0.1037	0.0249	−0.0239
HPCA-dim. *s-syn*	N–H···O inter	1.879	0.0291	0.1018	0.0241	−0.0227
	O–H···O intra	1.685	0.0499	0.1401	**0.0416**	**−0.0482**
HPCA-dim. *s-trans*	N–H···O inter	1.870	0.0299	0.1026	0.0244	−0.0231
	N–H···O intra	2.149	0.0186	0.0689	0.0152	−0.0131

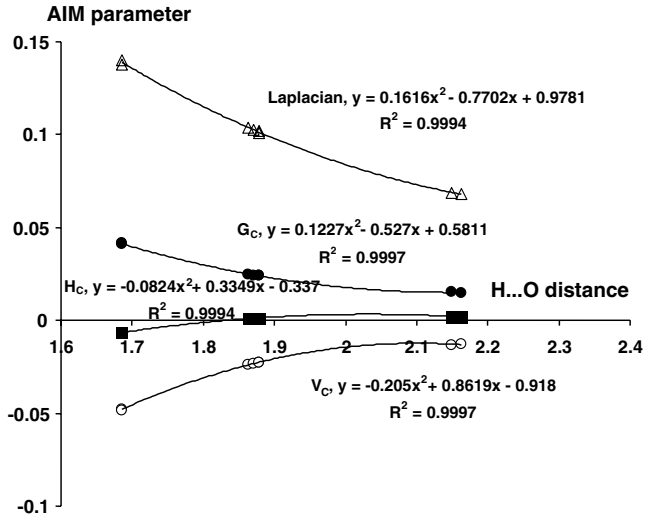

Fig. 8. The relationship between H···O distance (in Å) and the characteristics of the corresponding bond critical point such as, Laplacian, G_C, V_C and H_C (all in a.u.), different curves were fitted to show relationships.

Fig. 8 presents relationships between H···O distance and the other topological parameters. The same relations concerning C═O bond were linear (see previous section) while they are non-linear here (see Fig. 8), second order polynomials were fitted to indicate that generally monotonic non-linear relationships exist between H···O distance and any characteristic of the corresponding BCP. The explanation of such non-linearity is the same as for the correlation between H···O distance and the electron density at the corresponding BCP since the broad range of H···O distances is considered here.

The intermolecular interactions analyzed here are relatively strong, the binding energies are presented in Table 6 and they are within ⟨−11.5;−12.7⟩ kcal/mol range if the BSSE correction is included. It is worth to mention that the binding energies corresponding to *s-trans* conformers are greater (modulus of energy), thus interactions for these conformers are stronger. However *s-cis* conformers' dimers are of the lower energies than their *s-trans* counterparts. This is connected with the Leffler–Hammond postulate [42,43] that systems of stronger H-bonds are closer to transition states and hence they are of greater energies. It is worth mentioning that the binding energies of dimers analyzed here concern two symmetry equivalent N–H···O interactions. The intramolecular interactions are stronger than intermolecular ones; this is justified not only by the shorter proton-acceptor distances for intramolecular contacts but also by topological parameters.

Table 6
The binding energies (in kcal/mol) of dimers analyzed here, the energies with the BSSE corrections are also presented, the energies of systems in hartrees

System	Binding energy	Binding energy (BSSE included)	Energy of the system
HPCA – *s-syn*	−12.44	−11.75	−908.3939237
HPCA – *s-trans*	−12.93	−12.39	−908.3706538
MPCA – *s-syn*	−12.02	−11.49	−836.6471885
MPCA – *s-trans*	−13.14	−12.67	−836.6330081

It is known that for covalent bonds (shared interactions) [44,45] as well as for very strong hydrogen bonds [46] the Laplacian of the electron density for interacting pair of atoms is negative. Such negative Laplacian for H-bonds indicate their covalent character [46]. However, for strong hydrogen bonds, if Laplacian is positive but the total electron energy density at BCP (H_C) is negative thus it means that hydrogen bonding is partially covalent in nature [47]. This is in line with the following equations:

$$1/4\nabla^2\rho_C = 2G_C + V_C \quad (1)$$

$$H_C = G_C + V_C \quad (2)$$

G_C is the positive value while V_C is negative, the latter value is strongly connected with the delocalization energy of interaction and consequently with covalency. Table 5 shows that H_C values Eq. (2) are negative for intramolecular O–H···O interactions, for the remaining weaker hydrogen bonds H_C values are positive.

4. Summary

The calculations performed on the monomer and dimer structures of 1-methylpyrrole-2-carboxamide (MPCA) and 1-hydroxypyrrole-2-carboxamide (HPCA) show the existence of inter- and intramolecular interactions which may be classified as hydrogen bonds. For the proton accepting C═O carbonyl bond its length correlates with topological parameters of the corresponding bond critical point. The similar correlations are observed for H···O contact.

It was found that intramolecular O–H···O hydrogen bonds are the strongest ones and they occur in monomer and dimer of HPCA. The H_C values of BCPs of corresponding H···O interactions are negative indicating the partial covalency of these hydrogen bonds. The other interesting finding is that intra- and intermolecular hydrogen bonds of the systems analyzed here do not influence on each other. The binding energy is more influenced by the kind of conformer than by the type of compound (MPCA or HPCA), one can see this from Table 6.

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