J. Phys. Chem. A **2002,** *106,* 10613−10621 **10613**

Pyrrole-2-carboxylic Acid and Its Dimers: Molecular Structures and Vibrational Spectrum

Alina T. Dubis,[†] Sławomir J. Grabowski,*[,†,‡] Dorota B. Romanowska,[†]
Tomasz Misiaszek,[§,||] and Jerzy Leszczynski[||]

Institute of Chemistry, University of Białystok, Al. J. Piłsudskiego 11/4, 15-443 Białystok, Poland,
Department of Crystallography and Crystallochemistry, University of Łódź, ul. Pomorska 149/153,
90-236 Łódź, Poland, Institute of Physical and Theoretical Chemistry, Wrocław University of Technology,
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland, and Computational Center for Molecular Structure and
Interactions, Department of Chemistry, Jackson State University, Jackson, Mississippi 39217

Received: May 9, 2002; In Final Form: August 29, 2002

The infrared and Raman spectroscopic study of pyrrole-2-carboxylic acid (PCA) confirms the formation of the cyclic acid dimer species in the solid state. The molecular structure, vibrational frequencies, and binding energies of cyclic dimers have been also examined using the density functional theory (DFT) at the B3LYP/6-311+G(d) level. In addition, a complete vibrational assignment is proposed for the both s-cis and s-trans PCA conformers. The vibrational assignments are supported by normal coordinate calculations utilizing force constants predicted using the DFT method. The “atoms in molecules” theory of Bader is also used to characterize hydrogen bonds.

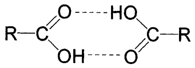
Introduction

One of the aims of crystal engineering is to understand intermolecular interactions and their role in crystal architectures.[1,2] It is well-known that hydrogen bonds play a dominant role in forming molecular networks in crystals.[3] There are a lot of reports and reviews on H-bond patterns in organic crystals.[4−6] Carboxyl groups are known as those which are often responsible for the arrangement of molecules in crystals.[7] Molecular packing modes of carboxylic acids have been studied in depth.[8,9] These studies on crystals of carboxylic acids were based on X-ray and neutron diffraction results. Carboxyl groups act as proton donors (OH bonds) and as proton acceptors (C═O bonds); hence they can form hydrogen bonds between each other as cyclic dimers or as open arrays forming, for example, catamer motifs.[8]

Sinha et al.[10] suggested that the combination of infrared and Raman spectroscopy is an ideal method to establish whether carboxylic acid molecules are hydrogen bonded as cyclic dimers or whether they form other patterns. For example, the infrared spectra of benzoic acid crystals have been demonstrated to show the coexistence of two kinds of cyclic configurations.[11] According to the Etter terminology[12] the cyclic dimers of carboxylic acids form the eight-membered ring (Chart 1) denoted as $R_2^2(8)$. This means that eight atoms (C═O···H−O−C═O···H−O) form two H-bonds usually related through the center of inversion.[8] The superscript designates the number of acceptor centers, and the subscript, the number of donors within the motif. The $R_2^2(8)$ motif often exists within crystal structures because it may be formed not only by O−H···O H-bonds but also by other bonds as well. For example, for the crystal structure of the phenazine-3,5-dinitrobenzoic acid complex the $R_2^2(8)$ motifs exist for phenazine−acid dimers connected by C−H···O and O−H···N bonds.[13]

The aim of this study is to investigate the conformations of pyrrole-2-carboxylic acid (PCA) using spectroscopic and theoretical methods. The PCA molecule contains not only a carboxyl group but also the N−H proton donating bond. Hence $R_2^2(8)$ motifs that may exist due to carboxyl groups may be replaced by other motifs owing to N−H donors; O−H···O bonds between PCA molecules may be replaced by N−H···O interactions. Such a situation is not novel in the crystal structures of organic compounds. For example, the existence of motifs containing N−H···O bonds was detected for the crystal structure of methyl 5-methyl-3,4-diphenyl-1*H*-pyrrole-2-carboxylate.[14] It is well-known that unlike the O−H···O hydrogen bonds, there are no examples of strong N−H···O bonds.[3] The experimental X-ray diffraction or neutron diffraction data support this statement because the N−H bond can be only slightly stretched by H-bond formation from 1.01 to 1.06 Å, in contrast to O−H···O systems[15] where for short H···O contacts of 1.2−1.3 Å the O−H bond length may be 1.15−1.2 Å. The elongation of the donating bond within H-bridges is often treated as a measure of H-bond strength.[16]

CHART 1: The Cyclic Dimers of Carboxylic Acids



The spectroscopic investigations of pyrrole-2-carboxylic acid have been performed earlier.[17] On the basis of vibrational spectra the possible arrangements of the molecules in crystals have been predicted. As mentioned above, the studies of PCA conformers and of the possible PCA dimers have been performed here using FT-IR and Raman spectroscopic methods, ab initio calculations, and the Bader atoms-in-molecules (AIM) theory.[18]

Experimental Section

Pyrrole-2-carboxylic acid was prepared by hydrolysis[19] of methyl pyrrole-2-carboxylate, MPC (prepared by Bailey’s method[20]). A sample of methyl pyrrole-2-carboxylate (0.8 mmol) was dissolved in 10 mL of methanol. The mixture was treated with a solution of 40 mmol of KOH in 2 mL of water and stirred overnight at 50 °C. The solution was acidified and extracted with ether. The extract was concentrated on a rotary evaporator,

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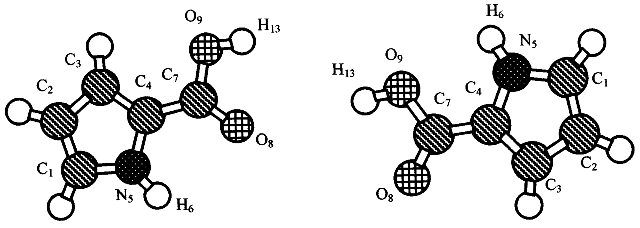
* Corresponding author. E-mail address: slagra@krysia.uni.lodz.pl.
[†] University of Białystok.
[‡] University of Łódź.
[§] Wrocław University of Technology.
[||] Jackson State University.

10.1021/jp0211786 CCC: $22.00

CHART 2: Structures of Pyrrole-2-carboxylic Acid Monomers: a) s-cis (syn) Conformer b) s-trans (anti) Conformer



and the obtained white solid was crystallized from methanol. Mp: 204−208 °C. The structure was proved by ^{1}H NMR and FT-IR spectra.

N-Methylpyrrole-2-carboxylic acid was prepared by hydrolysis of methyl *N*-methylpyrrole-2-carboxylate according to the procedure described for PCA.

The FT-IR spectra were recorded using a Nicolet Magna IR 550 Series II spectrometer. The sample was measured in CCl_4 solution (0.001M) in a KBr cell of 0.2 mm path length, as a KBr pellet and Nujol mull on KBr plates. A spectral resolution of 4 cm^{-1} was used.

The Raman spectrum was taken using a Jobin Yvone T64000 spectrograph equipped with a CCD camera cooled by liquid nitrogen as a detector. The 514.5 mn excited line of an Ar^+ laser was used. A powder sample was measured.

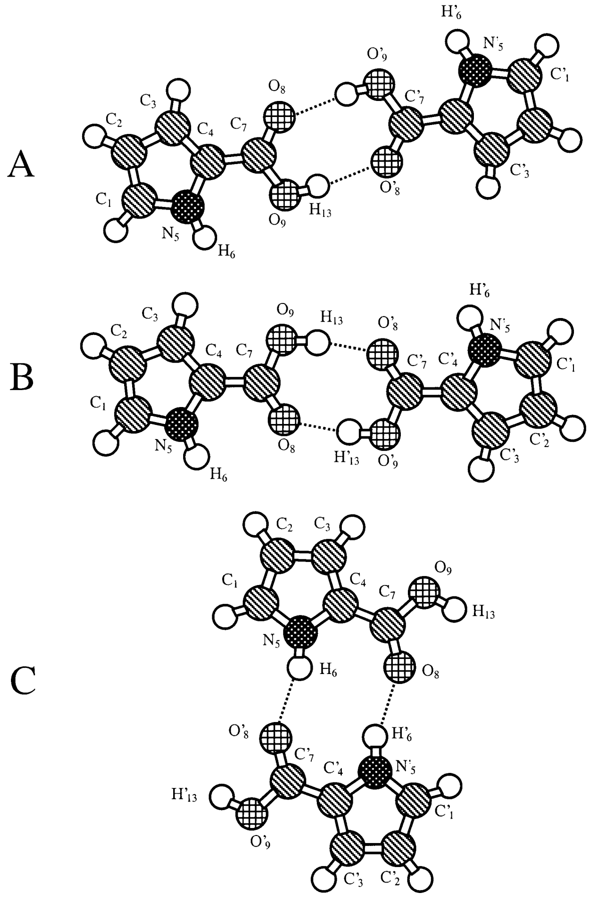
Computational Details

All DFT calculations were carried out using the Gaussian 98 program.[21] The geometry of conformers of pyrrole-2-carboxylic acid (PCA) considered in this paper (s-cis and s-trans conformers, Chart 2) has been optimized at the B3LYP/6-311+G(d) and B3LYP/6-311++G(d,p) levels of theory. The geometry optimizations have been performed for three PCA dimers (A, B, and C; Chart 3) at the B3LYP/6-311+G(d) level. However, in the case of dimers the optimizations were carried out with symmetry restrictions. The equivalence of monomers forming complexes was assumed. In other words, for each kind of dimer two associated monomers are related by the center of inversion. For the A and B dimers (Chart 3) the centers of inversion lie in the middle of the eight-membered rings and hence the centrosymmetric dimers are considered as is usual for dimers of carboxylic acids in crystals.[8] For the C dimer the center of inversion lies within a ten-membered ring.

H-bond energies were computed as the difference in energy between the complex, on one hand, and the sum of isolated monomers on the other hand. Basis set superposition error (BSSE) was corrected by the counterpoise procedure of Boys and Bernardi.[22] The IR spectra of monomers and dimers considered in this study were also calculated by applying the same codes of Gaussian 98.[21] The DFT (B3LYP) approach was used to predict the vibrational wavenumbers and intensities and the corresponding optimized geometries of the molecules. The predicted vibrational wavenumbers were scaled down by a single factor of 0.98. The aforementioned method overestimates the calculated harmonic frequencies, and for this reason, the scaling factors have been proposed in the literature to correct for anharmonicity.[23,24]

The transformation of the force field from Cartesian to internal coordinates was carried out. The internal coordinates following the UPAC recommendation[25] are given in Table 1. Such determined force constants were used to calculate the vibrational potential energy distribution (PED) among the normal coordinates.

CHART 3: Structures of the Possible Cyclic Dimers of the Pyrrole-2-carboxylic Acid



In addition, the atoms-in-molecules theory (AIM) of Bader[18] was applied for the localization of bond critical points (BCPs), which were analyzed in terms of electron densities and their Laplacians.[26]

Results and Discussion

Vibrational Spectra. The molecules of carboxylic acids usually exist as centrosymmetric dimers in crystals with the center of inversion within the eight-membered ring formed by two carboxyl groups[3,8] (Chart 1). The PCA molecule contains O—H, C═O, and N—H groups and hence may generate the formation of three types of hydrogen-bonded dimers (Chart 3). For the A and B cases the complexes are linked through two C═O···H—O bonds and for the C dimers there are two intermolecular interactions of N—H···O═C type. The last type of interaction is the so-called heterogenic association where the carboxyl group is hydrogen bonded to another functional group. For the A and B dimers there are $R_2^2(8)$ motifs containing two equivalent O—H···O hydrogen bonds[12] that are replaced by the $R_2^2(16)$ motif in the C dimer. It seems that the $R_2^2(16)$ motif is not as frequent as the $R_2^2(8)$ motif, and it is probably less stable. The C dimer could be also less stable than the A and B complexes because N—H···O bonds are not as strong as O—H···O ones.[15] This is in agreement with the spectroscopic results based on the shifts of the wavenumbers of the H-bonded O—H and N—H stretching absorption bands.[27]

The dimers considered here are of resonant type (resonance-assisted hydrogen bonds, RAHBs).[15] For dimers A and B O—

TABLE 1: Local Symmetry Coordinates of PCA (Atom Numbering as in Chart 2)

symmetry coordinate[a]	description[b]
$S_1 = r$(C1−N5)	ν_{CN}
$S_2 = r$(C1−C2)	ν_{CC}
$S_3 = r$(C2−C3)	ν_{CC}
$S_4 = r$(C3−C4)	ν_{CC}
$S_5 = r$(C4−N5)	ν_{CN}
$S_6 = r$(C4−C7)	ν_{CC}
$S_7 = r$(C7−O8)	ν_{CO}
$S_8 = r$(C7−O9)	ν_{CO}
$S_9 = r$(N5−H6)	ν_{NH}
$S_{10} = r$(O9−H13)	ν_{OH}
$S_{11} = r$(C1−H10)	ν_{CH}
$S_{12} = r$(C2−H11)	ν_{CH}
$S_{13} = r$(C3−H12)	ν_{CH}
$S_{14} = \beta$(C1−N5−H6) − β(C4−N5−H6)	δ_{NH}
$S_{15} = \beta$(N5−C1−H10) − β(C2−C1−H10)	δ_{CH}
$S_{16} = \beta$(C1−C2−H11) − β(C3−C2−H11)	δ_{CH}
$S_{17} = \beta$(C2−C3−H12) − β(C4−C3−H12)	δ_{CH}
$S_{18} = \beta$(C3−C4−C7) − β(N5−C4−C7)	δ_{CC}
$S_{19} = \beta$(O8−C7−C4) − β(O8−C7−O9)	δ_{CO}
$S_{20} = \beta$(O9−C7−C4) − β(O8−C7−O8)	δ_{CO}
$S_{21} = \beta$(H13−O9−C7)	δ_{OH}
$S_{22} = \beta$(C3−C4−N5) − 0.809β(C2−C3−C4) − 0.809β(C1−N5−C4) + 0.309β(C3−C2−C1) + 0.309β(C2−C1−N5)	δ_{ring}
$S_{23} = -1.118\beta$(C2−C3−C4) + 1.118β(C1−N5−C4) − 1.809β(C3−C2−C1) + 1.809β(C2−C1−N5)	δ_{ring}
$S_{24} = \gamma$(H6−N5−C4−C1)	γ_{CH}
$S_{25} = \gamma$(H10−C1−C2−N5)	γ_{CH}
$S_{26} = \gamma$(H11−C2−C1−C3)	γ_{CH}
$S_{27} = \gamma$(H12−C3−C2−C4)	γ_{CH}
$S_{28} = \gamma$(C7−C4−C3−N5)	γ_{CC}
$S_{29} = \gamma$(O8−C7−C4−C3)	γ_{CO}
$S_{30} = \gamma$(O9−C7−C4−C3)	γ_{CO}
$S_{31} = \gamma$(H13−C9−C7−C4)	γ_{OH}
$S_{32} = \tau$(C3−C2−C1−N5) + 0.309τ(N5−C4−C3−C2) + 0.309τ(C1−N5−C4−C3) − 0.809τ(C4−C3−C2−C1) − 0.809τ(C2−C1−N5−C4)	τ_{ring}
$S_{33} = -0.118\tau$(C2−C1−N5−C4) + 0.118τ(C4−C3−C2−C1) + 1.809τ(C1−N5−C4−C3) − 1.809τ(N5−C4−C3−C2)	τ_{ring}

[a] Normalization constants are not given here. Definitions are in terms of standard valence coordinates: r_{ij} is the bond length between atoms *i* and *j*; β_{ijk} is the valence angle between angle atoms *i*, *j*, and *k* with the *j* central atom, β_{ijkl} is the out-of plane angle between the *i*−*j* bond and the plane defined by the *j*, *k*, and *l* atoms; τ_{ijkl} is the torsion (dihedral) angle between planes defined by the *i*, *j*, *k* and *j*, *k*, *l* atoms. [b] Vibrational modes: ν, stretching; δ, bending in-plane; γ, bending out-of-plane; τ, torsion.

H···O hydrogen bonds are assisted by H13−O9−C7=O8 conjugated systems (see Chart 3) and can be called as R_1 rings [$R_2^2(8)$].[28] N−H···O hydrogen bonds of dimer C are assisted by two conjugated systems: the R_1 ring [$R_2^2(8)$] H6−N5−C4=C7−O8 and a more extended H6−N5−C1=C2−C3=C4−C7=O8 R_5 ring [$R_2^2(16)$], giving origin to a conjugated structure that can be called an (R_1+R_5) ring [$R_2^2(8)$ $R_2^2(16)$].[28] The similar intermolecular N−H···O hydrogen bonds assisted by resonance were investigated previously [28] for the crystal structures. However, the PCA or its simple derivatives were not investigated from the crystallographic point of view. The Cambridge Structural Database (CSD)[29] was searched in this study for the PCA structure and its derivative structures (all possible substituents instead of H-atoms within the pyrrole ring; only the N−H bond was kept); no entries were found.

The analysis of the observed bands in the IR and Raman spectra was supported by theoretical calculations. The frequencies and IR intensities of the s-cis and s-trans conformers of pyrrole-2-carboxylic acid were calculated; and the proposed description of bands is presented in Tables 2 and 3. Furthermore, the DFT PCA dimer frequencies are given in Table 4. The assignment of the majority of the pyrrole ring stretching and bending vibrational modes[30,31] is straightforward and therefore will not be discussed here.

Figure 1 presents the FT-IR spectra of pyrrole-2-carboxylic acid taken as a KBr pellet (curve a), Nujol mull (curve b), and diluted CCl_4 solution (curve c), displayed together to facilitate their comparison. The solubility of the PCA in nonpolar solvents is very low; however, the IR spectrum was successfully obtained.

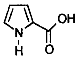
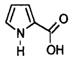
PCA shows a free ν_{NH} band at 3465 cm^{-1} in CCl_4 solution. The position of this band is exactly the same as for the s-cis conformer of methyl pyrrole-2-carboxylate (MPC). The experimental and theoretical IR studies of MPC were presented in our previous paper.[32] The theoretically estimated values of the free ν_{NH} modes are 3576 and 3593 cm^{-1} for the s-cis and s-trans PCA conformers, respectively (Table 3). The condensed phase spectrum of PCA (KBr pellet and Nujol mull) revealed strong absorptions at 3358 and 3356 cm^{-1}, respectively, attributed to the vibration of the hydrogen-bonded N−H group. The N−H out-of-plane bending mode additionally confirms involvement of the N−H group in intermolecular interactions. Solid-state spectra show an absorption band at 602 cm^{-1}, whereas dilute CCl_4 solution revealed the absence of a δ_{N-H} band of a bonded N−H group.[32]

Formation of associates causes typical changes in the vibrational frequency of the free O−H group. Even in quite dilute CCl_4 solution the PCA, as a large majority of carboxylic acids, exists essentially as a dimeric species. As a consequence, the spectrum in the condensed phase (KBr disk and Nujol mull) exhibits absorption due to the presence of the dimers. The bands at 2917, 2906, 2746, 2701, 2637, 2627, 2574, and 2515 cm^{-1} were observed. In very dilute solution only a small portion of the monomer is present, which was confirmed by a weak band of the stretching vibration of the free OH group at 3550 cm^{-1}. Another band characteristic of the dimeric acid species arises from the O−H out-of-plane deformation vibration, which appears as a broad band of intermediate intensity at 884 cm^{-1}. In the diluted solution this band is less intense.

In the spectrum of the KBr pellet ν_{CO} bands at 1685 and 1665 cm^{-1} are broad and overlapped (Figure 1a). The spectrum of the mull form also shows a broad and strong doublet at 1680 and 1661 cm^{-1} (Figure 1b) associated with the stretching vibration of a hydrogen-bonded carbonyl group. The spectrum of a diluted carbon tetrachloride solution (Figure 1c) revealed strong ν_{CO} absorption at 1671 cm^{-1}. The experimentally observed absorption of the carbonyl group can be confirmed by using DFT calculated vibrational frequencies. The lowest ν_{CO} frequency was theoretically estimated for the B dimer (Table 4). Its value of 1671 cm^{-1} is the closest to the experimental ν_{CO} frequency of 1670 cm^{-1} recorded in CCl_4 solution. Additionally, the IR spectrum of *N*-methylpyrrole-2-carboxylic acid, run as a CCl_4 solution, shows absorption of the carbonyl group at the same wavenumber, e.g., 1670 cm^{-1}, as PCA (Figure 2). It has been shown previously[33] that *N*-alkylpyrroles substituted in the α-position exist primarily in the more stable syn conformation (s-cis). Thus, in nonpolar solvents the N−H group takes no part in the hydrogen bond formation and, as a result, PCA forms a hydrogen bond via the carboxylic group. These observations indicate that in the condensed phase, the carbonyl oxygen of PCM is involved in two types of interactions B and C, whereas in tetrachloride solution the B dimer is dominant.

On the basis of the difference in wavenumbers of the acid ν_{CO} measured in the gas and crystal form, Lautié et al.[17] assumed that PCA is likely to associate in cyclic dimers. The obtained difference, around 4.5%, is close to the analogous values for

TABLE 2: Theoretical (B3LYP/6-311++G Level of Theory) Wavenumbers and IR Intensities for PCA**

								
Mode	ν^a (cm^{-1})	A (km mol^{-1})	PED^b (%)	Assignment	ν (cm^{-1})	A (km mol^{-1})	PED^b (%)	Assignment
1	3699	110.2	$S_{10}(100)$	ν_{OH}	3701	108.3	$S_{10}(100)$	ν_{OH}
2	3570	103.3	$S_9(100)$	ν_{NH}	3588	102.4	$S_9(100)$	ν_{NH}
3	3198	0.4	$S_{11}(43)$, $S_{12}(28)$, $S_{13}(28)$	ν_{CH}	3198	0.7	$S_{11}(36)$, $S_{12}(32)$, $S_{13}(31)$	ν_{CH}
4	3191	0.1	$S_{11}(39)$, $S_{13}(60)$	ν_{CH}	3190	0.0	$S_{11}(42)$, $S_{13}(57)$	ν_{CH}
5	3174	2.3	$S_{11}(17)$, $S_{12}(71)$, $S_{13}(11)$	ν_{CH}	3175	1.7	$S_{11}(21)$, $S_{12}(67)$, $S_{13}(11)$	ν_{CH}
6	1723	555.7	$S_7(77)$	ν_{CO}	1752	554.8	$S_7(80)$	ν_{CO}
7	1556	31.7	$S_2(16)$, $S_4(31)$, $S_6(10)$, $S_{14}(15)$	ν_{CC}, δ_{NH}	1561	56.6	$S_2(16)$, $S_4(36)$, $S_6(11)$, $S_{14}(14)$	ν_{CC}, δ_{NH}
8	1447	1.8	$S_1(28)$, $S_{15}(23)$	ν_{CN}, ν_{CC}, δ_{CH}	1446	33.8	$S_1(19)$, $S_2(11)$, $S_{15}(30)$	ν_{CN}, ν_{CC}, δ_{CH}
9	1431	53.4	$S_4(28)$, $S_5(20)$, $S_{14}(20)$	ν_{CC}, ν_{CN}, δ_{NH}	1435	59.2	$S_1(13)$, $S_4(20)$, $S_5(14)$, $S_{14}(28)$	ν_{CN}, ν_{CC}, δ_{NH}
10	1418	157.2	$S_2(25)$, $S_5(16)$, $S_6(12)$, $S_{16}(13)$, $S_{22}(13)$	ν_{CC}, ν_{CN}, $\delta_{CH,}$ δ_{ring}	1410	49.9	$S_2(22)$, $S_3(13)$, $S_5(19)$, $S_{16}(18)$, $S_{21}(13)$	ν_{CC}, ν_{CN}, $\delta_{CH,}$ δ_{OH}
11	1349	55.8	$S_3(20)$, $S_8(14)$, $S_{21}(14)$	ν_{CC}, ν_{CO}, δ_{OH}	1332	87.8	$S_3(18)$, $S_6(10)$, $S_8(10)$, $S_{30}(19)$	ν_{CC}, ν_{CO}, γ_{CO}
12	1255	22.5	$S_5(11)$, $S_{14}(18)$, $S_{15}(12)$, $S_{16}(17)$, $S_{17}(27)$	ν_{CN}, δ_{NH} δ_{CH}	1256	5.6	$S_{14}(14)$, $S_{16}(17)$, $S_{18}(32)$	δ_{NH}, δ_{CH}, δ_{CC}
13	1230	33.6	$S_1(12)$, $S_3(18)$, $S_{21}(41)$	ν_{CN}, ν_{CC}, δ_{OH}	1212	54.8	$S_3(13\%)$, $S_5(17\%)$, $S_{21}(42\%)$	ν_{CC}, ν_{CN}, δ_{OH}
14	1134	115.6	$S_2(11)$, $S_5(11)$, $S_8(20)$, $S_{14}(10)$, $S_{15}(18)$, $S_{21}(13)$	ν_{CC}, ν_{CN}, ν_{CO}, δ_{NH}, δ_{CH}, δ_{OH}	1117	50.7	$S_1(13\%)$, $S_2(17\%)$, $S_{14}(11\%)$, $S_{15}(39)$	ν_{CN}, ν_{CC}, δ_{NH}, δ_{CH}
15	1097	292.0	$S_1(40)$, $S_{14}(18)$, $S_{15}(16)$	ν_{CN}, δ_{NH}, δ_{CH}	1109	220.3	$S_1(29)$, $S_{14}(12)$, $S_{20}(14)$	ν_{CN}, δ_{NH}, δ_{CO}
16	1072	22.0	$S_2(29)$, $S_8(16)$, $S_{16}(24)$	ν_{CC}, ν_{CO}, δ_{CH}	1053	130.5	$S_2(15)$, $S_8(32)$, $S_{16}(18)$	ν_{CC}, ν_{CO}, δ_{CH}
17	1033	35.9	$S_3(35)$, $S_{16}(16)$, $S_{17}(40)$	ν_{CC}, δ_{CH}	1031	48.2	$S_3(36)$, $S_{16}(19)$, $S_{17}(40)$	ν_{CC}, δ_{CH}
18	945	19.5	$S_4(10)$, $S_5(13)$, $S_{16}(10)$, $S_{22}(46)$	ν_{CC}, $\nu_{CN,}$ δ_{CH} , δ_{ring}	938	45.6	$S_5(14)$, $S_8(12)$, $S_{22}(46)$	ν_{CN}, $\nu_{CO,}$ δ_{ring}
19	884	0.5	$S_{25}(12)$, $S_{26}(46)$, $S_{27}(42)$	γ_{CH}	889	1.0	$S_{25}(10)$, $S_{26}(42)$, $S_{27}(48)$	γ_{CH}
20	882	2.4	$S_{23}(94)$	δ_{ring}	881	6.7	$S_{23}(95)$	δ_{ring}
21	823	6.5	$S_{25}(39)$, $S_{26}(13)$, $S_{27}(42)$	γ_{CH}	827	5.4	$S_{25}(40)$, $S_{26}(19)$, $S_{27}(35)$	γ_{CH}
22	759	59.8	$S_{28}(11)$, $S_{29}(15)$, $S_{30}(60)$	γ_{CC}, γ_{CO}	751	60.00	$S_{29}(74)$	γ_{CO}
23	732	86.1	$S_{25}(50)$, $S_{26}(39)$	γ_{CH}	732	81.6	$S_{25}(52)$, $S_{26}(39)$	γ_{CH}
24	682	41.0	$S_6(10)$, $S_8(18)$, $S_{19}(27)$, $S_{20}(15)$, $S_{22}(15)$	ν_{CC}, ν_{CO}, δ_{CO}, δ_{ring}	677	36.6	$S_6(10)$, $S_8(19)$, $S_{19}(25)$, $S_{20}(16)$, $S_{22}(15)$	ν_{CC}, ν_{CO}, δ_{CO}, δ_{ring}
25	636	2.6	$S_{24}(25)$, $S_{32}(40)$, $S_{33}(32)$	γ_{CH}, τ_{ring}	636	0.2	$S_{24}(12)$, $S_{32}(35)$, $S_{33}(46)$	γ_{CH}, τ_{ring}
26	613	4.1	$S_{29}(12)$, $S_{32}(40)$, $S_{33}(48)$	γ_{CO}, τ_{ring}	608	0.8	$S_{30}(9)$, $S_{32}(57)$, $S_{33}(34)$	γ_{CO}, τ_{ring}
27	557	76.7	$S_{24}(69)$, $S_{32}(26)$	γ_{CH}, τ_{ring}	538	110.0	$S_{24}(81)$, $S_{32}(11)$	γ_{CH}, τ_{ring}
28	515	84.2	$S_{31}(90)$	γ_{OH}	508	58.3	$S_{31}(84)$, $S_{33}(13)$	γ_{OH}, τ_{ring}
29	507	2.3	$S_{18}(19)$, $S_{19}(31)$, $S_{20}(24)$	δ_{CC}, δ_{CO}	504	3.7	$S_{18}(20)$, $S_{19}(27)$, $S_{20}(39)$	δ_{CC}, δ_{CO}
30	409	14.6	$S_6(30)$, $S_{20}(32)$, $S_{22}(15)$	ν_{CC}, δ_{CO}, δ_{ring}	414	10.0	$S_6(32)$, $S_{19}(12)$, $S_{20}(28)$, $S_{22}(16)$	ν_{CC}, δ_{CO}, δ_{ring}
31	181	4.1	$S_{18}(64)$, $S_{19}(15)$, $S_{20}(18)$	δ_{CC}, δ_{CO}	190	0.1	$S_{18}(65)$, $S_{19}(17)$, $S_{20}(15)$	δ_{CC}, δ_{CO}
32	169	2.5	$S_{28}(85)$, $S_{29}(15)$	γ_{CC}, γ_{CO}	172	2.1	$S_{27}(82)$, $S_{30}(18)$	γ_{CH}, γ_{CO}
33	105	1.7	$S_{29}(45)$, $S_{30}(55)$	γ_{CO}	100	0.0	$S_{29}(38)$, $S_{30}(62)$	γ_{CO}

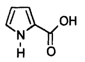
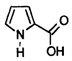
[a] Scaled by factor 0.98. [b] PED's lower than 10% are not included.

benzoic and trifluoroacetic acids, which are known to associate in cyclic forms. The theoretically calculated differences between ν_{CO} of the monomers and of the cyclic associates are 2.95%, 2.7%, and 1.7% for the A, B, and C dimers, respectively. This provides additional support for the experimental IR evidence.

Furthermore, the interactions of solvents of different polarities with pyrrole-2-carboxylic acid and *N*-methylpyrrole-2-carboxylic acid were also studied. It was observed that the shift of the ν_{CO} band of these two acids is of the same type in diethyl ether (1711 cm^{-1}), dioxane (1706, 1707 cm^{-1}), and acetonitrile (1713, 1710 cm^{-1}). The carbonyl band is symmetric and has a regular shape. This is another piece of evidence suggesting that the pyrrole-2-carboxylic acid, as well as its *N*-methyl derivative, exist in only one conformation in solution, most likely in the s-cis form.

Additional support for this conclusion is provided by the comparison of the calculated at B3LYP/6-311+G(d) level dipole moments of both conformers. The value for the s-cis form is 1.42 D, whereas for the s-trans form it amounts to 3.34 D. The dipole moments of selected pyrroles have been also calculated previously on the basis of a group's moments[34] and compared with their measured values. It was concluded that 2-acylpyrroles exist in solution almost exclusively in the syn conformation. Furthermore, Chadwick[33] pointed out that the greater stability of the syn- over the anti-rotamer of pyrrole-2-carbaldehyde and -2-ketones in a low polarity solvent is due to the lower dipole moment of this form. A similar conclusion may be drawn in the case of pyrrole-2-carboxylic acid. In this case the syn-rotamer has a much lower dipole moment than the anti rotamer.

TABLE 3: Theoretical (B3LYP/6-311+G* Level of Theory) IR Data for Pyrrole-2-carboxylic Acid Monomers

								
Mode	ν (cm^{-1})	ν^{a} (cm^{-1})	A (km mol^{-1})	Approximate description^{b}	ν (cm^{-1})	ν^{a} (cm^{-1})	A (km mol^{-1})	Approximate description^{b}
1	3732	3658	75.3	ν_{OH}	3744	3670	74.1	ν_{OH}
2	3649	3576	84.8	ν_{NH}	3667	3593	84.1	ν_{NH}
3	3262	3197	1.3	ν_{C-H}	3262	3196	1.7	ν_{C-H}
4	3255	3190	1.1	ν_{C-H}	3254	3189	0.9	ν_{C-H}
5	3236	3171	3.8	ν_{C-H}	3237	3173	2.9	ν_{C-H}
6	1759	1724	566.8	$\nu_{C=O}$	1791	1755	566.4	$\nu_{C=O}$
7	1595	1563	26.4	ν_{ring}, δ_{N-H}	1599	1567	52.2	$\delta_{N-H}, \nu_{ring}, \delta_{C-H}$
8	1483	1453	0.9	$\delta_{N-H}, \nu_{CC}, \delta_{C-H}$	1483	1453	17.2	$\delta_{N-H}, \nu_{ring}, \delta_{C-H}$
9	1466	1436	62.5	$\delta_{N-H}, \nu_{CC}, \nu_{CN}$	1471	1442	81.3	$\delta_{N-H}, \delta_{C-H}, \delta_{O-H}$
10	1451	1422	146.7	$\delta_{O-H}, \delta_{C-H}, \nu_{CC}, \nu_{CN}$	1443	1414	46.5	$\delta_{O-H}, \delta_{C-H}, \nu_{CN}, \nu_{CC}$
11	1383	1355	49.8	$\delta_{O-H}, \delta_{N-H}, \nu_{CC}, \delta_{C-H}$	1364	1337	76.8	$\delta_{O-H}, \delta_{C-H}, \delta_{N-H}, \nu_{CO}$
12	1291	1265	29.2	$\delta_{N-H}, \delta_{C-H}, \delta_{O-H}, \nu_{CN}$	1291	1265	7.4	$\delta_{N-H}, \delta_{C-H}, \delta_{O-H}$
13	1264	1239	49.7	$\delta_{O-H}, \delta_{C-H}, \nu_{CC}$	1245	1220	72.9	$\delta_{O-H}, \delta_{C-H}, \delta_{N-H}$
14	1163	1140	117.9	$\delta_{N-H}, \delta_{O-H}, \delta_{C-H}, \nu_{CC}$	1144	1121	38.7	$\delta_{N-H}, \delta_{O-H}$
15	1125	1103	280.9	$\delta_{N-H}, \delta_{C-H}, \nu_{CN}$	1138	1115	232.9	$\delta_{O-H}, \delta_{N-H}, \delta_{C-H}, \nu_{CO}$
16	1097	1075	26.3	$\delta_{C-H}, \delta_{N-H}, \nu_{CC}$	1077	1055	125.8	$\nu_{CO}, \delta_{N-H}, \delta_{C-H}$
17	1058	1037	35.6	δ_{C-H}, ν_{CC}	1056	1035	50.7	δ_{C-H}
18	965	945	19.9	$\delta_{ring}, \delta_{C-H}, \delta_{O-H}$	958	938	46.8	$\nu_{CO}, \delta_{C-H}, \delta_{ring}$
19	901	883	2.4	$\delta_{C-H}, \delta_{ring}, \delta_{N-H}$	901	883	6.5	δ_{ring}
20	894	876	0.6	δ^{oop}_{C-H}	899	880	1.3	δ^{oop}_{C-H}
21	834	817	5.8	$\delta^{oop}_{C-H}, \delta^{oop}_{N-H}$	836	819	5.1	$\delta^{oop}_{C-H}, \delta^{oop}_{N-H}$
22	780	765	70.1	$\delta^{oop}_{C-H}, \delta^{oop}_{CO}$	772	756	70.2	$\delta^{oop}_{C-H}, \delta^{oop}_{CO}$
23	741	726	92.5	$\delta^{oop}_{C-H}, \delta^{oop}_{N-H}$	740	725	85.2	δ^{oop}_{C-H}
24	697	683	41.4	$\delta_{O-H}, \delta_{C-H}, \nu_{CO}$	691	677	36.6	$\delta_{O-H}, \delta_{ring}$
25	651	638	0.3	$\delta^{oop}_{N-H}, \delta^{oop}_{C-H}, \delta^{oop}_{O-H}$	654	640	1.6	$\delta^{oop}_{N-H}, \delta^{oop}_{C-H}, \delta^{oop}_{O-H}$
26	631	618	9.1	$\delta^{oop}_{C-H}, \delta^{oop}_{O-H}, \delta^{oop}_{N-H}$	622	609	1.4	$\delta^{oop}_{C-H}, \delta^{oop}_{O-H}, \delta^{oop}_{N-H}$
27	565	553	117.1	$\delta^{oop}_{N-H}, \delta^{oop}_{C-H}, \delta^{oop}_{O-H}$	549	538	166.8	$\delta^{oop}_{N-H}, \delta^{oop}_{O-H}, \delta^{oop}_{C-H}$
28	548	537	51.8	$\delta^{oop}_{O-H}, \delta^{oop}_{N-H}$	531	520	12.6	$\delta^{oop}_{O-H}, \delta^{oop}_{N-H}, \delta^{oop}_{C-H}$
29	517	507	2.5	$\delta_{C-H}, \delta_{CO}, \delta_{N-H}$	514	503	3.4	$\delta_{N-H}, \delta_{CO}, \delta_{C-H}$
30	417	409	14.9	$\delta^{ip}_{COOH}, \delta^{ip}_{ring}, \delta^{ip}_{N-H}$	423	414	10.3	$\delta^{ip}_{COOH}, \delta^{ip}_{ring}$
31	186	182	4.1	$\delta^{ip}_{ring}, \delta^{ip}_{COOH}, \delta^{ip}_{C-H}$	194	190	0.1	$\delta^{ip}_{ring}, \delta^{ip}_{COOH}, \delta^{ip}_{N-H}$
32	175	171	2.6	$\delta^{oop}_{C-H}, \delta^{oop}_{ring}, \delta^{oop}_{O-H}$	176	172	2.3	$\delta^{oop}_{O-H}, \delta^{oop}_{ring}, \delta^{oop}_{C-H}$
33	109	107	1.8	$\delta^{oop}_{CO}, \delta^{oop}_{N-H}, \delta^{oop}_{C-H}$	104	102	0.01	$\delta^{oop}_{CO}, \delta^{oop}_{C-H}, \delta^{oop}_{N-H}$

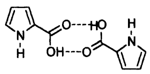
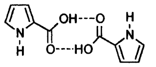
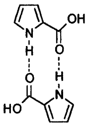
[a] Scaled by 0.98. [b] Vibrational modes: ν, stretching; δ, deformational (all kinds). Superscripts: s, symmetrical; as, asymmetrical; ip, in-plane; oop, out of plane.

In the study of the vibrational behavior of carboxylic acids, the combination of infrared and Raman spectroscopy seems to be a good method to decide whether a carboxylic acid is H-bonded through a cyclic dimer pattern. For instance, the $\nu_{C=O}$ band of the formic acid cyclic dimer was observed at 1754 cm^{-1} in the infrared and at 1670 cm^{-1} in the Raman.[35-37]

The calculated spectra of dimers A, B, and C revealed two carbonyl absorptions, which are assigned to the in phase (ν^{ip}_{CO}) and out of phase (ν^{op}_{CO}) stretching modes for intermolecular hydrogen-bonded CO groups. Their intensities differ significantly from each other in the Raman and IR spectra. The in phase, symmetrical stretching vibration of the CO group is active in the Raman. The ab initio calculated frequencies are 1672, 1651, and 1692 cm^{-1} for dimers A, B, and C, respectively, and their intensities are of medium strength (data concerning intensities are based on the HF calculations). The out of phase stretching vibration of the carbonyl group gives intensive bands at 1695, 1670, and 1703 cm^{-1} in the IR spectrum of dimer A, B, and C, respectively.

Figure 3 shows the Raman spectrum of the crystal PCA. The broad and medium intensity band at 1622 cm^{-1} is assigned to the stretching vibration ν^{ip}_{CO} of the H-bonded C═O group. The theoretically estimated ν_{CO} frequencies for three cyclic dimers are higher than Raman experimental frequencies by 73, 48, and 81 cm^{-1} for dimers A, B, and C, respectively. Thus, the experimental value of the ν_{CO} is closest to the theoretically predicted value for dimer B. The significant difference of 63 cm^{-1} between the in phase and out of phase stretching vibration of the CO groups may be treated as direct evidence of the existence of the cyclic dimers.

TABLE 4: Theoretical (B3LYP/6-311+G* Level of Theory) and Experimental IR and Raman Data for Pyrrole-2-carboxylic Acid Dimers

	dimer A 				dimer B 				dimer C 				
Mode	ν (cm^{-1})	ν[a] (cm^{-1})	A (km mol^{-1})	Approximate description[b]	ν (cm^{-1})	ν[a] (cm^{-1})	A (km mol^{-1})	Approximate description[b]	ν (cm^{-1})	ν[a] (cm^{-1})	A (km mol^{-1})	Approximate description[b]	Experimental[c] IR ν (cm^{-1})
1	3661	3588	172.5	ν_{NH}	3653	3580	166.7	ν_{NH}	3740	3665	146.1	ν_{OH}	3550[d]vw
2	3261	3196	0.02	ν_{C-H}	3262	3197	0.7	ν_{C-H}	3483	3413	1793.2	ν_{NH}	3465[d], 3358[e], 3356[f]
3	3254	3189	2.6	ν_{C-H}	3255	3190	1.9	ν_{C-H}	3262	3197	3.0	ν_{C-H}	3132
4	3237	3172	3.5	ν_{C-H}	3238	3173	233.8	ν_{C-H}, ν_{OH}	3255	3190	2.9	ν_{C-H}	3124
5	3220	3156	4999.5	ν_{OH}	3235	3171	2500.3	ν_{OH}, ν_{C-H}	3236	3171	9.7	ν_{C-H}	3108
6	1730	1695	1539.5	$\nu_{C=O}$	1705	1671	1465.4	$\nu_{C=O}$	1738	1703	1808	$\nu_{C=O}$	1685[e], 1680[f] 1665[e], 1661[f] 1744[d]w, 1671[d]
7	1602	1570	204.9	δ_{N-H}, ν_{ring}	1598	1566	133.8	δ_{N-H}, ν_{ring}	1596	1564	34.3	δ_{N-H}, ν_{ring}	1554
8	1484	1454	144.6	$\delta_{N-H}, \delta_{C-H}, \delta_{O-H}$	1486	1456	101.1	$\delta_{N-H}, \delta_{C-H}$	1504	1474	48.1	$\delta_{N-H}, \delta_{C-H}, \nu_{ring}, \delta_{O-H}$	
9	1480	1450	348.7	$\delta_{N-H}, \delta_{C-H}, \delta_{O-H}$	1481	1451	507.4	$\delta_{O-H}, \delta_{C-H}, \delta_{N-H}$	1470	1441	87.2	$\delta_{C-H}, \delta_{N-H}, \nu_{ring}$	1439
10	1451	1422	50.3	$\delta_{O-H}, \delta_{N-H}, \nu_{ring}$	1462	1432	51.9	$\nu_{ring}, \delta_{N-H}, \delta_{O-H}$	1447	1418	393	$\nu_{ring}, \delta_{O-H}, \delta_{N-H}$	
11	1420	1392	37.9	$\delta_{O-H}, \delta_{C-H}, \delta_{N-H}$	1423	1394	46.8	$\delta_{O-H}, \delta_{C-H}, \nu_{ring}$	1393	1366	77.3	$\delta_{O-H}, \delta_{N-H}, \nu_{ring}$	1391
12	1335	1309	632.2	$\delta_{O-H}, \delta_{C-H}, \nu_{CO}$	1355	1328	653.1	$\delta_{O-H}, \delta_{N-H}, \nu_{CO}$	1306	1280	37.6	$\delta_{N-H}, \delta_{C-H}, \delta_{O-H}$	1328
13	1285	1259	35.8	$\delta_{N-H}, \delta_{C-H}, \delta_{O-H}$	1286	1261	6.3	$\delta_{C-H}, \delta_{N-H}$	1270	1245	75.2	$\delta_{O-H}, \delta_{C-H}$	1264w
14	1203	1179	335	$\nu_{CC}, \delta_{N-H}, \delta_{O-H}$	1213	1189	280.3	$\delta_{N-H}, \delta_{C-H}, \delta_{O-H}$	1181	1158	68.4	$\delta_{N-H}, \delta_{C-H}, \delta_{O-H}$	1190
15	1141	1118	148.6	$\delta_{C-H}, \delta_{N-H}$	1136	1113	231.8	$\delta_{N-H}, \delta_{C-H}$	1150	1127	661.0	$\delta_{N-H}, \delta_{C-H}, \nu_{CO}$	1123
16	1099	1077	34.7	$\delta_{N-H}, \delta_{C-H}$	1104	1082	8.1	$\delta_{C-H}, \delta_{N-H}$	1097	1076	112.2	$\delta_{C-H}, \delta_{N-H}$	
17	1056	1035	107.5	δ_{C-H}	1058	1037	103.9	δ_{C-H}	1063	1042	66.3	δ_{C-H}	1037
18	967	947	61.9	$\delta_{C-H}, \nu_{CN}, \delta^{ip}_{ring}$	969	950	50.0	$\delta^{ip}_{ring}, \delta_{C-H}, \delta_{O-H}$	961	942	49.8	$\delta_{C-H}, \delta^{ip}_{ring}$	948
19	922	903	251.9	δ^{oop}_{O-H}	919	901	259.4	δ^{oop}_{OH}	902	884	4.7	δ^{ip}_{ring}	892[e,f], 884[d]
20	901	883	16.7	δ^{ip}_{ring}	902	884	10.1	δ^{ip}_{ring}	897	880	2.9	$\delta^{oop}_{C-H}, \delta^{oop}_{N-H}$	
21	899	881	1.1	δ^{oop}_{C-H}	897	879	4.9	δ^{oop}_{C-H}	886	868	125	$\delta^{oop}_{N-H}, \delta^{oop}_{O-H}$	
22	838	822	21.7	$\delta^{oop}_{N-H}, \delta^{oop}_{C-H}$	837	820	18.9	$\delta^{oop}_{OH}\ \delta^{oop}_{N-H}$	810	794	111.2	$\delta^{oop}_{N-H}, \delta^{oop}_{C-H}$	
23	780	765	41.7	$\delta^{oop}_{C-H}, \delta^{oop}_{N-H}, \delta^{oop}_{ring}$	779	764	34.1	$\delta^{oop}_{OH}, \delta^{oop}_{C-H}$	769	754	0.1	$\delta^{oop}_{N-H}, \delta^{oop}_{C-H}\ \delta^{oop}_{O-H}$	
24	759	744	36.4	$\nu_{CO}, \delta^{ip}_{CO},$	762	746	43.7	$\nu_{CO}, \delta^{ip}_{CO}, \delta_{C-H}$	749	734	149.1	$\delta^{oop}_{N-H}, \delta^{oop}_{C-H}$	756
25	742	728	191.9	δ^{oop}_{C-H}	743	728	193.9	δ^{oop}_{C-H}	707	693	82.7	$\delta^{ip}_{OH}, \nu_{CO}$	693
26	646	634	19.3	$\delta^{oop}_{N-H}, \delta^{oop}_{C-H}$	650	637	16.9	$\delta^{oop}_{N-H}, \delta^{oop}_{C-H}$	628	615	20.0	$\delta^{oop}_{C-H}, \delta^{oop}_{ring}, \delta^{oop}_{O-H}$	
27	618	606	8.3	$\delta^{oop}_{C-H}, \delta^{oop}_{O-H}, \delta^{oop}_{ring}$	618	606	10.9	$\delta^{oop}_{C-H}, \delta^{oop}_{ring}, \delta^{oop}_{O-H},$	619	606	21.1	$\delta^{oop}_{C-H}, \delta^{oop}_{N-H}$	602[e,f]
28	557	546	108.8	$\delta^{ip}_{CO}, \delta^{oop}_{C-H}, \delta^{oop}_{N-H}$	564	552	105.4	$\delta^{ip}_{CO}, \delta^{oop}_{N-H}, \delta^{oop}_{C-H}$	526	516	24.3	$\delta^{ip}_{C-H}, \delta^{ip}_{CO}, \delta^{ip}_{ring}$	557[e,f], 554[d]
29	555	544	108.4	$\delta^{oop}_{N-H}, \delta^{oop}_{C-H}$	559	548	66.8	$\delta^{ip}_{COOH}, \delta^{ip}_{C-H}, \delta_{N-H}$	525	514	200.0	δ^{oop}_{O-H}	
30	435	426	3.2	$\delta^{ip}_{CO}, \delta^{ip}_{ring}$	431	422	4.9	$\delta^{ip}_{ring}, \delta^{ip}_{CO}$	202	198	3.2	$\nu_{CO}, \delta^{ip}_{ring}, \delta^{ip}_{CO}$	
31	275	269	49.8	$\delta_{C-H}, \delta^{ip}_{CO}, \delta^{ip}_{CC}$	264	259	99.5	$\delta^{ip}_{CO}, \delta_{C-H}, \delta^{ip}_{CC}$	176	173	4.2	$\delta^{oop}_{ring}, \delta^{oop}_{O-H}, \delta^{oop}_{CO}$	
32	191	187	1.1	$\delta^{oop}_{C-H}, \delta^{oop}_{CO}, \delta^{oop}_{ring}$	188	185	1.2	$\delta^{oop}_{CO}, \delta^{oop}_{ring}, \delta^{oop}_{C-H}$	424	416	26.1	$\delta^{ip}_{CO}, \delta^{ip}_{OH}$	
33	117	115	0.2	$\delta^{oop}_{N-H}, \delta^{oop}_{CO},$ $\delta^{oop}_{C-H}\ \delta^{oop}_{CC}$	121	119	1.9	$\delta^{oop}_{CO}, \delta^{oop}_{ring},$ $\delta^{oop}_{CC}\ \delta^{oop}_{N-H},$	137	134	0.6	$\delta^{oop}_{CO}, \delta^{oop}_{C-H}$	
34	64	62	8.9	$\delta^{ip}_{CC}, \delta^{ip}_{N-H}, \delta^{ip}_{C-H}$	64	63	1.1	$\delta^{ip}_{CC}, \delta^{ip}_{C-H}, \delta^{ip}_{N-H}$	85	84	8.4	$\delta^{ip}_{C-H}, \delta^{ip}_{ring}, \delta^{ip}_{CO}, \delta^{ip}_{CC}$	
35	47	46	3.2	$\delta^{oop}_{N-H}, \delta^{oop}_{C-H},$ $\delta^{oop}_{CO}, \delta^{oop}_{CC}$	45	44	1.1	$\delta^{oop}_{CO}, \delta^{oop}_{N-H},$ $\delta^{oop}_{C-H}, \delta^{oop}_{CC}$	35	34	0.3	$\delta^{oop}_{N-H}, \delta^{oop}_{CO}, \delta^{oop}_{C-H}$	
36	22	21	2.2	$\delta^{oop}_{C-H}, \delta^{oop}_{CO}$	22	21	1.2	$\delta^{oop}_{CO}, \delta^{oop}_{C-H}$	16	16	0.2	$\delta^{oop}_{CO}, \delta^{oop}_{ring}$	

[a] Scaled by 0.98. [b] Vibrational modes: ν, stretching; δ, deformational (all kinds). Superscripts: s, symmetrical; as, asymmetrical; ip, in-plane; oop, out of plane. [c] Abbreviation used: s, strong; m, medium; w, weak; v, very. [d] Measured as CCl_4 solution. [e] Measured as KBr pellet. [f] Measured as Nujol mull.

Other bands that may assist in the identification of acid dimers are the coupled vibrations involving the C=O stretching and OH in plane deformation vibrations. The δ_{OH} band at 1391 cm^{-1} is rather weak in both spectra. The intensity of the ν_{C-O} band at 1328 cm^{-1} in IR is high, whereas in the Raman spectrum a weak band was observed. Additionally, the broad and medium intense γ_{OH} band is visible only in the IR spectrum of solid PCA.

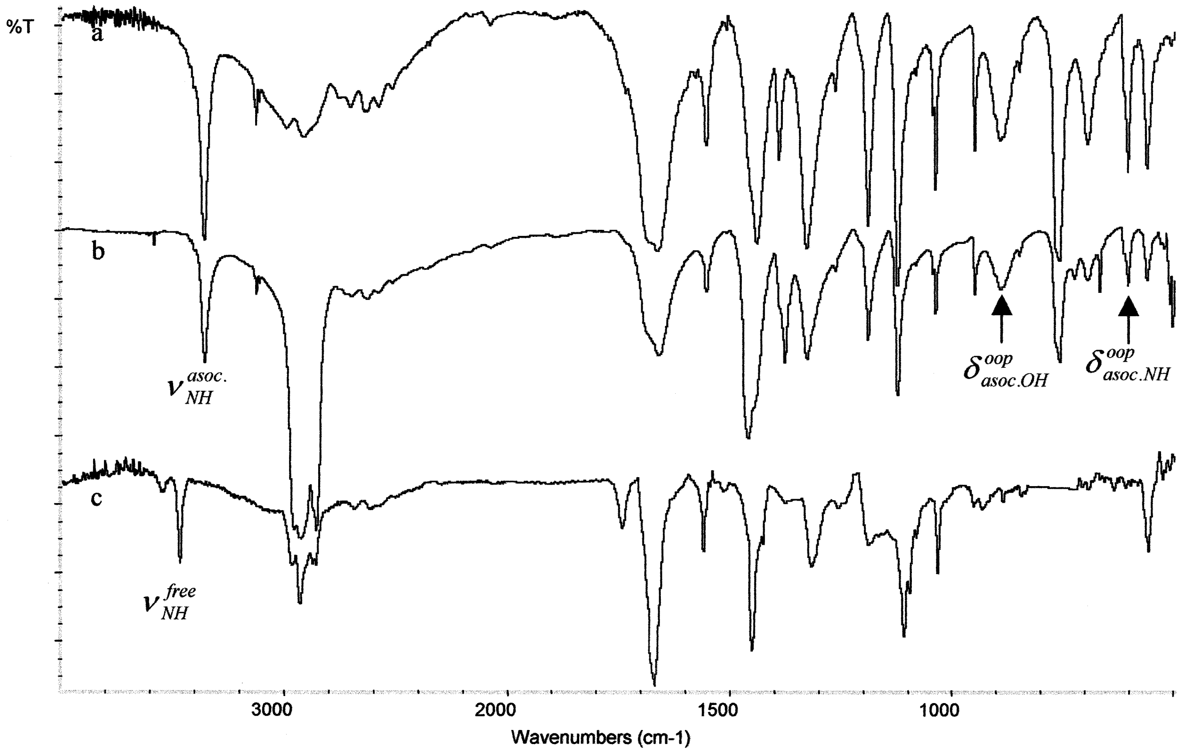


Figure 1. IR spectra of pyrrole-2-carboxylic acid: (a) KBr pellet; (b) Nujol mull; (c) 0.001 M CCl_4 solution.

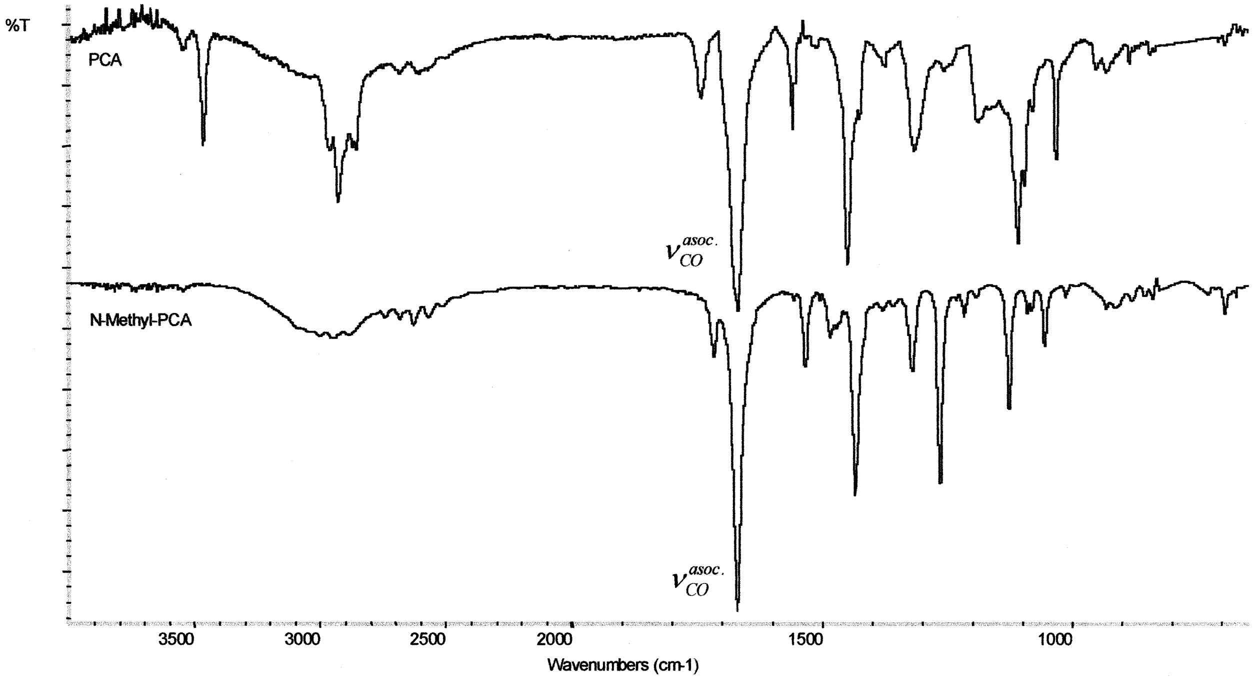


Figure 2. IR spectra of pyrrole-2-carboxylic acid (PCA) and *N*-methylpyrrole-2-carboxylic acid (0.025 M; CCl_4).

Geometries and Energetics. The results of the B3LYP/6-311+G(d) level calculations indicate that the s-cis monomer conformer is more stable than the s-trans conformer. The difference in energies of these conformers amounts to 0.97 kcal/mol. It was pointed out in the previous section that the B dimer is dominant in solution. Table 5 presents some of the geometrical parameters of complexes considered in this study. The results show that the dimers formed through O—H···O bonds are more stable than the complex formed through N—H···O bonds. The elongation due to the H-bond formation of the O—H proton donors (0.027−0.028 Å) is greater than the elongation of the N—H bond (0.010−0.011 Å). A similar situation is observed for the C═O bond; its elongation is smaller for the C dimer than for the A and B complexes. It was pointed out earlier[38] on the basis of neutron diffraction results taken from the Cambridge Structural Database[29] that in the case of C═O···H—O interactions there is a correlation between the H···O distance and C═O bond length: the shorter the H···O distance, the longer the C═O bond.

Interestingly, the O−H···O angles are greater than N−H···O angles (Table 5) and it is well-known that linear H-bonds and those that approach linearity are usually stronger than the

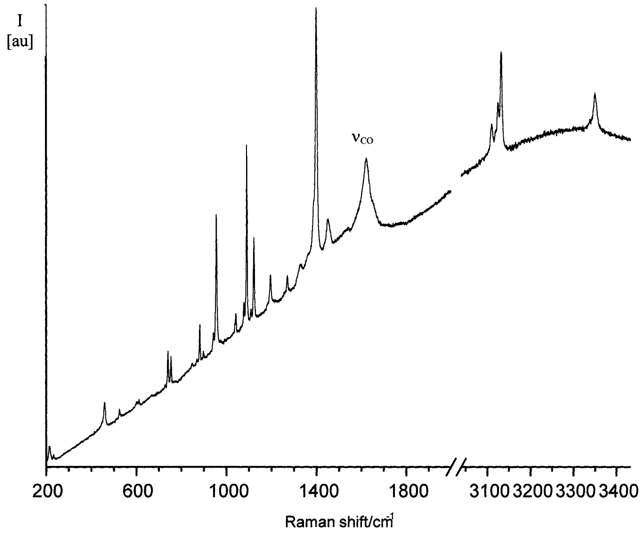


Figure 3. Raman spectrum of solid pyrrole-2-carboxylic acid (PCA).

TABLE 5: Geometrical (Ångstroms and Degrees) and Energy (kcal/mol) Parameters of the PCA Dimers Considered in This Study (Results Obtained at B3LYP/6-311+G* Level of Theory, H-Bond Energies Corrected for BSSE)

cyclic dimer	X−H*	H···O	C=O	X−H···O	H-bond energy
A	0.997	1.688	1.230	178.6	−8.3
B	0.996	1.697	1.237	178.9	−7.7
C	1.019	1.892	1.226	163.9	−5.7

[a] NH bond length for monomeric PCA amounts to 1.008 Å (s−E) and 1.009 Å (s−Z); OH bond length amounts to 0.969 Å for both conformers.

bonds where the X−H···Y angle is far from 180°. Additionally, H···O distances for the A and B complexes are shorter than this distance for the C complex.

The B3LYP/6-311+G(d) H-bond energies corrected for BSSE are also given in Table 5. The single O−H···O and N−H···O binding energies are provided. One can see that H-bonds are of the medium strength, as mentioned in the previous section, and they are assisted by conjugated systems. For the all cases considered here two H-bonds stabilize each of the complexes. One can conclude that the energetic results confirm the geometrical data; the A and B complexes are more stable. Additionally, the O−H···O bond within the complex formed by the s-trans conformers is stronger than such an O−H···O bond within the s-cis conformers dimer.

Figure 4 presents the contour maps of electron density for the considered dimers. The positions of attractors, bond critical points and ring critical points are also displayed. Table 6 presents the topological parameters of the bonds involved in H-bond formation (C=O, O−H, and N−H bonds): electron densities at BCPs and their Laplacians. The same topological parameters of H···O contacts are also given.

It is well-known that the electron density at H···Y (Y is the accepting center within the X−H···Y bridge) well correlates with the H-bond energy; thus the stronger the H-bond, the greater the $\rho_{H\cdots Y}$ value.[39−41] Such a relationship is mainly fulfilled for homogeneous samples.[42] One can conclude that the $\rho_{H\cdots O}$ values (Table 6) are in an agreement with the corresponding H-bond energies.

All the results presented here indicate that the O−H···O bonds are stronger than the N−H···O ones and that the A and B complexes are more stable than the C complex. These results are also supported by the values of the electron densities at the ring critical points. It was shown recently[43] that for intermolecular H-bonds, greater ρ_{RCP} (electron density at the ring critical point) values are observed for stronger H-bonds. For such systems, the considered ring critical points are associated with the ring created due to intermolecular H-bond formation. The value of ρ_{RCP} for the eight-membered ring of PCA dimers (A and B) amounts to 0.008 au and for the ten-membered ring of the C dimer it is only 0.003 au

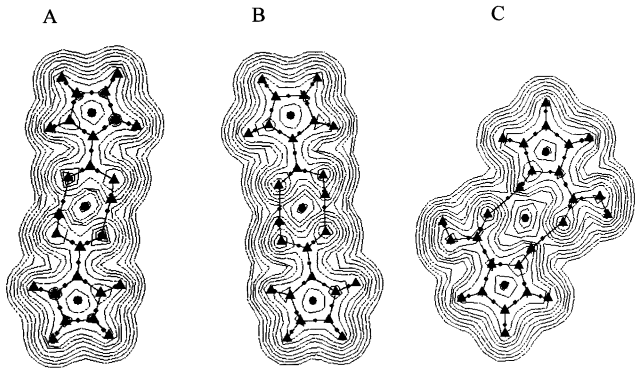


Figure 4. Contour maps of the electron density for the pyrrole-2-carboxylic acid dimers A, B, and C: (▲)nuclear attractor NA; (●) ring critical point RCP; (•) bond critical point BCP.

TABLE 6: Topological Parameters (Obtained from B3LYP/6-311+G* Wave Functions) for Complexes of the PCA (All Values in au)

cyclic dimer	ρ_{XH}	$\nabla^2\rho_{XH}$	$\rho_{H\cdots O}$	$\nabla^2\rho_{H\cdots O}$	$\rho_{C=O}$	$\nabla^2\rho_{C=O}$
A	0.3147	−2.0832	0.0462	0.1449	0.3961	−0.3413
B	0.3163	−2.0977	0.0454	0.1435	0.3902	−0.3667
C	0.3243	−1.7270	0.0264	0.1094	0.4000	−0.3098

Conclusions

On the basis of spectroscopic investigations using both IR and Raman techniques, we have revealed that the pyrrole-2-carboxylic acid (PCA) forms cyclic acid dimers in the solid state. The theoretically estimated IR frequencies for the B and C dimers are very close to the experimentally observed absorptions. Pyrrole-2-carboxylic acid exists in solution and in the solid state in only one conformation, most likely in the s-cis form.

Acknowledgment. This work was supported by State Committee of Scientific Research of Poland (KBN), grants 3 T09A 061 19 and 4 TO9A 163 22. The authors wish to acknowledge the Interdisciplinary Centre for Mathematical and Computational Modeling (Warsaw University) and Wrocław Supercomputing and Networking Center for computational facilities. This work was facilitated in part by the NSF grant No. 9805465 & 9706268, Wrocław University of Technology Grant, and the Army High Performance Computing Research Center under the auspices of the Department of the Army, Army Research Laboratory cooperative agreement number DAAH04-95-2-0003/contract number DAAH04-95-C-0008.

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