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Infrared, Density-Functional Theory, and Atoms in Molecules Method Studies on Conformers of Some 2-Substituted 1*H*-Pyrroles

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Methyl pyrrole-2-carboxylate (MPC), pyrrole-2-carbaldehyde (PC), methyl *N*-methylpyrrole-2-carboxylate (MPC-NMe), and *N*-methylpyrrole-2-carbaldehyde (PC-NMe) are investigated. Experimental and theoretical IR spectra and density-functional theory calculations concerning energetic and geometrical properties of molecular structures show that for all species s-cis conformers are more stable than s-trans ones. The existence of intramolecular N−H···O hydrogen bonds for s-cis conformers of MPC and PC is controversial; the topological analysis based on Bader theory shows that such hydrogen bonds do not exist.

Introduction

Conformational isomers and the dimeric form of the methyl pyrrole-2-carboxylate (MPC) have been studied previously by means of IR spectroscopy and ab initio (HF/6-311++G**) calculations.[1,2] IR spectroscopy revealed a higher concentration of s-cis conformer than s-trans conformer in CCl_4 solution. Additionally, ab initio calculations have shown that the s-cis conformer, where the carbonyl group is located on the same side as the N−H group, is 1.3 kcal/mol more stable than the s-trans conformer. This location of the carbonyl and N−H groups favors the formation of centrosymmetric dimers with two equivalent N−H···O═C hydrogen bonds. The calculated hydrogen-bond energy for the MPC dimer is 9.4 kcal/mol, and its strength is comparable to the hydrogen-bond energy found for typical acid dimers. The vibrational spectrum of solid-state MPC may be explained by assuming that cyclic dimers exist in crystals.[2] A similar situation was detected recently by Gale et al.[3] who presented crystallographic evidence that some 2-substituted 1*H*-pyrroles form dimeric aggregates in the solid state as a result of pyrrole-N−H−carboxyl-O hydrogen bonds.

Meakins et al.'s study[4] revealed unusual behavior of carbonyl absorption after methylation of MPC and pyrrole-2-carbaldehyde (PC). After conversion of the N−H group to NCH_3, the ν_{CO} absorption moves to higher wavenumber, from 1701 to 1710 cm^{-1} in the case of MPC and from 1666 to 1671 cm^{-1} in the case of PC. Meakins et al. explained these shifts, which are opposite to predictions based on the inductive effect of the methyl group, by the formation of weak N−H···O═C intramolecular hydrogen-bond interactions for PC or MPC and the lack of such interaction for *N*-methyl derivatives.

However, our recent studies using Bader theory on MPC show that it is not possible to find the critical point of H···O intramolecular contact within the N−H···O═C system.[1] This means that the presence of intramolecular hydrogen bonds in the MPC molecule is rather doubtful.

To characterize the parameters influencing the spectroscopic properties of the above-mentioned compounds, detailed analyses of the experimental and theoretical IR spectra of MPC, PC, and their *N*-methyl derivatives are the subject of the present study. Additionally, density-functional theory (DFT) calculations were performed to find the optimized geometry of the molecules and to analyze the energetic relationships. The atoms in molecules (AIM) theory of Bader[5] was also applied in the analysis of the molecular structures to explain the controversial hypothesis that for MPC and PC molecules intramolecular N−H···O═C bonds are responsible for the vibrational spectra in the solid state.

Computational Details

MPC, PC, methyl *N*-methylpyrrole-2-carboxylate (MPC-NMe), and *N*-methylpyrrole-2-carbaldehyde (PC-NMe) molecules were fully optimized using the Gaussian 98 program.[6] For all of these molecules two conformers, s-cis and s-trans, were optimized. DFT calculations were carried out using the B3LYP method, which has been shown[7] to provide reliable information on both the structures and the energies of different kinds of hydrogen-bonded clusters. Additionally, the centrosymmetric dimer of the s-cis conformer of PC is considered in this study. The calculations for it were performed in the following way: Two molecules are connected by two equivalent N−H···O═C bonds; there is an inversion center between monomers, and hence, the molecules are geometrically equivalent. Despite such symmetry restrictions, the geometrical parameters of the N−H···O═C bonds in the PC dimer were optimized. The DFT (B3LYP/6-311++G**) approach was used to predict the vibrational wavenumbers, intensities, and the corresponding optimized geometries of the molecules. The predicted wavenumbers were scaled down by a single factor of 0.98. The aforementioned method overestimates the calculated harmonic frequencies, and for this reason, scaling factors have been proposed to correct for anharmonicity.[8,9] Scaling of the predicted wavenumbers is a frequently used procedure, especially for results at the Hartree−Fock (HF) level of theory. Raw frequency values computed at the HF level contain systematic errors because electron correlation is neglected, which result in overestimations of about 10−12%. Therefore, it is usual to scale HF frequencies by an empirical factor of 0.8929. It has been demonstrated that the use of this factor leads to the agreement

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of theoretical values with experimental results for a wide range of systems. Similarly, frequencies computed with methods other than the Hartree−Fock method are also scaled to eliminate systematic error, and scale factors for different levels of theory have been proposed.[8,10]

The analyses in this study are based on the geometrical parameters and energies obtained theoretically for fully optimized species; the only exception is the above-mentioned dimer of the s-cis conformer of PC for which the symmetry constraints were applied. Additionally, theoretical IR results are compared with experimental IR data.

To get more precise insight into the characteristics of molecules, the topological theory of Bader[5] was also applied. The bond critical points (BCPs) and the ring critical points (RCPs) were located using the AIM2000 program.[11] The electron densities at those points (ρ's) and their Laplacians ($\nabla^2\rho$'s) were calculated as parameters describing the properties of bonds and intermolecular or intramolecular contacts. Hydrogen bonds are the subject of special attention in this study.

Results and Discussion

IR Spectrum of MPC in Organic Solvents. Previous theoretical and spectroscopic studies on conformations of MPC show that there are some doubts concerning the assignment of the ν_{CO} band.[4] The absorption band at 1730 cm^{-1} was assigned to the s-trans form, whereas the band at 1717 cm^{-1} was assigned to the Fermi resonance. According to our spectroscopic and theoretical investigations,[1] the reverse order of assignment appears more probable than that proposed earlier.

It was recognized previously[12] that the position of equilibrium between alternative rotational isomers of a particular molecule is medium-dependent. So, solvent effects play an important role in determining equilibrium constants. Theoretical study of solvent effects shows their weak influence on geometrical properties and their much greater influence on thermodynamic properties, including enthalpy, free energy, and total energy.[13] Polar solvents stabilize the more polar form causing its higher proportion; in less interactive solvents its lower proportion was observed. Cheng et al.[12] explained such behavior as resulting from the reduction of the free energy difference between the s-cis and the s-trans forms. Furthermore, the frequency shifts of the carbonyl group depend on the solvent dielectric constants, solvent−solute interactions such as hydrogen bonds, and steric effects. The ν_{CO} shifts are also sensitive to the solvent acidity.[14,15] Therefore, some solvents with low hydrogen-bond donor acidity values and diversified dielectric constants were chosen in this study.

The IR spectrum of MPC has been investigated in organic solvents of various polarities. Figure 1 shows the IR spectrum of MPC in carbon tetrachloride, ethyl ether, acetonitrile, and methylene chloride. Some of the vibrational modes, especially the proton donor and acceptor groups, are sensitive to the polarity of the solvent. The absorption bands of the free carbonyl groups at 1701 and 1717 cm^{-1} observed in carbon tetrachloride move to slightly higher frequencies at 1703 and 1719 cm^{-1} in more polar acetonitrile and to 1706 and 1720 cm^{-1} in the case of ethyl ether solution. Furthermore, the ratio of the integrated intensities of the ν_{CO} stretching vibrations of the s-cis and s-trans conformers also changes. As we proposed previously,[1] on the basis of ab initio calculations, the absorption band at higher frequency (1719 cm^{-1}) was ascribed to the less stable s-trans conformer and the band at 1701 cm^{-1} to the s-cis form. According to the IR data concerning conformational analysis,[12,16] the population of the more polar form increases with the polarity of the solvent. Thus, the ratio $A_{C=O}^{s-cis}/A_{C=O}^{s-trans}$ of integrated intensities of the carbonyl bands of MPC conformers in CCl_4 is 1.59, whereas in the more polar acetonitrile it is 1.43 and is close to unity for 10^{-3} M ethyl ether solution. The larger value of this ratio observed in carbon tetrachloride solution indicates that the carbonyl band at higher frequency (1717 cm^{-1}) originates from the more polar form. The values of the calculated dipole moments of the analyzed conformers are listed in Table 1. The dipole moments for the s-cis and s-trans form of MPC are equal to 0.75 and 3.43 D. The stabilization of the s-trans conformation of MPC in acetonitrile may be related to the energy of the complexes formed between the solute and the solvent.

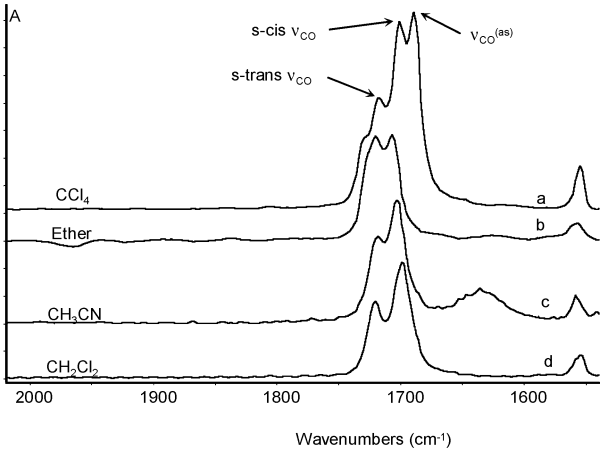


Figure 1. IR spectra of 0.001 M solutions of MPC in (a) carbon tetrachloride, (b) ethyl ether, (c) acetonitrile, (d) methylene chloride.

TABLE 1: Values of Dipole Moments (Calculated at the B3LYP/6-311++G Level of Theory), Energies, Barrier Heights, and Δ*E* for the s-cis and s-trans Conformers of PC, MPC, PC-NMe, and MPC-NMe**[a]

compound	μ [D]	*E* [hartree]	barrier height [kcal/mol]	Δ*E* [kcal/mol]
s-cis PC	3.02	−323.598 697 8	16.21	3.84
s-trans PC	4.70	−323.592 580 1		
ts PC[b]		−323.572 861 5		
s-cis PC-NMe	3.04	−362.915 304 3	15.31	4.52
s-trans PC-NMe[c]	5.11	−362.908 095 0		
ts PC-NMe[b]		−362.890 905 6		
s-cis MPC	0.75	−438.185 377 7	12.35	1.06
s-trans MPC	3.43	−438.183 686 7		
ts MPC[b]		−438.165 700 6		
s-cis MPC-NMe	0.86	−477.500 841 6	125.05	1.93
s-trans MPC-NMe	3.83	−477.497 765 7		
ts MPC-NMe[b]		−477.301 555 0		

[a] The energies of the optimized molecular structures of the species analyzed are presented here. The energies (in hartree) of both conformers as well as of the transition states (those systems for which the angle of rotation of COH or $CO(OCH_3)$ around C−C (aromatic) is equal to 90°) are given. The barrier heights (in kcal/mol) are also given. Δ*E* is the difference between the s-trans conformer energy and the energy of the more stable s-cis conformer. [b] Transition state. [c] There is one imaginary frequency for the s-trans PC-NMe structure; the optimized structure has not been found.

Vibrational Spectrum of MPC-NMe. The experimental and calculated IR normal modes for the MPC-NMe conformers are presented in Table 2. The theoretical absorption frequencies for the stretching vibrations of the methyl groups attached to pyrrole nitrogen and ester oxygen are very close to each other. The IR spectrum revealed that these bands are overlapped and no splitting was observed.

TABLE 2: Experimental IR Data (0.001 M CCl_4 Solutions) and the Theoretical Frequencies (B3LYP/6-311++G Level of Theory) for Optimized Structures of the s-cis and s-trans Conformers of MPC, MPC-NMe, PC, and PC-NMe**

	$\nu_{N-H}{}^{a}$ [cm^{-1}]			$\nu_{CO}{}^{a}$ [cm^{-1}]			$\nu_{ring}{}^{a}$ [cm^{-1}]			$\delta^{oop}_{N-H}{}^{a}$ [cm^{-1}]		
compound	s-trans	s-cis	exp	s-trans	s-cis	exp	s-trans	s-cis	exp	s-trans	s-cis	exp
MPC	3589	3571	3465	1736	1705	1719 1701 1689^{b}	1559	1555	1554	553	558	557 607^{b}
MPC-NMe				1717	1705	1711	1537	1531	1532			
PC	3576	3565 3321^{c}	3460 3274^{b} 3272^{d}	1712	1685 1668^{c}	1666 1656^{b} 1659^{d}	1553	1554	1552	499	566	568 605^{b}
PC-NMe				1694	1689	1670	1533	1531	1528			

[a] Scaled by 0.98. [b] Measured as a 0.1 M solution in CCl_4. [c] Calculated wavenumbers for the PC dimer. [d] Measured as a 0.1 M solution in cyclohexane.

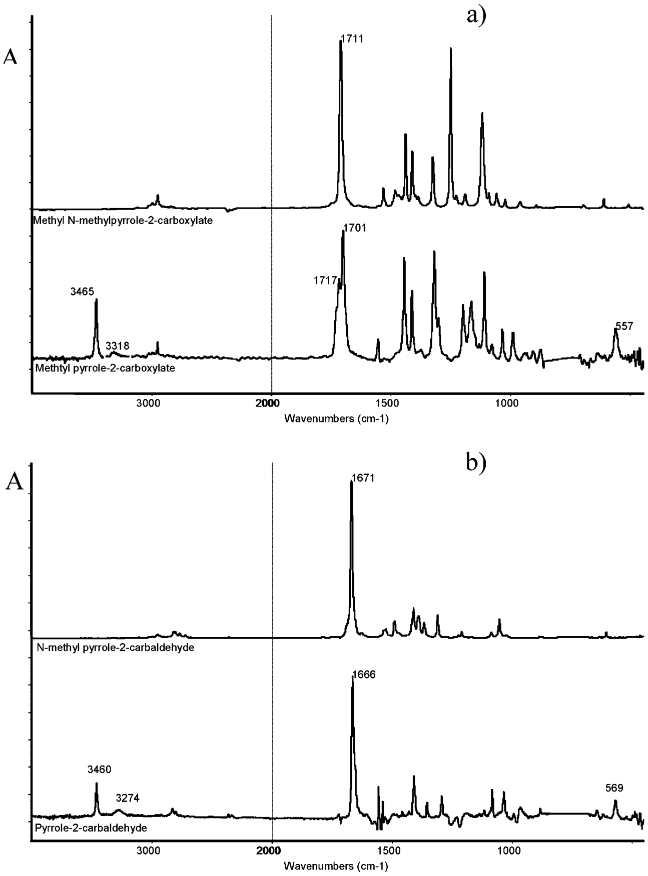


Figure 2. IR spectra of 0.001 M solutions of (a) MPC and *N*-methyl MPC and (b) PC and *N*-methyl PC.

The ν_{CO} band appears as a single, symmetrical component at 1711 cm^{-1} in CCl_4 solution (Figure 2a). Change of solvent from cyclohexane to acetonitrile does not split the carbonyl band. This means, according to earlier data,[17] that MPC-NMe exists in solution in one form, probably the s-cis one. The calculated energy differences between the s-trans conformer energy and the energy of the more stable s-cis conformer are given in Table 1. Table 1 reveals that the s-cis form is 1.93 kcal/mol more stable than the s-trans form. The calculated dipole moments for eight analyzed structures are also presented in Table 1. In all cases, the dipole moments are lower for the s-cis form, in which the component dipoles of the pyrrole ring and the carbonyl group[12] are in the antiparallel arrangement.

The theoretically predicted difference of the carbonyl absorption by the MPC-NMe s-cis and s-trans conformers is 12 cm^{-1} (Table 2). On the basis of the above calculations, it seems that both forms would not have the same carbonyl absorption. Additionally, our observation of the behavior of carbonyl absorption in different solvents revealed the same shift direction of the ν_{CO} band for MPC-NMe as was observed for the ν_{CO} band of the s-cis form of MPC (Table 2).

It is intriguing that the carbonyl absorption of MPC-NMe (Table 2) is shifted by 10 cm^{-1} toward higher wavenumber in comparison with MPC. This effect may be explained by a decrease in the conjugation of the ester group with the pyrrole ring.[18] On the opposite side, the calculated ring bond lengths remain almost unchanged, but the skeletal vibration of the pyrrole ring moves to a lower wavenumber and occurs at 1528 cm^{-1} like the unsubstituted pyrrole ring (Table 2). Additionally, calculated frequencies of the IR absorption by the s-cis MPC and s-cis MPC-NMe conformers show the same values of ν_{CO}. Taking into consideration the fact that the distance between the hydrogen atom of the methyl group and the carbonyl oxygen for conformer s-cis of MPC-NMe is short (2.66 Å), increasing hindrance may be occurring. This may cause the ν_{CO} and δ_{CH3} vibrations to require more energy.[19] Thus, carbonyl absorption is shifted by 10 cm^{-1} toward higher wavenumber, and δ_{CH3} appears at 1483 cm^{-1} in comparison with 1443 cm^{-1} for MPC.

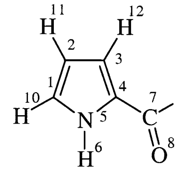
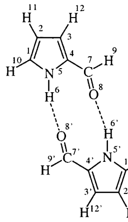
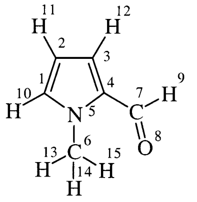
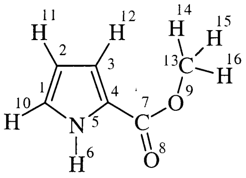
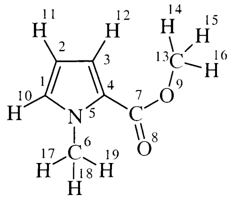
Some authors[4,20] have suggested that intramolecular hydrogen bonding, $N-H\cdots O=C$, in α-substituted N−H pyrroles may occur and influence the frequency of the ν_{CO} absorption. The shift of the carbonyl band in the *N*-methyl derivatives appears as a consequence of removal of weak intramolecular hydrogen bonding. The possibility of the existence of intramolecular hydrogen bonds is investigated with the use of Bader theory[5] in the next sections.

Vibrational Spectra of PC and PC-NMe. The frequencies and IR intensities of the normal modes of the PC and PC-NMe conformers were calculated at the B3LYP/6-311++G** level of theory, and proposed descriptions of the bands are presented in the Supporting Information (experimental IR data are also included).

The aldehydic C−H weak absorptions at 2829 and 2755 cm^{-1} were observed experimentally. The single ν_{C-H} normal mode for the s-cis and s-trans conformers of PC was predicted theoretically, at 2871 and 2786 cm^{-1}, respectively. The appearance of low-frequency bands in the IR spectrum is the effect of the Fermi resonance between the fundamental aldehyde stretching vibration and the first overtone of the aldehyde C−H deformation band.

The IR spectra of CCl_4 solutions of PC studied in this work reveal a single absorption of the free carbonyl group at 1666 cm^{-1}, whereas absorption of the associated CO group was observed at 1655 cm^{-1}. The theoretically estimated CO frequency is 1685 cm^{-1} for the s-cis conformer and 1712 cm^{-1} for the s-trans form of PC. The experimental CO frequency is much closer ($\Delta\nu = 19$ cm^{-1}) to the calculated CO frequency

TABLE 3: Selected Bonds for Conformers of PC, PC-NMe, MPC, and MPC-NMe Obtained at the B3LYP/6-311++G Level of Theory**[a]

												
	s-cis PC	s-trans PC	PC dimer		s-cis PC-NMe	s-trans PC-NMe		s-cis MPC	s-trans MPC		s-cis MPC-NMe	s-trans MPC-NMe
N5-H6	1.00	1.008	1.024				N5-H6	1.009	1.008			
C7-O8	1.22	1.215	1.231	C7-O8	1.22	1.218	C7-O8	1.217	1.210	C7-O8	1.217	1.212
H6-O8	2.63			O8-H15	2.727		H6-O8	2.57		O8-H19	2.662	
H6-O8’			1.835									
C4-C7-O8	123.9	125.7		C4-C7-O8	126.3	124.2	C4-C7-O8	123.8	125.7	C4-C7-O8	125.8	123.9
N5-H6-O8’			164.4	C6-H15-O8	90.4		N5-H6-O8	93.2		C6-H19-O8	89.9	
N5-H6-O8	91.8			C6-H15-H9		124.1						

[a] Bond lengths in Å and angles in deg.

for the s-cis form than for the s-trans ($\Delta\nu = 46$ cm^{-1}) form. This confirms earlier experimental results. The conformational preferences of some heteroaromatic aldehydes and their *N*-methyl derivatives were recognized previously on the basis of various physical methods: ^{1}H, ^{13}C NMR,[21-23] measurements of dipole moments,[12] molar Kerr constants,[24] ab initio studies,[25] and IR spectral investigations.[4,18] These studies showed a very strong preference for the s-cis arrangement of the N−H and CO groups. Furthermore, it was demonstrated that for PC-NMe the s-cis conformer is a dominant form (95%).[18,23] The IR spectroscopic investigations[1,4] revealed the presence of one absorption band for the free carbonyl group.

Replacement of the N−H group by the N−CH$_3$ group causes shifts of the ν_{CO} band to higher wavenumber (Table 2). From the B3LYP/6-311++G** level of theory, the predicted shift of the wavenumber associated with the CO mode of the s-cis form amounts to 4 cm^{-1}, from 1685 cm^{-1} for PC to 1689 cm^{-1} for PC-NMe. The shift obtained from experiment is the same, from 1666 to 1670 cm^{-1}.

This unexpected shift of the ν_{CO} band of PC-NMe toward higher wavenumber in comparison with the ν_{CO} band of PC may be correlated with the influence of C4−C7−O8 angle changes. Introduction of the N−CH$_3$ group leads to this angle increasing from 123.9° to 126.3° in the case of the s-cis form of PC and from 123.8° to 125.8° in the case of the s-cis MPC molecule (Table 3). The angle deviations of the C7 sp^2 hybridized orbital result in steric strain effects that cause the frequency of absorption of the carbonyl group to be shifted to higher values.

Table 2 also lists calculated frequencies and intensities for the normal modes of the PC dimer. The calculated IR spectrum of the dimeric form of PC is very close to the experimental spectrum recorded for the concentrated CCl$_4$ solution. The IR spectrum of PC has also been investigated in cyclohexane and hexane solutions. The intensity of the N−H associated band decreases slowly with dilution in favor of the free N−H band. Even for strongly diluted cyclohexane solutions, the intensive bands of the N−H and C=O associated groups were observed at 3272 and 1659 cm^{-1}, respectively. Furthermore, the bands at 604 and 568 cm^{-1} corresponding to the bound and free N−H group (δ^{oop}_{N-H}) were also observed. A similar observation was ascribed [1] for the dimeric form of MPC, where bands at 607 and 557 cm^{-1} were detected. Characteristic out-of-plane-bending bands seem to be suitable key bands for recognition of intermolecular interactions of pyrroles.

The above observations indicate that PC centrosymmetric dimers with two N−H···O hydrogen bonds are stable in solution. The shift in position of the N−H vibrations for experimental IR data of 0.001 and 0.1 M CCl$_4$ solutions (Table 2) is equal to 186 cm^{-1} indicating that this group is involved in rather strong intermolecular interaction. A similar trend to form cyclic dimers was already observed in the related system of MPC.[2] To compare the strength of the hydrogen bonds of dimers formed by MPC and PC, one may determine the experimental value of $\Delta\nu_{N-H}$ for the free and associated groups. In the case of the MPC dimer, $\Delta\nu_{N-H}$ is equal to 147 cm^{-1}. The shift of the N−H band is 39 cm^{-1} higher for the PC dimer. This may suggest that the hydrogen bond is a little stronger for the PC dimer than for the MPC one.

DFT Calculation Results. Table 3 presents the selected geometrical parameters for the molecular structures of PC, PC-NMe, MPC, and MPC-NMe optimized within the B3LYP/6-311++G** level of theory. The optimizations were performed for both the s-cis and s-trans forms of these species as well as for the PC dimer. The results concerning possible intramolecular N−H···O=C hydrogen bonds are not conclusive. The C=O bonds for the s-cis conformers are slightly longer than the corresponding C=O bonds for the s-trans conformers. This may suggest the existence of weak intramolecular hydrogen bonds; however, the difference between the corresponding bond lengths is not significant. Additionally, there is no difference in the length between the possible N−H donors (the differences are about 0.001 Å), and it is well-known that the elongation of the proton-donating bond is treated as evidence for the existence of hydrogen bonding.[26,27] Table 3 shows the significant elongation of the C=O and N−H bonds for the dimer of PC (s-cis form) for which the double connection through two N−H···O hydrogen bonds exists. According to the assumptions for the calculations presented in the previous section, both hydrogen bonds are equivalent. The H···O contact length for them amounts to 1.835 Å, and N−H···O angle is equal to 164.4°, which is close to linearity. For comparison, for the intramolecular N−H···O contact of the s-cis conformer of PC, the H···O length amounts to 2.631 Å and N−H···O angle is equal to 91.8°; these values for intramolecular contact do not manifest the existence of a hydrogen bond.

The B3LYP/6-311++G** results show that the energy of the single N−H···O interaction within the dimer amounts to −6.9 kcal/mol; this value of energy is corrected for basis-set superposition error (BSSE) according to the counterpoise method of Boys and Bernardi.[28]

The calculations also show that for all species studied here the s-cis conformers are more stable than the s-trans conformers (Table 1). This is in agreement with the IR experimental and theoretical results analyzed in the previous sections. The relationships between the energy and the angle of rotation of the CHO or C(OCH$_3$)O group around the C−C (aromatic) bond for all four species were investigated here. The angle of rotation amounts to zero for the s-cis conformation; for the angle of rotation equal to 180° there is the s-trans conformer. Table 1 presents the real energies for the s-cis conformers and for the greatest energies obtained during the rotation of the CHO or C(OCH$_3$)O group. The greatest energies correspond to angles of rotation of 90° and may be treated as transition states for reactions of transformation of conformations from the s-cis form to the s-trans form. The barrier heights for those reactions are about 12−16 kcal/mol except for MPC-NMe for which it is 125 kcal/mol; this is probably due to steric effects.

Analysis of the Bond Critical Points. Earlier[29,30] and recent investigations[31−33] show that Bader theory is a powerful method for the analysis of hydrogen bonds. The topological criteria have been given for the existence of such interactions.[34] According to published reports, the bond critical point (BCP) for H···Y (where Y is a proton-acceptor center within the X−H···Y hydrogen bond) should exist. Additionally, for this BCP the electron density ($\rho_{\mathrm{H\cdots Y}}$) should be in the range from 0.002 to 0.035 au, and the range of the corresponding Laplacian ($\nabla^2\rho_{\mathrm{H\cdots Y}}$) is from 0.024 to 0.139 au. The topological analysis shows that there are no intramolecular hydrogen bonds for the s-cis conformers of PC and MPC, opposite to suggestions given by Meakins et al.;[4] for these cases it was not possible to find the bond critical points corresponding to H···O contacts. In contrast, there are such BCPs for the dimer of PC, and the corresponding $\rho_{\mathrm{H\cdots O}}$ and $\nabla^2\rho_{\mathrm{H\cdots O}}$ values are 0.030 and 0.114 au. We see that these values are within the ranges proposed by Koch and Popelier[34] that are indicative of the existence of hydrogen bonding. Figure 3 presents the contour maps of the electron density for the s-syn and s-trans conformers of PC and for the PC dimer (the dimer of the s-cis conformer). We see the existence of H···O BCPs for the dimer which indicates the connection through two hydrogen bonds. Because the electron density at the BCP is a property which decays exponentially with increasing distance,[5] it may be treated not only as evidence of hydrogen-bond interaction but also as a measure of hydrogen-bond strength. For example, for the linear (trans) conformation of the water dimer this value amounts to 0.024 au for the B3LYP/6-311++G** wave function, and the H···O distance calculated at this level is equal to 1.933 Å; the hydrogen-bond energy for the water dimer is about 5−6 kcal/mol. The greater value of the electron density for the H···O BCP of the PC dimerand the shorter H···O contact of 1.835 Å indicate that the single hydrogen bond for the PC dimer is stronger than the one for the water dimer.

The use of Bader theory allows us to detect intramolecular hydrogen bonds for PC-NMe and MPC-NMe. For example, Figure 4 (structure E) shows the contour map of the s-cis form of PC-NMe; there is the C−H···O intramolecular hydrogen bond. Table 4 shows the topological parameters for the intramolecular hydrogen bonds studied here; the electron densities of contacts and corresponding Laplacians are given. The values of $\rho_{\mathrm{H\cdots O}}$ and $\nabla^2\rho_{\mathrm{H\cdots O}}$ are within ranges which guarantee the existence of hydrogen bonding. However, these values correspond to the transition states because the calculations at the B3LYP/6-311++G** level of theory show one imaginary frequency for these structures. Figure 4 also shows the contour map of the optimized structure of the s-cis conformer of PC-NMe (structure F). For this case there is the bond path connecting the oxygen atom of the CHO group and the carbon atom of the CH$_3$ group. A similar situation was found earlier;[35] it was detected that for the C$_3$H$_7$TiCl$_2$$^+$ molecular structure there is the intramolecular agostic C−H···Ti bond, but the optimized geometry corresponds rather to the structure for which the C···Ti bond path exists. In such a case the carbon atom is a five-coordinated carbon like the structure presented in Figure 4 (structure F). These observations concerning five-coordinated carbon atoms are not controversial in view of the maturity of hypercarbon chemistry.[36] A situation similar to that found for the s-cis conformer of PC-NMe occurs for both conformers of MPC-NMe; there are C−H···O intramolecular contacts for the transition states (one imaginary frequency for each molecular structure), and for the optimal molecular structures without imaginary frequencies, the C···O bond paths exist.

A very interesting situation is observed in this study for the molecular structure of the s-trans conformer of PC-NMe. Figure 4 (structure D) shows the contour map of that structure. We see the bond path for the H···H intramolecular interaction. It may be treated as an unconventional C−H···H hydrogen bond known as the dihydrogen bond[37] because the hydrogen atom acts here as a proton acceptor. However, there is one imaginary frequency for that system showing that it is not stable and that

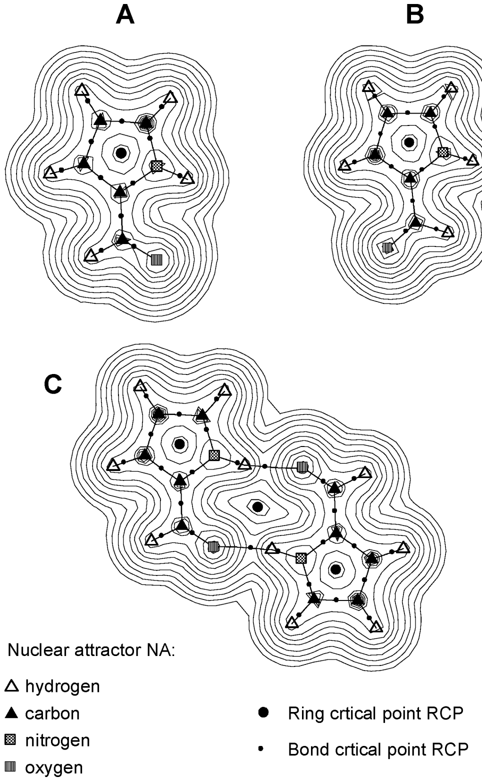


Figure 3. Contour maps of the electron density of PC: (A) cis form; (B) trans form; (C) PC dimer. The density contours in these figures increase in electron charge inward approximately in the progression of $2^n \times 10^{-3}$, where $n = 1, 2, 3, ..., 20$ (the following increase may be detected starting from the external line: 0.001; 0.002; 0.004; 0.008; 0.02; 0.04; 0.08; 0.2; 0.4; 0.8; 2.0 au).

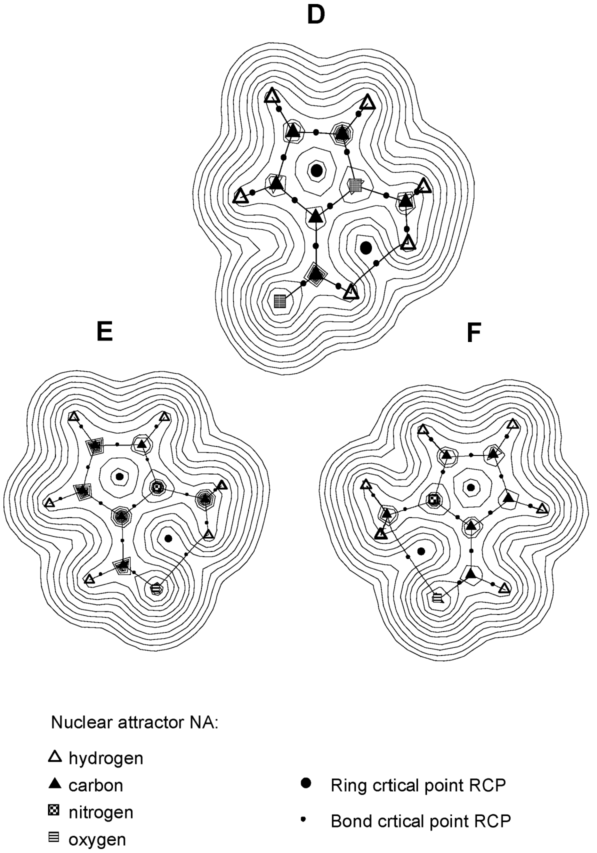


Figure 4. Contour maps of the electron density of the s-trans and the s-cis forms of PC-NMe. (D) corresponds to the first-order transition state for the s-trans form of PC-NMe, (E) corresponds to the first-order transition state for the s-cis form of PC-NMe, and (F) corresponds to the optimized geometry for the s-cis form of PC-NMe. The density contours increase in charge in the same way as for Figure 3.

TABLE 4: Topological Parameters (in au) for the Intramolecular Hydrogen Bonds for the Transition State Systems[a]

system	type of hydrogen bond	$\rho_{H\cdots Y}$	$\nabla^2\rho_{H\cdots Y}$
PC-NMe, s-cis	C−H···O	0.017	0.058
PC-NMe, s-trans	C−H···H	0.012	0.040
MPC-NMe, s-cis	C−H···O	0.019	0.067
MPC-NMe, s-trans	C−H···O	0.020	0.076

[a] Those structures for which one imaginary frequency was detected.

it may be related to the transition state. Dihydrogen bonds were investigated both experimentally[38] and theoretically,[39] and it was pointed out that for some cases such interactions are as strong as medium or even strong typical hydrogen bonds.[39] Intramolecular B−H···H−N hydrogen bonds have also been found in boronated heterocycles, for example, *N*-1-(cyanoboryl)cytosine.[40] Similar intramolecular B−H···H−O interactions have been investigated recently using different levels of theory up to MP2/6-311++G(3d,3p).[41] The calculations have been performed for a (1*Z*)-2-borylethen-1-ol molecule and its derivatives[41] to show that in this case an effect similar to that of the intramolecular O−H···O bonds known as resonance-assisted hydrogen bonds (RAHBs) may be detected.[42,43]

The system found in this study is an unconventional hydrogen bond for two reasons: the unconventional proton-donating bond, C−H, and the unconventional proton acceptor. Such systems have not been investigated yet. For the s-trans conformer of PC-NMe analyzed here, the electron density and its Laplacian for H···H intramolecular contact within the C−H···H hydrogen bond amount to 0.012 and 0.040 au, respectively (Table 4). This means that this kind of interaction may be treated as a hydrogen bond according to the topological criteria given by Koch and Popelier.[34]

Conclusions

The experimental and theoretical results show that for all species investigated here, MPC, PC, MPC-NMe, and PC-NMe, the s-cis conformer is dominant in solution, and it is more stable than the s-trans conformer. It was shown that there are no intramolecular hydrogen bonds for the PC and MPC species. The use of Bader theory indicates the lack of these interactions. The shift of carbonyl absorptions of PC-NMe and MPC-NMe toward higher wavenumber in comparison with ν_{CO} absorptions of PC and MPC may be correlated with the influence of C4−C7−O8 angle changes.

Intramolecular hydrogen bonds exist for *N*-methyl derivatives. However, all systems for which the intramolecular hydrogen bonds were detected correspond to transition states (Table 4). This means that for stable conformers of 2-substituted 1*H*-pyrroles corresponding to optimized structures the existence of intramolecular hydrogen bonds is not preferable. For the s-trans conformer of PC-NMe there is an intramolecular C−H···H hydrogen bond for the transition state.

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Supporting Information Available: Theoretical and experimental IR data for conformers of some 2-substituted 1*H*-pyrroles. This material is available free of charge via the Internet at http://pubs.acs.org.

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