

Spectroscopic and theoretical studies on the monomeric and dimeric forms of methyl pyrrole-2-carboxylate

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Received (in Montpellier, France) 13th August 2001, Accepted 9th October 2001

First published as an Advance Article on the web

The infrared spectra of a very dilute solution and a KBr pellet of methyl pyrrole-2-carboxylate (MPC) are compared with the theoretical spectra of monomeric and dimeric forms of MPC obtained at the RHF/6-311+G* level of theory, showing that dimers connected through N–H...O interactions are dominant in the solid state. *Ab initio* calculations are used for the analysis of geometries of both monomeric and dimeric forms of MPC. The H-bond energy for MPC dimer is calculated and the basis set superposition error (BSSE) is corrected by the counterpoise method of Boys and Bernardi. The Bader theory is also used to analyse N–H...O interactions within the MPC dimer. The experimental IR spectra, results of *ab initio* calculations and the analysis of topological parameters obtained from the Bader theory show that H-bonds of MPC dimer are of medium strength. The N–H...O interactions of MPC are also compared with a sample of other conventional and unconventional H-bonds and a measure of the H-bond strength introduced recently is applied in this study.

Peramine and some other pyrrolopyrazine compounds are produced in plants containing endophytic fungi. These alkaloids are responsible for antiherbivory effects and are an antifeedant agent for insects.¹ An antifeedant is a feeding deterrent that inhibits feeding or causes a cessation of feeding but does not directly kill the insects. In seeking antifeedant compounds a few peramine derivatives were synthesised² according to the modified Dumas method.³ Methyl pyrrole-2-carboxylate (MPC) is one of the intermediate products. The structure of MPC has been the subject of detailed study on the basis of both experimental IR spectra and *ab initio* HF calculations.⁴ 6-31G** and 6-311++G** basis sets were used in the study. IR spectra reveal that in CCl₄ solution the concentration of one of the conformers is higher than the concentration of the second conformer. *Ab initio* calculations show that such a conformer is more stable than the second one. In the more stable conformer the carbonyl group is located on the same side as the NH group.⁴ Such a location favours the formation of centrosymmetric dimers with two N–H...O hydrogen bonds. For these H-bonds N–H is the proton donor and the C=O carbonyl group is the accepting centre. Such C=O...H–N interactions often exist in biological structures.⁵ Knowledge of them allows the understanding of complicated processes resulting in the tertiary structure of proteins, interactions within DNA chains and the reaction mechanisms of some biologically active compounds.

Hence the aim of this study is the analysis of C=O...H–N interactions within the dimer of MPC. The geometrical, topological and energetic properties of the dimer are compared with the same properties of monomeric MPC. Additionally, experimental and theoretical IR spectra are analysed for the monomer and dimer of MPC.

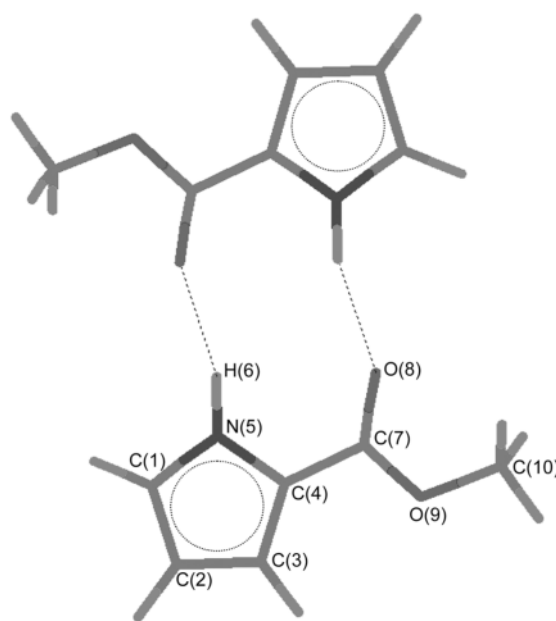
Experimental

Methyl pyrrole-2-carboxylate (MPC) was synthesised according to the method of Bailey *et al.*⁶ The crude product was crystallised from a mixture of hexane and ethyl acetate (1 : 1; V : V). The structure was proved by ¹H NMR and FT-IR

spectra. The FT-mid-IR spectra were recorded using a Nicolet Magna IR 550 Series II spectrometer equipped with KBr beamsplitter and DTGS (deuterated triglycine sulfate) detector. The sample was measured in a CCl₄ solution (0.001 M) in a KBr cell of 0.1 mm pathlength and in a KBr pellet.

Computational details

The calculations were performed with the Gaussian 98 program⁷ at the RHF/6-311+G* level of theory. For all complexes and monomers the geometry was fully optimised. For the MPC dimer the molecules are connected by two equivalent N–H...O=C H-bonds; there is an inversion centre between



Scheme 1 The projection of the dimer of methyl pyrrole-2-carboxylate.

moieties of the dimer and hence the molecules are geometrically equivalent. In spite of such restrictions the geometrical parameters of N–H...O bonds in the MPC dimer were optimised. In other words, the only constraints were connected with the equivalency of two double H-bonded MPC molecules. The H-bond energies were computed as the difference in energy between the complex, on the one hand, and the sum of isolated monomers, on the other hand.⁸ Basis set superposition error (BSSE) was corrected by the counterpoise method of Boys and Bernardi.⁹ The hydrogen bonding properties predicted on the basis of the Bader theory¹⁰ were obtained from AIM-PAC programs.¹¹

Results and discussion

Analysis of IR spectra

As a continuation of our previous study⁴ we have compared the monomeric and dimeric forms of methyl pyrrole-2-

carboxylate using FT-IR spectroscopy and *ab initio* calculations at the RHF/6-311+G* level of theory.

The energy calculations for the optimised geometry of two rotameric forms of MPC showed⁴ that the molecule was more stable in the Z-conformation around the single bond between the pyrrole ring and the methoxycarbonyl group. The location of the carbonyl group on the same side as the N–H bond suggested that the formation of the cyclic dimer shown in Scheme 1 should be dominant. As a consequence, the IR spectrum exhibits a band corresponding to N–H engaged in H-bonding even in a very dilute solution. The frequencies and IR intensities of the monomer and dimer of MPC were calculated and the proposed description of the bands is presented in Table 1. The scale factor of 0.8929 was used.¹²

The theoretically estimated NH stretching mode frequencies of the monomer and of the dimer of MPC are located at 3498 and 3417 cm^{−1}, respectively. The infrared spectra of a very dilute solution and of a KBr pellet revealed a ν_{NH} absorption band at 3465 and 3290 cm^{−1}, respectively. The relatively large

Table 1 Theoretical (calculated using the RHF/6-311+G* level of theory) and experimental IR data of monomeric and dimeric forms of methyl pyrrole 2-carboxylate

Mode	Monomer					Dimer				
	<i>v</i> / cm ^{−1}	<i>v</i> ^a / cm ^{−1}	IR int./ km mol ^{−1}	Approx. description ^b	Exp. ^c <i>v</i> / cm ^{−1}	<i>v</i> / cm ^{−1}	<i>v</i> ^a / cm ^{−1}	IR int./ km mol ^{−1}	Approx. description ^b	Exp. ^d <i>v</i> / cm ^{−1}
1	3918	3498	115.9	ν _{N–H}	3465	3827	3417	1270	ν _{N–H}	3290
2	3429	3062	2.8	ν _{C–H}	3098	3429	3062	6.7	ν _{C–H}	3138
3	3421	3055	5.1	ν _{C–H}	3070	3421	3055	10.9	ν _{C–H}	3122
4	3400	3036	5.8	ν _{C–H}	2994	3399	3035	14.5	ν _{C–H}	3004
5	3325	2969	28.1	ν _{CH₃} ^{as}	2951	3325	2969	63.0	ν _{CH₃} ^{as}	2978
6	3304	2950	33.4	ν _{CH₃} ^{as}	2905	3303	2949	66.1	ν _{CH₃} ^{as}	2953
7	3226	2880	50.3	ν _{CH₃} ^s	2840	3226	2880	94.9	ν _{CH₃} ^s	2844
8	1931	1724	564.7	ν _{CO}	1701	1899	1696	1727.1	ν _{CO}	1676
9	1749	1562	33.7	δ _{N–H} , ν _{ring}	1554	1745	1558	67.1	δ _{N–H} , ν _{ring}	1557
10	1638	1463	6.1	δ _{CH₃}		1638	1463	7.4	δ _{CH₃} , δ _{N–H}	
11	1628	1454	6.9	δ _{CH₃}		1631	1456	203.6	δ _{N–H} , δ _{CH₃} , δ _{CH}	
12	1622	1448	77.4	δ _{CH₃} , δ _{N–H}	1443	1629	1455	15.2	δ _{CH₃}	
13	1603	1431	16.2	δ _{CH} ^{ip}		1615	1442	37.0	δ _{CH₃} , δ _{N–H}	1445
14	1600	1429	21.7	δ _{N–H} , ν _{ring} , δ _{CH₃}	1411	1605	1433	46.8	δ _{N–H} , δ _{CH} ^{ip}	1406
15	1551	1385	234.2	ν _{ring} , δ _{CH₃}		1535	1371	614.1	δ _{CH} ^{ip} , δ _{CH₃} , δ _{N–H}	
16	1459	1302	517.1	δ _{N–H} , ν _{C–O–C} , δ _{CH₃} , ν _{ring}	1319	1471	1313	819.0	δ _{N–H} , δ _{CH₃}	1321
17	1393	1244	3.0	δ _{N–H} , δ _{CH} ^{ip}		1402	1252	21.9	δ _{N–H} , δ _{CH} ^{ip}	1265
18	1346	1202	52.7	δ _{CH₃} , δ _{N–H}	1198	1350	1205	186.6	δ _{CH₃} , δ _{N–H}	1203
19	1298	1159	137.4	δ _{CH₃} , ν _{C–O–C} , δ _{N–H}	1163	1306	1166	243.7	δ _{CH₃} , ν _{C–O–C}	1169
20	1296	1157	3.4	δ _{CH₃}	1130	1295	1156	6.3	δ _{CH₃}	1128
21	1221	1090	104.4	δ _{N–H} , δ _{CH} ^{ip}	1108	1237	1105	244.4	δ _{N–H} , δ _{CH} ^{ip}	
22	1199	1071	16.5	δ _{N–H} , δ _{CH} ^{ip}	1084	1200	1071	21.9	δ _{CH} ^{ip}	1087
23	1116	996	30.1	δ _{CH} ^{ip}	1033	1121	1001	77.3	δ _{CH} ^{ip}	1029
24	1101	983	54.3	ν _{C–O–C} , δ _{CH} ^{ip}	988	1103	985	89.5	ν _{C–O–C} , δ _{N–H}	980
25	1028	918	4.0	ν _{C–O–C} , δ _{ring} ^{ip}	928	1027	917	18.3	δ _{ring} ^{ip} , δ _{CH₃}	925
26	1006	898	1.1	δ _{CH} ^{oop}		1010	902	0.15	δ _{CH} ^{oop} , δ _{N–H}	892
27	968	864	6.3	δ _{ring} ^{ip} , δ _{CH₃}		978	873	31.8	δ _{N–H} ^{oop} , δ _{CH} ^{oop}	876
28	960	857	3.0	δ _{CH} ^{oop}		969	865	10.4	δ _{ring} ^{ip}	849
29	882	788	10.8	δ _{CH₃} , δ _{COO} ^{ip}		888	793	8.7	δ _{COO} ^{ip} , δ _{CH₃}	796
30	873	779	59.2	δ _{CH} ^{oop} , δ _{COO} ^{oop} , δ _{N–H}		886	791	239.6	δ _{N–H} ^{oop} , δ _{CH} ^{oop}	772
31	834	745	109.6	δ _{CH} ^{oop} , δ _{N–H} ^{oop}		848	757	132.8	δ _{N–H} ^{oop} , δ _{CH} ^{oop}	746
32	694	620	3.5	δ _{N–H} ^{oop} , δ _{ring} ^{oop}	636	823	735	21.2	δ _{N–H} ^{oop} , δ _{CH} ^{oop}	
33	670	598	0.9	δ _{CH} ^{oop}		671	599	0.7	δ _{ring} ^{oop}	
34	595	531	86.8	δ _{N–H} ^{oop} , δ _{CH} ^{oop}	557	666	595	40.8	δ _{N–H} ^{oop} , δ _{ring} ^{oop}	607
35	544	486	4.0	δ _{COO} , δ _{ring} ^{oop}	500	548	489	12.0	δ _{ring} ^{ip} , δ _{COC} ^{ip} , δ _{N–H}	510
36	419	374	0.08	δ _{COO} , δ _{ring}		423	378	0.6	δ _{ring} ^{ip} , δ _{COC} ^{ip}	
37	340	304	25.2	δ _{COC} , δ _{CH₃}		349	312	61.6	δ _{COC} ^{ip} , δ _{CH₃}	
38	234	209	0.9	δ _{CH₃} , δ _{ring} ^{oop} , δ _{COO} ^{oop}		230	205	1.5	δ _{CH} ^{oop} , δ _{CH₃}	
39	174	155	0.05	δ _{CH₃}		182	163	0.09	δ _{CH₃}	
40	159	142	3.8	δ _{CH₃} , δ _{ring} ^{ip}		166	148	6.9	δ _{CH₃} , δ _{N–H} , δ _{CH} ^{ip}	
41	116	104	1.6	δ _{ring} ^{oop} , δ _{CH₃}		132	118	0.7	δ _{CH₃} , δ _{CH} ^{oop}	
42	100	89	7.0	δ _{ring} ^{oop} , δ _{CH₃} , δ _{CO}		112	100	10.5	δ _{CH₃} , δ _{CH} ^{oop}	
43						61	55	2.3	δ _{CH} ^{ip} , δ _{CH₃}	
44						31	28	1.1	δ _{N–H} ^{oop} , δ _{CH} ^{oop}	
45						14	13	0.01	δ _{CH₃} , δ _{CH} ^{oop} , δ _{ring} ^{oop}	

^a Scaled by 0.8929. ^b Vibrational modes: *v*, stretching; *δ*, deformational (all kinds); superscripts: *s*, symmetrical, *as*, asymmetrical; *ip*, in-plane; *oop*, out-of-plane. ^c Measured as a CCl₄ solution (0.001 M). ^d Measured from a KBr pellet.

shift of 175 cm^{-1} in the position of the NH stretching band towards lower wave numbers in the solid spectrum indicates rather strong intermolecular interactions.¹³ These observations are in good agreement with the calculated frequencies and intensities. For example, calculations show that the associated NH band is much more intense than the free NH band; 1270 and 116 km mol^{-1} , respectively (Table 1).

There is also agreement between theoretical and experimental frequencies for the C=O group. The theoretically estimated C=O frequency for the dimer at 1696 cm^{-1} is close to the experimental value of 1676 cm^{-1} . For the monomer the theoretical C=O frequency of 1724 cm^{-1} is comparable to the experimental one of 1701 cm^{-1} . The dimer C=O stretching mode shows a marked shift of 25 cm^{-1} (experimental value) to lower frequency in comparison with the monomer C=O stretching mode.

The 1558 and 1562 cm^{-1} theoretically obtained modes for the dimer and the monomer are not simple N–H bending modes, but they are the result of coupling with pyrrole aromatic ring stretching vibrations. The experimental dimer frequency at 1557 cm^{-1} is similar to the theoretical value of δ_{NH} ($\Delta\nu = 1\text{ cm}^{-1}$). The *ab initio* calculated monomer C–O–C stretching mode at 1159 cm^{-1} moves to a higher frequency at 1166 cm^{-1} for the dimer. The theoretically estimated ν_{COC} dimer frequency agrees with the experimental value ($\Delta\nu = 3\text{ cm}^{-1}$).

The NH out-of-plane bending band shows a very high sensitivity to the hydrogen bond interaction.¹⁴ This vibration is observed in dilute CCl_4 solution as a band of medium intensity at 557 cm^{-1} (theoretical value 531 cm^{-1}) and is shifted towards a higher frequency at 607 cm^{-1} (theoretical value of 595 cm^{-1}) in the solid state.

Shifts in position of C=O and NH vibrations indicate that these groups are involved in rather strong intermolecular interactions in the solid state. Considerable shifts in band position occur on passing from the monomer to the dimer. Thus, the NH and C=O stretching bands show marked shifts to lower frequencies, while the NH bending and C–O–C stretching modes move to higher frequencies. IR spectra calculated at the RHF/6-311+G* level of theory give additional support for the presumption that the dimer is the dominant form of MPC in the solid state.

Ab initio and AIM results for monomeric and dimeric forms of methyl pyrrole-2-carboxylate

To get a better insight into the nature of N–H...O=C interactions within the MPC dimer, *ab initio* RHF/6-311+G* calculations have been performed for this study. Table 2 shows selected geometrical parameters of the Z-conformation of monomeric MPC and of the MPC dimer (Scheme 1). We see the elongation of the N–H bond from 0.992 \AA to 0.997 \AA due to H-bond formation. Elongation is also observed for the C=O carbonyl group—from 1.191 \AA to 1.199 \AA . The H...O intermolecular distance amounts to 2.012 \AA , less than the corresponding sum of van der Waals radii (2.6 \AA , 1.4 \AA for the oxygen atom and 1.2 \AA for the hydrogen atom). Such an intermolecular distance suggests the existence of a H-bond of medium strength. Table 3 shows the net atomic charges within the H-bonded ring of the MPC dimer; the net charges of the monomeric form are also given, showing a meaningful charge fluctuation due to H-bond formation.

Table 4 presents the topological parameters obtained from the Bader theory;¹⁰ the electronic densities at the bond critical points, ρ , and their Laplacians, $\nabla^2\rho$. The same topological values for the monomer of MPC are also given in Table 4. AIM calculations in this study were based on RHF/6-311+G* wave functions obtained for the monomeric and dimeric MPC.

Table 2 Selected geometrical parameters of monomeric and dimeric forms of MPC; both forms were optimized within the RHF/6-311+G* level of theory; bond lengths in \AA , angles in degrees. The atom numbering is the same as in Scheme 1

Parameter	Monomer	Dimer
C1–C2	1.368	1.372
C2–C3	1.417	1.411
C3–C4	1.365	1.370
C1–N5	1.348	1.342
C4–N5	1.366	1.366
C4–C7	1.463	1.456
C7–O8	1.191	1.198
C7–O9	1.318	1.316
O9–C10	1.415	1.415
N5–H6	0.992	0.997
C1–C2–C3	106.9	106.6
C2–C3–C4	107.1	107.0
C3–C4–N5	108.1	108.2
C1–N5–C4	109.4	109.1
N5–C1–C2	108.6	109.1
N5–C4–C7	119.3	120.8
C3–C4–C7	132.6	131.0
C4–C7–O8	123.1	124.1
C4–C7–O9	113.0	113.0
O8–C7–O9	123.9	122.9
C7–O9–C10	117.4	117.8

Table 3 Selected net atomic charges (in au) of monomeric and dimeric forms of MPC. The atom numbering is the same as in Scheme 1

Atom	Monomer	Dimer
N5	–0.385	–0.517
H6	0.486	0.720
C4	0.251	0.421
C7	–0.510	–0.539
O8	–0.405	–0.541
O9	–0.100	–0.075

A decrease of the ρ values is connected with an increase in the bond lengths. This is observable for the N–H and C=O bonds in the MPC dimer in comparison with the same bonds in the monomer. Popelier proposed¹⁵ a range for values of an electronic density at the H...Y bond critical point, $\rho_{\text{H}\cdots\text{Y}}$, and a range of its Laplacian, $\nabla^2\rho_{\text{H}\cdots\text{Y}}$, for H-bonds within X–H...Y systems. These proposals may be treated as topological criteria of the existence of H-bonding. The ranges are from 0.002 to 0.035(0.04) au for the electronic density values and from 0.024 to 0.139 au for the Laplacians. The $\rho_{\text{H}\cdots\text{O}}$ and $\nabla^2\rho_{\text{H}\cdots\text{O}}$ values for the bond critical point of the H...O

Table 4 Selected topological parameters (electronic densities at bond critical points and their Laplacians both in au) of monomeric and dimeric forms of MPC. The atom numbering is the same as in Scheme 1. The values for the monomer are given in parentheses

Bond	Electronic density	Laplacian
C1–C2	0.329 (0.332)	–1.034 (–1.046)
C2–C3	0.306 (0.303)	–0.903 (–0.890)
C3–C4	0.331 (0.334)	–1.040 (–1.055)
C1–N5	0.322 (0.316)	–0.388 (–0.353)
C4–N5	0.308 (0.306)	–0.402 (–0.358)
C4–C7	0.297 (0.294)	–0.933 (–0.918)
C7–O8	0.427 (0.435)	0.050 (0.087)
C7–O9	0.319 (0.318)	–1.332 (–1.297)
O9–C10	0.238 (0.237)	0.134 (0.132)
N5–H6	0.346 (0.353)	–2.158 (–2.077)

intermolecular contact of the MPC dimer amount to 0.018 and 0.088 au, respectively; they are within the ranges described above.

The binding energy was also calculated for MPC as the difference between the dimer energy and that of two monomers;⁸ it amounts to $-9.38 \text{ kcal mol}^{-1}$, which corresponds to two equivalent $\text{N-H}\cdots\text{O}$ H-bonds. Hence the H-bond energy is $-4.69 \text{ kcal mol}^{-1}$; the correction for BSSE according to Boys and Bernardi⁹ was included.

Comparison of the MPC dimer with other H-bonded systems

The geometrical, energetic and topological parameters describing the nature of the H-bond within the MPC dimer are compared with the same parameters of other simple H-bonded systems. The following complexes are considered here: $(\text{H}_2\text{O})_2$ (water, linear *trans* dimer), $(\text{F}\cdots\text{H}\cdots\text{F})^-$, $(\text{C}_2\text{H}_2)_2$ (T-shaped configuration), $\text{H}_2\text{CO}\cdots\text{HF}$, $(\text{HCOOH})_2$, $\text{H}_3\text{N}\cdots\text{HF}$, $\text{H}_2\text{CO}\cdots\text{HCCH}$, $\text{LiH}\cdots\text{HF}$. We see different types of hydrogen bonds: conventional ones such as $\text{O-H}\cdots\text{O}$, $\text{F-H}\cdots\text{O}$, $\text{F-H}\cdots\text{N}$ and unconventional ones such as $\text{C-H}\cdots\text{O}$, $\text{C-H}\cdots\pi$ or the dihydrogen bond $-\text{F-H}^{+\delta}\cdots\text{H}^{-\delta}$. There is also an $(\text{F}\cdots\text{H}\cdots\text{F})^-$ system in the sample which represents the strongest known H-bond interaction.¹⁶ The $\text{H}_2\text{CO}\cdots\text{HF}$ and $\text{H}_2\text{CO}\cdots\text{HCCH}$ complexes have C_{2v} symmetry, the same as a free water molecule. This means that for both complexes the mirror plane contains all atoms. For the $\text{H}_2\text{CO}\cdots\text{HF}$ dimer there is a twofold rotation axis going through the oxygen atom of the accepting molecule and through the atoms of the donating molecule. For the $\text{H}_2\text{CO}\cdots\text{HCCH}$ dimer the two-fold rotation axis runs through the atoms of the donor and through the oxygen atom of the formaldehyde molecule. Similarly, the $\text{H}_3\text{N}\cdots\text{HF}$ complex is of C_{3v} symmetry. The centrosymmetric dimer of formic acid is also considered here, in which two equivalent $\text{O-H}\cdots\text{O}$ bonds exist. The centrosymmetric dimers of carboxylic acids were often the subject of studies, both experimental¹⁷ as well as theoretical.¹⁸ The sample also contains the case of the unconventional dihydrogen bonded system— $\text{LiH}\cdots\text{HF}$ where HF is the proton donating molecule and LiH is the proton acceptor. The hydrogen atom of the LiH molecule has a net negative charge and is a Lewis base centre. Such dihydrogen bonded systems have also been investigated extensively, both from the experimental¹⁹ as well as from the theoretical point of view.²⁰ We see that the chosen sample contains different conventional and unconventional H-bonds. Such a choice is conditioned by one of the aims of this study—a comparison of $\text{N-H}\cdots\text{O}$ interactions existing in the MPC dimer with different H-bonds known from earlier studies.

Table 5 contains the H-bond parameters of the systems enumerated above: H-bond energies, proton donating bond parameters like bond lengths (X-H), the electronic densities at X-H bond critical points, ρ_{HX} , and the Laplacians, $\nabla^2\rho_{\text{HX}}$. The parameters of the $\text{Y}\cdots\text{H}$ contacts are also given: $\text{H}\cdots\text{Y}$

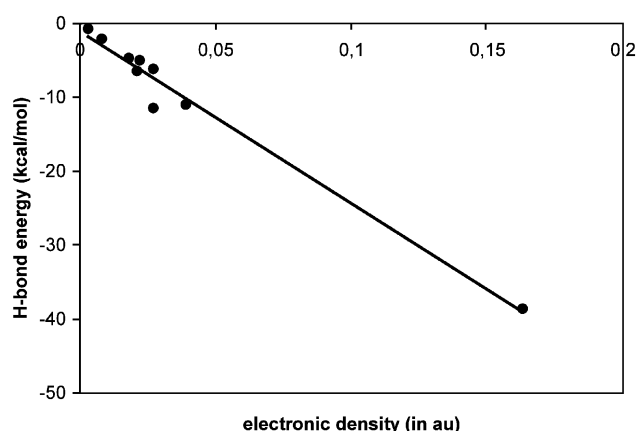


Fig. 1 The relation between H-bond energy and the electronic density at the $\text{H}\cdots\text{Y}$ bond critical point.

distance, $\rho_{\text{Y}\cdots\text{H}}$, and $\nabla^2\rho_{\text{Y}\cdots\text{H}}$. The comparison of the parameters presented in Table 5 with those of the MPC dimer shows that the $\text{N-H}\cdots\text{O}$ bonds are of medium strength. The $\text{N-H}\cdots\text{O}$ H-bond energy is only a little less than the $\text{O-H}\cdots\text{O}$ bond energy within a water dimer but it is stronger than almost all of the unconventional H-bonds presented here. The $\text{F-H}^{+\delta}\cdots\text{H}^{-\delta}$ dihydrogen bond is an exception ($-11.25 \text{ kcal mol}^{-1}$ for the binding energy) but it was pointed out earlier that dihydrogen bonds often belong to the category of strong H-bonds.^{20c}

Fig. 1 presents the dependence between the H-bond energy and the electronic density at the $\text{H}\cdots\text{Y}$ bond critical point. The linear correlation coefficient amounts to 0.989. There is a good correlation in spite of the fact that the sample investigated here is heterogeneous. It was pointed out earlier that the topological parameter $\rho_{\text{Y}\cdots\text{H}}$ may be treated as a measure of the H-bond strength but this was for homogenous samples of related complexes.²¹

A new measure of H-bond strength has been introduced recently.²² It is based on the geometrical and topological parameters of the X-H proton donating bond within an $\text{X-H}\cdots\text{Y}$ H-bonded system:

$$A_{\text{com}} = \left\{ \left[(r_{\text{X-H}} - r_{\text{X-H}}^0) / r_{\text{X-H}}^0 \right]^2 + \left[(\rho_{\text{X-H}}^0 - \rho_{\text{X-H}}) / \rho_{\text{X-H}}^0 \right]^2 + \left[(\nabla^2\rho_{\text{X-H}} - \nabla^2\rho_{\text{X-H}}^0) / \nabla^2\rho_{\text{X-H}}^0 \right]^2 \right\}^{1/2} \quad (1)$$

where $r_{\text{X-H}}$, $\rho_{\text{X-H}}$ and $\nabla^2\rho_{\text{X-H}}$ correspond to the parameters of the proton donating XH bond involved in H-bonding: the bond length, the electronic density at the HX bond critical point, and the Laplacian of that density, respectively; $r_{\text{X-H}}^0$, $\rho_{\text{X-H}}^0$ and $\nabla^2\rho_{\text{X-H}}^0$ correspond to the same parameters of the XH bond not involved in H-bond formation (*i.e.*, of the free molecule). It was pointed out that this parameter well describes the H-bond strength both for homogeneous samples as

Table 5 Geometrical (in Å) and topological (in au) parameters of XH proton donating bonds and $\text{H}\cdots\text{Y}$ contacts for $\text{X-H}\cdots\text{Y}$ H-bonded complexes. H-bond energies (corrected for BSSE) are also given (in kcal mol^{-1}). The results for the MPC dimer are included

Complex	XH bond length	ρ_{XH}	$\nabla^2\rho_{\text{XH}}$	$\text{H}\cdots\text{Y}$ distance	$\rho_{\text{H}\cdots\text{Y}}$	$\nabla^2\rho_{\text{H}\cdots\text{Y}}$	H-bond energy
$(\text{C}_2\text{H}_2)_2$	1.057	0.292	-1.120	3.062	0.003	0.009	-0.72
$(\text{H}_2\text{O})_2$	0.945	0.375	-2.757	1.985	0.022	0.096	-5.00
$(\text{F}\cdots\text{H}\cdots\text{F})^-$	1.133	0.163	-2.909	1.133	0.163	-2.909	-38.62
$\text{H}_2\text{CO}\cdots\text{HF}$	0.904	0.375	-3.012	1.898	0.021	0.111	-6.44
$(\text{HCOOH})_2$	0.956	0.356	-2.657	1.883	0.027	0.113	-6.16
$\text{H}_3\text{N}\cdots\text{HF}$	0.919	0.351	-2.726	1.821	0.039	0.119	-10.99
$\text{H}_2\text{CO}\cdots\text{HCCH}$	1.059	0.292	-1.133	2.358	0.008	0.038	-2.11
$\text{LiH}\cdots\text{HF}$	0.917	0.354	-2.745	1.590	0.027	0.063	-11.47
MPC	0.997	0.346	-2.158	2.012	0.018	0.088	-4.69

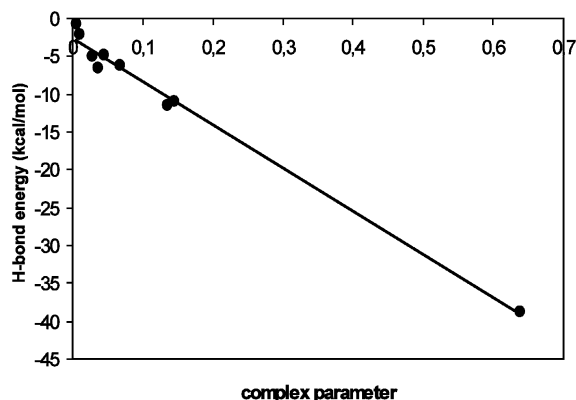


Fig. 2 The relation between H-bond energy and the complex parameter Δ_{com} .

well as for heterogeneous ones.²² A similar situation is observed here. Fig. 2 shows the correlation between the H-bond energy and the parameter described above (Δ_{com}). The linear correlation coefficient amounts to 0.995 in spite of the heterogeneous sample considered here. This correlation is presented only to compare MPC interactions with different H-bonds. However, it also confirms the earlier conclusions²² that the Δ_{com} parameter is a good descriptor of the H-bond strength.

Conclusions

The experimental IR spectra for the monomeric and dimeric forms of methyl pyrrole-2-carboxylate were compared with the complex theoretical studies based on *ab initio* calculations and topological parameters derived from the AIM theory of Bader. All results show that dimers are dominant in the solid state and that N-H...O H-bonds connecting moieties within the MPC dimer are of medium strength. The findings concerning the strength of H-bonds in the MPC dimer are supported by the studies on a sample of different types of H-bonds.

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