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Structure, Energetics, and Vibrational Frequencies of the Pyrazole-Water Complex

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Summary. The structure, energetics, and vibrational frequencies of the pyrazole-water complex is investigated within the framework of the ab initio self-consistent field method. Full optimization at DZP and TZP quality of the complex and its constituents has been carried out. The results indicate that a cyclic structure is the most stable with SCF/MP2 binding energies of −5.7/−7.0 kcal/mol. Using appropriate scaling factors, we can predict a complete set of vibrational spectra of isolated subunits as well as of the hydrogen-bonded complex and compare them with experimental data where available.

Keywords. Ab initio; Pyrazole-water; Structure; Vibrational frequencies; SCF; MP2.

Struktur, Energiezustände und Vibrationsfrequenzen des Pyrazol-Wasser-Komplexes

Zusammenfassung. Es wurden die Struktur, die energetischen Zustände und die Vibrationsfrequenzen des Pyrazol-Wasser-Komplexes mittels einer ab initio self consistent field Methode untersucht. Es wurde die volle Optimierung des Komplexes und seiner Komponenten in DZP- und TZP-Qualität durchgeführt. Dabei war eine cyclische Struktur mit SCF/MP2-Bindungsenergien von −5.7/−7.0 kcal/mol am stabilsten. Unter Verwendung geeigneter Skalierungsfaktoren kann man einen vollständigen Satz der Vibrationsspektren der isolierten Untereinheiten und des Wasserstoffbrücken-gebundenen Komplexes voraussagen und – falls vorhanden – mit den experimentellen Daten vergleichen.

Introduction

Hydrogen bonding is of prime importance for the structure, conformation and particularly the stability of biomolecules. This has motivated a number of theoretical and experimental studies of the corresponding intermolecular interactions [1–6]. A nitrogen containing ring system such as pyrazole is of interest, since it is ubiquitous in biological systems. Thus, the study of H-bonding of pyrazole-water should provide valuable insights into the interaction in more complex systems containing these remarkable subunits.

Few ab initio calculations for heterocycle-water systems have been reported [7]. Most of the works were constrained to a rather small basis set, the gradient method and electron correlation were not taken into account. In this study, full geometry optimization of the pyrazole-water complex has been carried out using DZP and

TZP basis sets for the first time. The binding energies are corrected for BSSE (Basis Set Superposition Error) by means of the counter-poise procedure [8] and for electron correlation effects via the second-order Moller-Plesset perturbation theory (MP2) [9–10].

Method

All calculations have been carried out using the TURBOMOLE [11] package of programs, which is based on the "direct SCF and two-electron integral transformation method" [12–14]. The two-electron repulsion integrals are re-computed when needed rather than being stored.

In order to increase efficiency, the algorithm includes improved integral estimation, selective storage of extensive and frequently used integrals, and minimization of difference density matrices as described in detail in Ref. [14].

In the present study, the following basis sets of Contracted Gauss Type Orbitals (CGTO) type and the corresponding contraction schemes, together with the exponents of polarization functions have been employed in the computations (primitive GTOs from Ref. [15]).

DZP

C: (8, 4, 1)/[4, 2, 1] $n_d = 0.80$
N: (8, 4, 1)/[4, 2, 1] $n_d = 1.00$
O: (8, 4, 1)/[4, 2, 1] $n_d = 1.20$
H: (4, 1)/[2, 1] $n_p = 0.80$

TZP

C: (9, 5, 1)/[5, 3, 1] $n_d = 0.80$
N: (9, 5, 1)/[5, 3, 1] $n_d = 1.00$
O: (9, 5, 1)/[5, 3, 1] $n_d = 1.20$
H: (5, 1)/[3, 1] $n_p = 0.80$

Gradient optimization techniques [16] have been employed to fully optimize the complex and its constituent at DZP and TZP levels. Geometry optimization were terminated when the gradient norm with respect to internal coordinates was smaller than 10^{-3} $E_h a^{-1}$. The energy change was then below $5 \cdot 10^{-6}$ E_h and the changes in the bond lengths and angles less than 0.05 pm and 0.01°, respectively.

The optimized structures were later used as equilibrium structures in the calculations of the harmonic force field (analytical second derivatives of the electronic energy with respect to coordinates). The force constants obtained were used to determine harmonic vibrational frequencies.

Results and Discussion

Structure and Energetics

The fully optimized structures of the pyrazole complex and their constituents obtained with the SCF method employing DZP and TZP basis sets are illustrated in Fig. 1.

Isolated Monomers: Comparison of Computed and Experimental Structures

Table 1 lists the DZ, DZP, TZP SCF structures for pyrazole and compares them with available experimental data [17]. There are only minor differences between DZP and TZP results (bond distances differ by at most 0.6 pm and angles by 0.3°).

Table 1. Experimental gas phase and theoretical structure of pyrazole (cf. Fig. 1 for numbering of atoms)

Bond	Bond length (pm)			
	TZP	DZP	DZ	Exp. [23]
N1-N2	132.9	132.3	135.0	134.9
N2-C3	129.9	130.0	131.4	133.9
C3-C4	141.4	141.4	141.9	141.6
C4-C5	136.0	136.4	136.8	137.2
C5-N1	136.0	136.4	136.8	137.2
N1-H1	99.1	99.6	99.4	99.9
C3-H3	107.0	107.7	107.1	108.7
C4-H4	106.8	107.5	107.1	108.2
C5-H5	106.9	107.6	107.2	108.4
Angle	**Bond angle (degree)**			
	TZP	DZP	DZ	Exp. [23]
N2-N1-C5	112.9	112.6	112.1	113.1
N1-C5-C4	106.5	106.6	106.5	106.4
C5-C4-C3	103.8	104.0	104.9	104.5
C4-C3-C2	111.5	111.6	111.0	111.9
C3-N2-N1	105.3	105.2	105.4	104.1
H1-N1-C5	127.6	127.8	128.4	–
H5-C5-C4	131.7	131.6	131.2	–
H4-C4-C3	128.4	128.2	127.6	–
H3-C3-N2	120.1	120.2	120.4	–

The deviations between the TZP SCF and the experimental geometry are less than 1.2 pm for C–C bonds, 2.0 pm for the N–N bond and upto 4.0 pm for the N2–C3 bond. Ring angles at this level differ by at most 1.2° from experiment. The most appreciable deviation between experiment and SCF calculation concerns the N2–C3 distance in the ring system, as already noted for imidazole [18–19]. These deviations probably reflect effects of electron correlation since the TZP result should be relatively close to the SCF limit.

Hydrogen-Bonded Complex

The structures of the pyrazole-water complex have been fully optimized under C_s and without C_1 symmetry constraints. Changes in the complexation are relatively small, and are documented in Table 2. The most stable C_s structure is not shown since it is similar to the C_1 structure (Fig. 1) except that H7 and H6 atoms of water are out of the molecular plane. Other possible C_s structures like a "bifurcated structure" or a planar structure where the N–H of pyrazole points towards the O atom of water are less stable by about 0.95 kcal/mol and 1.18 kcal/mol, respectively.

Vibrational analysis yields one imaginary frequency for the most stable C_s structure (out of plane motion of the non hydrogen-bonded proton (H7) of water). This indicates that the true minimum may be reached from this C_s structure by movement of H7 which is not involved in hydrogen bond formation.

Although, the C_1 structure is 0.5 kcal/mol lower in energy than the C_s configuration (DZP/SCF, no BSSE correction) this difference virtually vanishes after the BSSE correction (difference less than 0.1 kcal/mol, see Table 3). The results

Table 2. SCF optimized structure parameters for pyrazole-water (see Fig. 1 for atom numbering)

Bond	Bond length (pm)		
	TZP (C_s)	DZP (C_s)	DZP (C_1)
N1–N2	132.9	129.6	132.3
N2–C3	130.1	130.2	130.2
C3–C4	141.0	141.1	141.1
C4–C5	136.4	136.7	136.7
C5–N1	136.6	136.6	136.6
C3–H3	107.0	107.7	107.7
C4–H4	106.8	107.5	107.5
C5–H5	106.9	107.6	107.6
H1–01	227.2	223.8	218.0
H6–N2	222.7	225.4	223.5
N1–O1	291.1	283.3	287.6
O1–H6	94.7	95.1	95.1
O1–H7	94.1	94.4	94.6
N1–H1	99.5	100.0	100.1

Angle	Bond angle (degree)		
	TZP (C_s)	DZP (C_s)	DZP (C_1)
N2–N1–C5	112.4	112.6	112.6
N1–C5–C4	106.9	106.8	106.7
C5–C4–C3	103.8	103.9	103.8
C4–C3–C2	111.4	111.3	111.2
C3–N2–N1	105.4	105.6	105.6
H1–O1–H6	79.9	82.3	77.9
O1–H6–N2	128.8	125.7	130.2
H6–N2–N1	91.4	88.7	88.2
N2–N1–H1	118.8	118.4	117.9
N1–H1–O1	121.1	125.0	125.2
H6–O1–H7	107.8	106.5	105.1
N2–N1–H1–O1	0.0	0.0	−1.3
N2–N1–H1–H6	0.0	0.0	−3.8
N2–N1–H1–H7	0.0	0.0	19.2

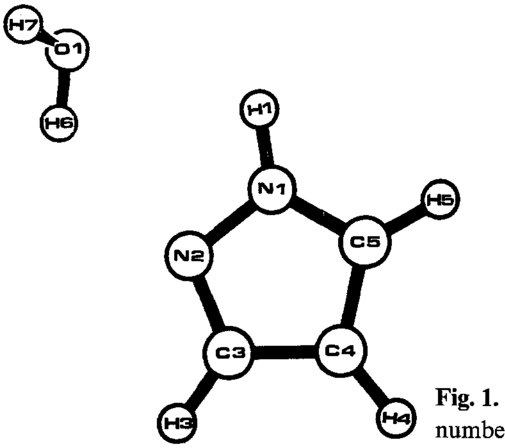

Fig. 1. Schematic representation of geometry and atom numbering for the pyrazole-water complex

Table 3. Computed SCF and MP2 interaction energies and Basis Set Super position Errors (kcal/mol)

Basis sets	SCF		MP2		ΔE^a
	$-\Delta E^b$	BSSE	$-\Delta E^b$	BSSE	$\Delta E^{SCF} + \Delta E^{MP2}$
DZP[c]	5.71	2.70	1.33	1.93	7.04
DZP[d]	5.78	2.04	1.32	1.44	7.10
TZP[d]	6.18	0.76	1.39	0.96	7.57

[a] $\Delta E = \Delta E^{SCF} + \Delta E^{MP2}$; [b] BSSE corrected; [c] C_1 structure; [d] C_s structure

of intermolecular interaction energies, obtained at the DZP structure given in Fig. 1, are as follows:

$$\text{SCF/DZP;} \quad \Delta E^{SCF} = -5.7\,\text{kcal/mol} \tag{1}$$

$$\text{MP2/DZP;} \quad \Delta E^{MP2} = -1.3\,\text{kcal/mol.} \tag{2}$$

If we combine ΔE^{SCF} and the correlation interaction we estimate the total interaction energy

$$\Delta E = \Delta E^{SCF} + \Delta E^{MP2} = -7.0\,\text{kcal/mol} \tag{3}$$

we note that ΔE^{SCF} results obtained from the two basis sets (DZP and TZP) differ by 0.4 kcal/mol (cf. Table 3). Inclusion of the correlation stabilizes the complex by 0.47 kcal/mol in TZP relative to DZP. The optimized N(H)...O distance is 283.3 pm, the (O) H...N distance is 225.4 pm.

Vibrational Frequency: Comparison of Computed and Experimental spectra

Even with relatively large basis sets there is a discrepancy between the computed and experimental frequencies. This discrepancy is in part due to the use of the Hartree–Fock approximation and in part to the fact that calculated frequencies are harmonic frequencies whereas the experimental ones are anharmonic.

Table 4. Comparison of the calculated and experimental vibrational frequencies of pyrazole (in cm^{-1})

No.	Sym.	Approx. assignment	Theoretical data		Experimental data [23]
			DZP-Frequ.	Scaled Frequ.	Vapour [23]
1	A″	NH wagging	593	534	515
2	A″	Ring torsion	694	625	612
3	A″	Ring torsion	754	679	668
4	A″	CH wagging	851	766	744
5	A″	CH wagging	983	885	833
6	A″	CH wagging	1022	920	879
7	A′	Ring def.	905	815	910
8	A′	Ring def.	1001	900	931
9	A′	CH def.	1020	918	1021
10	A′	CH def.	1125	1013	1057
11	A′	NH def.	1154	1039	1121
12	A′	Ring def.	1247	1122	1164
13	A′	CH def.	1382	1244	1253
14	A′	Ring def.	1529	1376	1359
15	A′	Ring def.	1544	1390	1394
16	A′	Ring def.	1631	1468	1446
17	A′	Ring def.	1741	1567	1530
18	A′	CH stretch	3400	3060	3074
19	A′	CH stretch	3417	3075	3090
20	A′	CH stretch	3425	3083	3140
21	A′	NH stretch	3896	3506	3500

The calculated frequencies of pyrazole-water, pyrazole, and water are listed in Table 4 together with the available experimental frequencies. The frequencies of pyrazole are higher than those of the ones observed with an error of about 10% as ordinary results of the ab initio calculations [20]. This is a systematic deviation which is the basis for the success of various scaling methods. Schaefer et al. [21] have used a constant scaling factor while Pulay et al. [22] have used different scaling factors assigned to each diagonal force constant matrix element labeled with different internal coordinates of the molecule. In Table 5 two scaling factors were used. A scaling factor was determined by dividing the observed frequency of a subunit by the calculated frequency of each corresponding vibration of the subunit. Scaled frequencies of pyrazole-water were therefore evaluated by multiplying DZP frequencies by these scaling factors. The DZP single scaled factor of 0.9 was also used and tabulated in the last column of Table 5. With these appropriate scaling factors we can predict the frequency shifts induced by complexation. The symmetrical stretching vibration of water is at 3654 cm^{-1} with a red-shift of 62 cm^{-1}. The asymmetrical stretching vibration of water is red-shifted by 41 cm^{-1} to lower value. The bending mode is blue-shifted by 20 cm^{-1}. The major changes of frequencies of pyrazole involve the N–H motions. The N–H stretching mode, originally located at about 3500 cm^{-1} in the monomer, occurs at 3451 cm^{-1} in the

Table 5. Computed vibrational frequencies of pyrazole, water and the pyrazole-water complex

Approx. assignment	*Py*H[a] vapour	*Py*H[b] factor	*Py*H/H_2O[c] cal	*Py*H/H_2O[d] SCF scale
1 N–H wagging	515	0.868	580	601
2 ring torsion	612	0.882	639	652
3 ring torsion	668	0.886	714	725
4 CH wagging	744	0.874	748	770
5 CH wagging	833	0.847	836	888
6 CH wagging	879	0.860	880	921
7 ring def.	910	1.006	1008	902
8 ring def.	931	0.930	944	914
9 CH def.	1021	1.001	1045	940
10 CH def.	1057	0.940	1061	1016
11 NH def.	1121	0.971	1122	1040
12 ring def.	1164	0.933	1162	1133
13 CH def.	1253	0.907	1263	1254
14 ring def.	1359	0.887	1361	1378
15 ring def.	1394	0.903	1395	1391
16 ring def.	1446	0.887	1461	1482
17 ring def.	1530	0.879	1527	1563
18 CH stret.	3074	0.904	3076	3063
19 CH stret.	3090	0.904	3091	3077
20 CH stret.	3140	0.917	3144	3086
21 NH stret.	3500	0.898	3443	1600
22 bending	1649	0.939	1670	3451
23 sym. stret.	3832	0.928	3768	1600
24 Asym. stret.	3943	0.931	3901	3654

[a] Ref. [23]; [b] factor = ν_{obs}/ν_{cal}; [c] scaled with pyrazole scale factors (b); [d] scaled with optimized SCF scale factor

hydrogen bonded complex. The N–H wagging is found at about 600 cm^{-1} with a blue shift of 67 cm^{-1}.

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