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REGULAR ARTICLE

Coupled cluster, B2PLYP and M06-2X investigation of the thermochemistry of five-membered nitrogen containing heterocycles, furan, and thiophene

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Abstract Herein, the thermochemical properties of five-membered rings heterocycles were studied employing the CCSD(T) methodology coupled with the correlation consistent basis sets and including corrections for relativistic and core-valence effects as well as anharmonicities of the potentials. For pyrrole, furan, imidazole, pyrazole, 1H-1,2,4-triazole, and 1H-tetrazole, the mean absolute deviation (MAD) of the $\Delta H^{o}_{f,298}$, computed at the CCSD(T) level, is 0.5 kcal/mol with respect to the experimental values. In the case of 1H-1,2,3-triazole, 2H-1,2,3-triazole, 4H-1,2,3-triazole, 4H-1,2,4-triazole, 2H-tetrazole, and pentazole, we propose the following $\Delta H^{o}_{f,298}$: 62.6, 59.2, 85.0, 54.2, 77.7, and 107.5 kcal/mol, respectively. For thiophene, we revisit our previous result and propose a value of 26.0 kcal/mol. The theoretical estimations were used to study the performance of the M06-2X and B2PLYP functionals. Also, the convergence toward the complete basis set limit (CBS) was analyzed. M06-2X did not show a smooth convergence toward the CBS limit. Particularly, for the cc-pVTZ and cc-pVQZ basis sets, some problems were detected. Yet, along the cc-pVQZ, cc-pV5Z, and cc-pV6Z basis sets, the TAE smoothly decreased. The diminution of the TAE upon increase in basis set was not expected because the opposite behavior is more frequently observed. The MAD of the total atomization energies determined at the M06-2X level was 0.42 kcal/mol, with respect to the CCSD(T) results. In the case of the double hybrid B2PLYP functional, a smooth convergence toward the CBS limit was detected, even though the performance seriously degradated when the basis set was increased. At the CBS limit, the MAD with respect to the CCSD(T) TAEs was 8.26 kcal/mol.

Keywords Coupled clusters · Correlation consistent basis sets · Entahlpies of formation · Density functional theory · M06-2X · Five-membered ring heterocycles

1 Introduction

The determination of enthalpies of formation of five-membered ring heterocycles has been the focus of theoretical [1–3] and experimental investigations [4–25]. The number of experimental investigations is significantly superior to those conducted by means of accurate first principle calculations. Among the latter, we can highlight the pioneering coupled cluster investigation of furan derivatives published in 2000 by Feller et al. [3], and the studies on five-membered nitrogen-containing heterocycles by Gutowski et al. [1] and da Silva et al. [2], at the CCSD(T) and G3 levels, respectively. The main reason for the scarcity of a large number of theoretical determinations is that the CCSD(T) calculations become intractable as the size of the molecules is increased. In addition, the loss of symmetry seriously affects the performance of the computational codes rendering unfeasible calculations that could have been performed if at least a mirror plane of symmetry is present. It is important to stress that a large number of theoretical articles are necessary to motivate new experimental investigations. That is the case of the HOOO radical, for which tens of theoretical investigations [26] were performed, but it was not until 2010 when an experimental [27] work confirmed the theoretical results (see [26, 27] and references therein for details). Over the last decade, it has been possible for us [28–38] and several

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other research groups [39–77] to achieve levels of accuracy as small as 0.3–0.5 kcal/mol for the determination of enthalpies of formation of small molecules. Considering the success that theory has achieved for small molecules it is expected that theorists would study larger molecules to shed light into their thermochemical properties. Previous theoretical works investigated furan [3], benzene [70, 71], and octane [72]. Herein, we continue the work initiated by the study of thiophene [36], and thus we have applied the state-of-the-art methodologies to perform a detailed analysis of the thermochemistry of pyrrole, furan, thiophene as well as seven nitrogen-containing five-membered ring heterocycles: imidazole, pyrazole, 1H-1,2,3-triazole, 2H-1,2,3-triazole, 4H-1,2,3-triazole, 1H-1,2,4-triazole, 4H-1,2,4-triazole, 1H-tetrazole, 2H-tetrazole, and pentazole. The results obtained show that much like previously observed for small molecules, it is possible to obtain an error smaller than 1 kcal/mol when measuring $\Delta H^{o}_{f,298}$. When experimental data are available for comparison purposes, we determined that the mean absolute deviation with respect to experiment is only 0.5 kcal/mol. For the molecules whose enthalpy of formation is not available, we recommend new values. The benchmark results obtained herein are employed to assess the performance of two recently proposed density functionals: M06-2X and B2PLYP. In addition, we investigated the convergence of these two functionals when correlation consistent basis sets up to sextuple zeta are employed. For M06-2X/cc-pV6Z, the MAD is 0.42 kcal/mol, with respect to the coupled cluster results. However, for B2PLYP, the performance is seriously deteriorated when basis set larger than quadruple zeta is used. Finally, while for B2PLYP, we observed a smooth convergence toward the complete basis set limit that was not the case for M06-2X, which showed some oscillations around the cc-pVQZ basis set. We expect that this work would trigger several experimental and theoretical determinations of the enthalpies of formation of heterocycles, which would allow the construction of a reliable database of enthalpies of formation that can be used to model atmospherical and combustion processes as well as to parameterize new density functionals.

2 Theoretical methods

Coupled cluster theory with single-, double-, and perturbative treatment of triple excitations, namely CCSD(T), was the methodology of choice [78–81], along with the cc-pVXZ and cc-pVXZ X = D, T, Q, 5, 6 [82] basis sets. In the case of thiophene, the basis sets augmented with a tight d function [83] were used because of the well-known problems associated with the estimation of the enthalpies of formation of molecules containing second row atoms. The frozen core approximation was used for the UCCSD(T) calculations. Core-valence correlation effects were estimated as the difference between the full and frozen core UCCSD(T) calculations employing the cc-pwCVXZ basis sets X = T, Q [84]. It is important to note that the 1-s electrons of sulfur were not correlated because the cc-pwCVXZ basis sets were not designed to include those electrons, since they are expected to lie too low in energy to make a significant contribution. The extrapolation of correlation energies to the complete basis set limit was carried out employing the two parameter expression $E = B + C/l^3$ [85], and the HF energy was computed with the cc-pV6Z or cc-pV(6 + d)Z basis set. Scalar relativistic effects were estimated using perturbative techniques at the MVD2 level as implemented in CFOUR [86, 87] and using the cc-pwCVTZ basis set. The spin–orbit splitting for atoms was taken from Moore [88]. Geometry optimizations were undertaken for basis sets up to cc-pV(Q + d)Z, except for the cc-pV(X + d)Z X = 5, 6 ones, for which the cc-pV(Q + d)Z geometry was employed. In the case of the CCSD(T)/cc-pwCVQZ calculations, the CCSD(T)/cc-pwCVTZ geometry was selected. Calculations performed using the cc-pwCV5Z basis set for pentazole indicated that the use of the latter basis set is unnecessary. Indeed, the core-valence correction is increased by 0.03 kcal/mol when the basis set is extended from cc-pwCVQZ to cc-pwCV5Z. The harmonic vibrational frequencies were determined analytically at the CCSD(T)/cc-pV(T + d)Z and B3LYP levels. To evaluate anharmonic contributions to zero-point energy corrections, we computed fundamentals at the B3LYP/6-311 + (3df,2p) level [89–91]. All the CCSD(T) calculations were done with CFOUR [86, 87], whereas the M06-2X [92] and B2PLYP [93] calculations were carried out with Gaussian 2009 [94]. For the M06-2X and B2PLYP calculations, we did geometry optimizations for all basis sets up to cc-pV6Z.

3 Results and discussion

3.1 Enthalpies of formation determined at the CCSD(T) level

The $\Delta H^{o}_{f,298}$ estimated for the three most important five-membered ring heterocycles: furan, pyrrole, and thiophene are presented in Table 1. In the case of pyrrole, we are aware of two experimental results by Hubbard et al. [8] and Zaheeruddin et al. [6]. Both values differ by 9 kcal/mol, thus theory can help decide which is the correct one. Our estimation is 25.0 kcal/mol, only 0.88 kcal/mol lower than the experimental result of Ref. [8], thus supports the work by Hubbard et al. [8]. Although obtained at the G3 level, the result by da Silva et al. [2] is only 0.22 kcal/mol larger than the experimental $\Delta H^{o}_{f,298}$. Turning our attention to furan, we found three experimental determinations of its $\Delta H^{o}_{f,298}$. The fourth $\Delta H^{o}_{f,298}$ was proposed by Pedley [4] considering earlier investigations. The best agreement between experiment and theory is observed with the value proposed by the same group that studied pyrrole [7]. The deviation here is only 0.01 kcal/mol, although when considering Pedley′s revised value the discrepancy is increased to 0.3 kcal/mol. Further extension of the basis set to cc-pV6Z reduces the estimated $\Delta H^{o}_{f,298}$ by only 0.16 kcal/mol. This small change shows the efficiency of the extrapolation approach selected. Overall, the agreement between experiment and theory is superb. Finally, for thiophene, the deviation is larger: 1.5 kcal/mol. Our new $\Delta H^{o}_{f,298}$ for thiophene is 0.85 kcal/mol larger than our previous computation [36]. The reason for the new estimation is that we used an older $\Delta H^{o}_{f,298}$ for the carbon atom. Despite the larger value that we propose now, the deviation with respect to experiment is significantly larger as compared with furan, pyrrole, and other molecules investigated at this level. In line with our previous recommendations, we suggest that a new experimental investigation on the $\Delta H^{o}_{f,298}$ of thiophene would be desirable. It has to be noted that we expect further reduction in our result if connected quadruple excitations are considered since in most cases these excitations have the effect of decreasing enthalpies of formation [37, 73–77].

Table 1 Total atomization energies (kcal/mol) and enthalpies of formation determined for pyrrole, furan, and thiophene (kcal/mol), at the CCSD(T) level

	Pyrrole	Furan	Thiophene
CCSD(T)/∞(5,Q)[a]	1,068.55	990.67	961.24
CCSD(T)/∞(Q,T)[a]	1,068.92	991.37	961.73
CCSD(T)/∞(6,5)[a]		990.51	
M06-2X/cc-pV6Z	1,073.57		
TAE_e	1,068.55	990.67	961.24
Core-valence	5.83	5.31	5.51
Scalar relativistic	1.00	0.96	1.09
Spin–orbit	0.32	0.54	0.88
$ZPE_{harmonic}$	51.71	43.83	41.71
$ZPE_{anharmonic}$	51.10	43.32	41.36
TAE_{0K}	1,021.96	951.16	923.42
$\Delta H^{o}_{f,0}$	29.0	945.71	29.0
$\Delta H^{o}_{f,298}$	**25.0**	**−8.6**	**26.0**
Exp.	25.88 ± 0.12[a]	−8.29[f]	27.47 ± 0.24[g]
Exp.	34.23[b]	−7.12[e]	
		−6.62[b]	
		−8.61[d]	
Theory	26.1[c]		
Theory			

[a] Ref. [8], [b] Ref. [6], [c] Ref. [2], [d] Ref. [7], [e] Ref. [5], [f] Ref. [4], [g] Refs. [9, 10]

The $\Delta H^{o}_{f,298}$ of ten nitrogen-containing five-membered rings is presented in Table 2 and their structures in Fig. 1. For these series of compounds, the experimental values are more dispersed, and without the aid of theoretical calculations, it is almost impossible to decide which is the correct one. Of the ten molecules considered, only for imidazole, pyrazole, 1H-1,2,4 triazole, and 1H-tetrazole, we have found experimental data. For imidazole, our estimation is bracketed by the experimental results by Bedford et al. [12] and Guthrie et al. [13], namely 31.8 ± 0.1 kcal/mol and 30.6 ± 1.8 kcal/mol, respectively. On the other hand, the value by Jimenez et al. [11] viz. 33.29 kcal/mol falls outside the range defined by the other two $\Delta H^{o}_{f,298}$ and thus it will be no longer considered. Our best estimation is 31.2 kcal/mol, being closer to that measured by Bedford et al. [12], which is the same group that performed the aforementioned determinations for furan, pyrrole, and thiophene. Other theoretical computations by da Silva et al. [2] and Gutowski et al. [1] at the G3 and CCSD(T) levels, respectively, support Bedford′s value. For pyrazole, the structural isomer of imidazole, we observe again that our calculation is closer to Bedford′s report. The deviation of our calculations for imidazole and pyrrole is close to 0.6 kcal/mol in both cases, smaller than the usual 1 kcal/mol desired. The G3 estimation by da Silva [2] is also in excellent agreement with the experiment.

The next structural isomers considered are the five triazoles. For 1H-1,2,3 triazole, the best $\Delta H^{o}_{f,298}$ available is the G3 calculation by da Silva et al. [2], viz. 63.7 kcal/mol. In this case, our $\Delta H^{o}_{f,298} = 62.6$ kcal/mol, is lower by 1.1 kcal/mol. We expect that the true value should be bracketed by these two estimations. For 1H-1,2,4 triazole, two experimental [11, 14] measurements have been reported which differ only by 0.2 kcal/mol. Our calculation is less than 0.3 kcal/mol far so; for this molecule, the agreement between experiment and theory is excellent. For 2H-1,2,3-triazole, 4H-1,2,3 triazole, and 4H-1,2,4-triazole determined the following $\Delta H^{o}_{f,298}$: 59.2, 85.0, and 54.2 kcal/mol, respectively. As regards the 1H and 2H tetrazole isomers, only the former (which is the least stable) has its enthalpy of formation experimentally determined. The spread of the experimental results is important in this case (3 kcal/mol), which precludes recommendation. The closest agreement with our prediction, viz. 79.4 kcal/mol, is that recommended by Pedley [4], which is only 0.5 kcal/mol larger than ours, even though the

Table 2 Total atomization energies (kcal/mol) and enthalpies of formation of (kcal/mol) of nitrogen-containing heterocycles, determined at the CCSD(T) level

	Imidazole	Pyrazole	1H-1,2,3-Triazole	2H-1,2,3-Triazole	4H-1,2,3-Triazole	1H-1,2,4-Triazole	4H-1,2,4-Triazole
TAE/∞(5,Q)	946.78	935.89	799.54	803.56	776.24	816.79	808.19
TAE/∞(Q,T)	947.24	936.36	799.45	803.53	775.76	816.78	808.0
TAE_e	946.78	935.89	799.64	803.47	776.24	816.79	808.19
Core-valence	5.28	5.12	4.39	4.28	3.68	4.38	4.28
Scalar relativistic	1.12	1.11	1.07	1.11	0.88	1.14	1.05
Spin–orbit	0.24	0.24	0.16	0.16	0.16	0.16	0.16
$ZPE_{anharmonic}$	44.05	44.11	36.54	37.0	34.9	37.07	36.6
$ZPE_{harmonic}$	44.60	44.65	37.00	37.4	35.3	37.50	37.0
TAE_{0K}	906.65	895.55	766.16	769.57	744.38	782.37	774.66
$\Delta H^{o}_{f,0}$	35.1	46.2	66.4	63.0	88.2	50.2	57.9
$\Delta H^{o}_{f,298}$	**31.2**	**42.3**	**62.6**	**59.2**	**85.0**	**46.4**	**54.2**
Exp.	31.8 ± 0.1^{c}	43.3 ± 2.1^{c}				46.3 ± 0.45^{f}	
Exp.	30.6 ± 1.8^{d}	42.9 ± 0.2^{e}				46.1 ± 0.2^{e}	
Exp.	33.29 ± 0.45^{e}						
Theory[a]	31.9	42.8	63.7			46.8	
Theory[b]	31.6					46.4	

	1H-Tetrazole	2H-Tetrazole	Pentazole
TAE/∞(5,Q)	667.03	669.13	522.96
TAE/∞(Q,T)	666.44	668.42	521.88
TAE/∞(6,5)			522.62
TAEe	666.95	669.13	522.96
Core-valence	3.47	3.49	2.65
Scalar relativistic	1.04	1.08	0.98
Spin–orbit	0.08	0.08	0
$ZPE_{anharmonic}$	29.07	20.45	21.39
$ZPE_{harmonic}$	29.39	29.78	21.66
TAE_{0K}	640.35	641.91	503.46
$\Delta H^{o}_{f,0}$	83.1	81.4	111.0
$\Delta H^{o}_{f,298}$	**79.4**	**77.7**	**107.5**
Exp.	78.1^{g}		
Exp.	76.6 ± 0.7^{h}		
Exp.	79.9^{i}		
Theory[a]	81.0	79.0	108.9
Theory[b]	80.2		

[a] Ref. [2], [b] Ref. [1], [c] Ref. [12], [d] Ref. [13], [e] Ref. [11], [f] Ref. [14], [g] Ref. [15], [h] Ref. [16], [i] Ref. [4]

deviation with respect to the other $\Delta H^{o}_{f,298}$ reported is three to five times larger. Previous theoretical estimations at the G3 [2] and CCSD(T) [1] levels are 1.6 and 0.8 kcal/mol larger, respectively. Despite these differences, both values are closer to Pedley′s recommended value. For 2H tetrazole, our best computation is 77.7 kcal/mol, about 1.3 kcal/mol lower than the G3 result mentioned elsewhere [2]. The last molecule is pentazole, which does not have any carbon atoms. For this molecule, we recommend a $\Delta H^{o}_{f,298} = 107.5$ kcal/mol. This value is 1.4 kcal/mol lower than the G3 one. For pentazole, we performed additional CCSD(T) calculations using the cc-pV6Z basis set. The estimated enthalpy of formation was decreased by 0.34 kcal/mol. This value is small for the size of the molecules considered but reflect that in order to reach the 1 kJ/mol accuracy 7Z basis sets would be required. It is

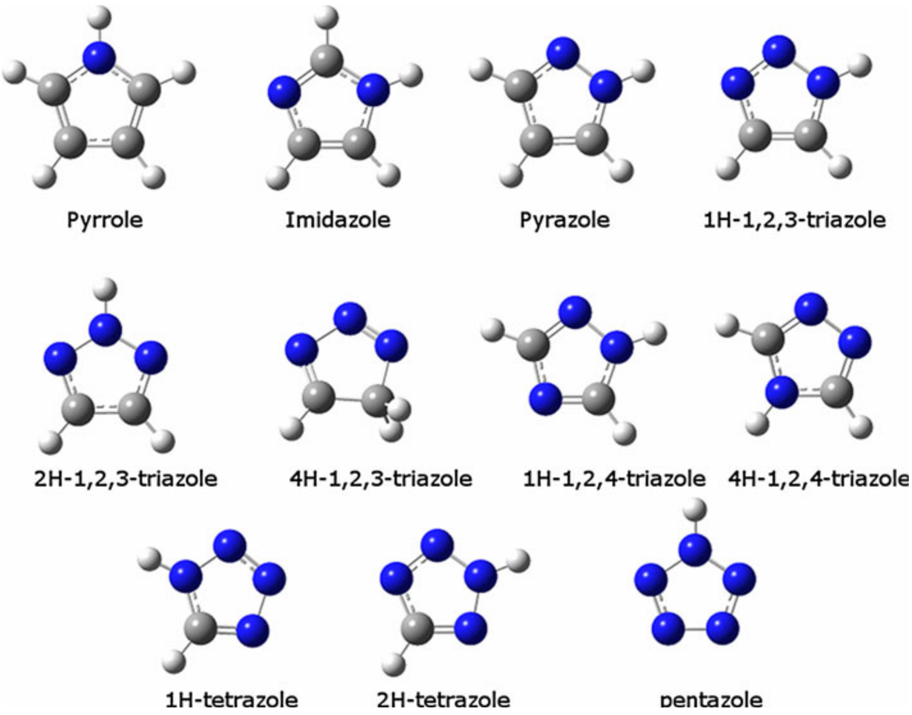

Fig. 1 Nitrogen-containing five-membered rings studied in this work (nitrogen is *blue*, carbon is *gray*, and hydrogen is *white*)

interesting to note that when the number of nitrogen atoms is increased to 4 and 5, larger deviations between the CCSD(T) and G3 methodologies are observed, and also the G3 results deviate more from experiment as discussed for pyrazole 1H-1,2,4 triazole and 1H tetrazole. For the sake of completeness, we plotted in Fig. 2 the $\Delta H^{o}_{f,298}$ vs the number of nitrogen atoms. As noted by da Silva et al. [2], an almost linear relationship is apparent, even when pentazole is included in the plot. It is worth to mention that this trend is observed only if imidazole and the 1,2,4 triazoles are excluded from the liner plot. The reason is related to the fact that in these isomers, the number of N–N bonds is not increased with respect to the compound with $n-1$ nitrogen atoms. For example: pyrazole and imidazole have 2 nitrogen atoms but only pyrazole has one N–N bond. In the same line, the 1,2,3 triazoles and 1,2,4 triazoles have three nitrogen atoms, but the 1,2,3 isomers show 2 N–N bonds whereas the 1,2,4 ones have only one. A proof of this hypothesis is confirmed by comparing the enthalpies of formation of 1H and 2H tetrazole, which differ by 1.7 kcal/mol and thus both can be included in the linear fit. We have previously observed a similar relationship for the enthalpies of formation of HOOH, HOOOH, and HOOOOH. In effect, the $\Delta H^{o}_{f,298}$ was reduced by 10 kcal/mol for each oxygen atom added [26].

In summary, for pyrrole, furan, imidazole, pyrazole, 1,2,4 tetrazole, and 1H-tetrazole, the mean absolute deviation (MAD) of our CCSD(T) results and experiment was 0.5 kcal/mol with the largest deviation being equal to 0.9 kcal/mol (pyrrole). This level of agreement is excellent if we take into account the size of the molecules considered and the problems faced. For example, the zero-point energy corrections are quite large, close to 50 kcal/mol in some cases as we show in Table 3. However, the agreement between the harmonic vibrational frequencies computed at the CCSD(T)/cc-pVTZ and B3LYP/6-311 + G(3df,2p) levels is excellent. Indeed, the mean absolute deviation of the harmonic ZPEs estimated at the DFT level is only 0.04 kcal/mol with respect to the CCSD(T)/cc-pVTZ values. Should we expect a similar agreement if force fields were calculated at the CCSD(T) levels? Preliminary calculations for smaller molecules indicate that this would be the case. Returning to one of the main focus of this work, the determination of thermochemical properties, the excellent agreement observed for the aforementioned enthalpies of formation makes us confident enough to propose new values for 1H-1,2,3-triazole, 2H-1,2,3-triazole, 4H-1,2,3-triazole, 4H-1,2,4-triazole, 2H-tetrazole, pentazole and also to recommend revision for thiophene as the deviation is more than three times the MAD determined.

3.2 Performance of M06-2X and B2PLYP

Due to the low computational cost of DFT as compared with wavefunction-based methodologies, several new functionals are proposed every year. In this work, we studied the performance of two of them at determining the $\Delta H^{o}_{f,298}$ of five-membered ring nitrogen-containing

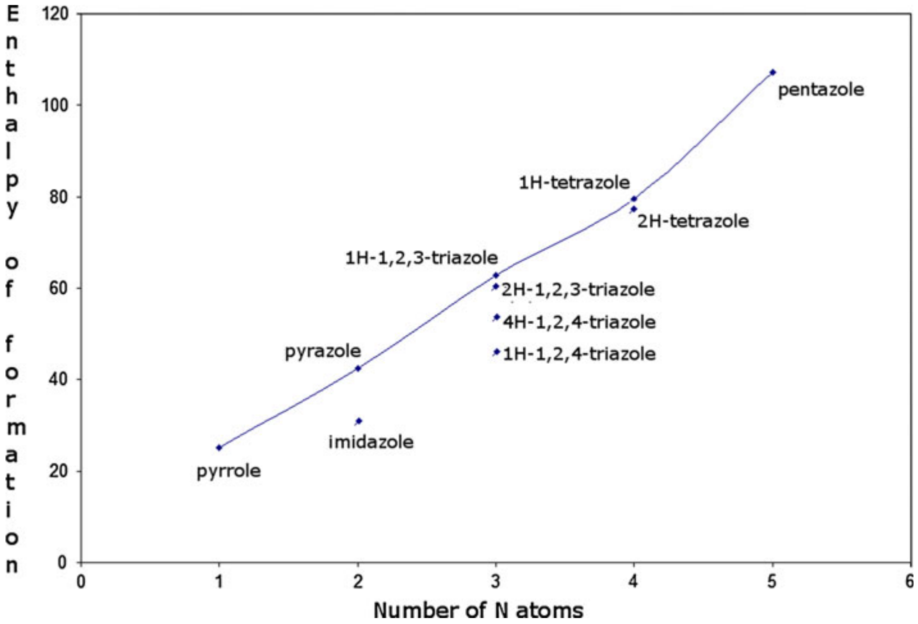

Fig. 2 Enthalpies of formation determined for the nitrogen-containing five-membered rings

Table 3 Zero-point energies (kcal/mol) determined at the CCSD(T)/cc-pVTZ and B3LYP/6-311 + G(3df,2p) levels

	CCSD(T)/ cc-pVTZ	B3LYP/6-311 + G(3df,2p)	
	Harmonic	Harmonic	Anharmonic
Furan	43.81	43.83	43.32
Pyrrole	51.62	51.72	51.10
Imidazole	44.61	44.60	44.05
Pyrazole	44.63	44.65	44.11
1H-1,2,3-triazole	36.96	37.00	36.54
1H-1,2,4-Triazole	37.54	37.50	37.07
1H-Tetrazole	29.36	29.39	29.03
2H-Tetrazole	29.79	29.78	29.45
Pentazole	21.59	21.66	21.39

heterocycles. This comparison is useful because we have constructed a small set of seven molecules and determined their enthalpies of formation with the state-of-the-art theoretical methodologies, thus we got rid of the uncertainties inherent to the experimental investigations. We note that for molecules as small as S_2, we [28, 32] and Feller et al. [68] found serious discrepancies between experiment and theory, which motivated further experimental investigations that confirmed our predictions. Therefore, the use of accurate Coupled Cluster TAE is essential to gauge the performance of density functionals.

When comparing the DFT and CCSD(T) values, the question that arises is what should be actually compared? Enthalpies of formation corrected by relativistic effects, core-valence, and the rest of the corrections or just electronic ones? We have decided to compare with the total atomization energies determined at the CCSD(T) level, extrapolated to the CBS limit, and including only the core corrections. The reason for that decision is that relativistic effects were not considered in the DFT treatments. In Table 4, we show the total atomization energies determined at the M06-2X and B2PLYP levels employing basis sets up to sextuple zeta. In Table 5, the mean absolute deviation determined by each method and basis set is reported. In the case of M06-2X, we observe that the convergence against the cardinal number of the basis set is not smooth. In effect, the TAE determined with the cc-pVQZ basis set is larger than those computed with the cc-pVTZ and cc-pV5Z basis sets. However, going through the cc-pVQZ, cc-pV5Z, and cc-pV6Z series of basis sets the TAE decreases. Therefore, the compatibility problem between the correlation consistent basis sets and M06-2X is observed for the triple and quadruple zeta basis sets only. The MAD computed for M06-2X indicates that the performance is improved as the basis set is increased. When using the cc-pV6Z basis set, the MAD is 0.42 kcal/mol, exceptionally low and a confirmation of the great improvements made with the design of this functional.

We also studied the behavior of B2PLYP. This method shows a stronger basis set dependence than M06-2X but smaller than CCSD(T) as we can appreciate in Fig. 3. In contrast with the result obtained for M06-2X, a well-behaved convergence toward the complete basis set limit is observed. On the contrary, the results seriously worsen when the basis set is increased. For the cc-pVQZ basis set, the MAD reaches its smallest value, viz. 3.47 kcal/mol, 8 times larger than for M06-2X. When the basis set is increased to cc-pV6Z level, the MAD becomes 6.67 kcal/mol, and if extrapolation is performed to the

Table 4 Total atomization energies (kcal/mol) determined at the CCSD(T)/∞, M06-2X and B2PLYP levels

	Imidazole	Pyrazole	1H-1,2,3-Triazole	1H-1,2,4-Triazole	1H-Tetrazole	2H-Tetrazole	Pentazole
CCSD(T)/cc-pVTZ	922.27	911.34	773.02	790.36	638.67	641.03	492.71
CCSD(T)/cc-pVQZ	940.50	929.49	791.70	809.05	657.71	659.95	512.12
CCSD(T)/cc-pV5Z	946.41	935.38	797.93	815.22	664.22	666.37	518.92
CCSD(T)/∞ + Core	**951.96**	**940.91**	**803.84**	**821.09**	**670.42**	**672.55**	**525.61**
B2PLYP/cc-pVTZ	945.13	934.60	799.61	816.47	667.90	670.57	525.02
B2PLYP/cc-pVQZ	**952.35**	**941.77**	**807.11**	**823.97**	**675.61**	**678.17**	**532.91**
B2PLYP/cc-pV5Z	954.53	943.95	809.38	826.19	677.95	680.43	535.33
B2PLYP/cc-pV6Z	955.40	944.83	810.30	827.09	678.91	681.37	536.37
B2PLYP/∞	956.60	947.00	812.21	828.33	680.23	682.66	537.80
M06-2X/cc-pVTZ	950.91	939.21	801.55	819.86	667.76	670.19	521.66
M06-2X/cc-pVQZ	954.93	943.21	806.18	824.45	672.99	675.30	527.53
M06-2X/cc-pV5Z	953.28	941.55	804.35	822.61	670.95	673.22	525.23
M06-2X/cc-pV6Z	**952.60**	**940.91**	**803.67**	**821.88**	**670.22**	**672.48**	**524.53**
M06-2X/Pople[a]	953.81	941.81	804.64	823.27	671.36	673.67	525.07

Bold values are the best values for each level of theory used

[a] Pople = 6-311 + G(3df,2p) basis set

Table 5 Mean absolute deviation (kcal/mol) of M06-2X and B2PLYP with respect to the CCSD(T)/∞ + Core total atomization energies

	MAD
B2PLYP/cc-pVTZ	4.04
B2PLYP/cc-pVQZ	**3.47**
B2PLYP/cc-pV5Z	5.74
B2PLYP/cc-pV6Z	6.67
B2PLYP/∞	8.26
M06-2X/cc-pVTZ	2.35
M06-2X/cc-pVQZ	2.43
M06-2X/cc-pV5Z	0.83
M06-2X/cc-pV6Z	**0.42**
M06-2X/Pople[a]	0.96

Bold values are the best values for each method

complete basis set limit using Halkier′s formula, the MAD is 8.26 kcal/mol. Consequently, with the parameters employed in Gaussian 2009, B2PLYP displays a bad performance at the CBS limit and it is outperformed by M06-2X with all basis sets. Further, tuning of the empirical parameters may improve the B2PLYP determinations but the rather large basis set effect is expected to be maintained because of the MP2 correlation that is included in this method.

4 Conclusions

We studied the thermochemical properties of five-membered rings heterocycles employing the CCSD(T) methodology coupled with the correlation consistent basis sets and including corrections for relativistic and core-valence effects as well as anharmonicities of the potentials. The results obtained were employed to gauge the performance of the recently proposed functionals M06-2X and B2PLYP. The following are the most important findings:

1. For pyrrole, furan, imidazole, pyrazole, 1H-1,2,4 triazole, and 1H-tetrazole, the mean absolute deviation with respect to experiment of $\Delta H^{o}_{f,298}$ computed at the CCSD(T) level is 0.5 kcal/mol and the maximum deviation is 0.88 kcal/mol, for pyrrole.
2. In the case of 1H-1,2,3-triazole, 2H-1,2,3-triazole, 4H-1,2,3-triazole, 4H-1,2,4-triazole, 2H-tetrazole, and pentazole, we propose the following $\Delta H^{o}_{f,298}$: 62.6, 59.2, 85.0, 54.2, 77.7, and 107.5
3. In line with the results we previously found for thiophene [36], we observed a rather large deviation with respect to the experimental value. For thiophene, we propose a $\Delta H^{o}_{f,298}$ of 26.0 kcal/mol.
4. The harmonic ZPEs determined at the B3LYP/6-311 + G(3df,2p) level are extremely close to those computed at the CCSD(T)/cc-pVTZ level. The mean absolute deviation is 0.04 kcal/mol.
5. The M06-2X functional did not show a smooth convergence toward the complete basis set limit. Particularly, for the cc-pVTZ and cc-pVQZ basis sets, some problems were detected. Yet, along the cc-pVQZ, cc-pV5z, and cc-pV6Z series, the TAE showed a smooth convergence. The diminution of the TAE upon increase in basis set was not expected because the opposite behavior is more frequently observed.

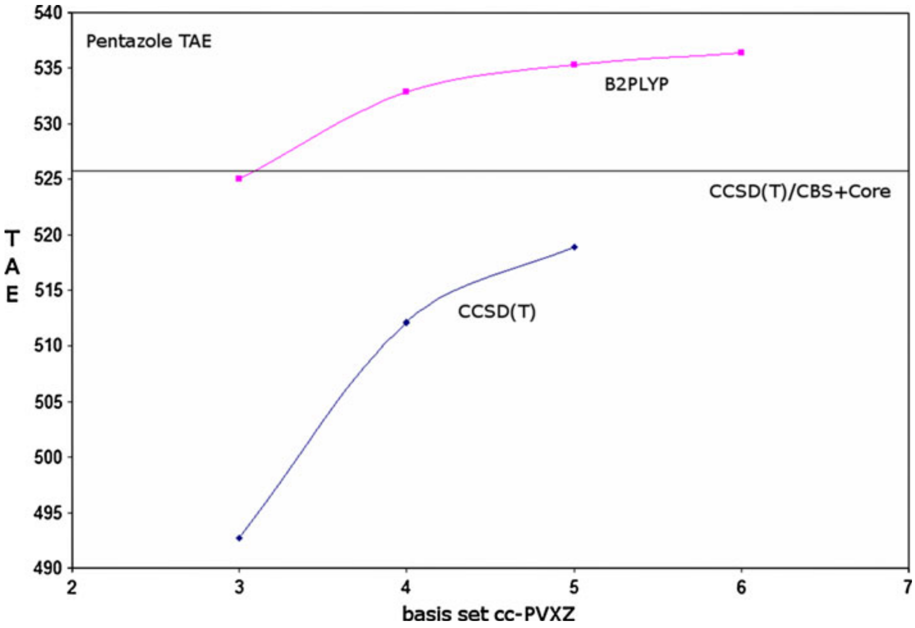

Fig. 3 Total atomization energy determined for pentazole at the CCSD(T) and B2PLYP levels

6. The MAD of the total atomization energies determined at the M06-2X level, with respect to the CCSD(T) results, was 0.42 kcal/mol.
7. The double hybrid B2PLYP functional showed a smooth convergence toward the CBS limit, even though the performance seriously degradated when the basis set was increased. At the CBS limit, the MAD with respect to the CCSD(T) TAE was 8.26 kcal/mol.

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