REGULAR ARTICLE

Daniel Glossman-Mitnik

CHIH-DFT determination of the molecular structure and infrared and ultraviolet spectra of azathiophenes

Abstract In this work, we make use of a new model chemistry within Density Functional Theory, which is called CHIH-DFT (Chihuahua Heterocycles-Density Functional Theory), to calculate the molecular structure of the azathiophenes, as well to predict their infrared and ultraviolet spectra. The calculated values are compared with the experimental data available for these molecules as a mean of validation of our proposed chemistry model. The predicted results are in excellent agreement with the experimental ones.

Keywords Azathiophenes · CHIH-DFT · Molecular structure · Infrared spectrum · Ultraviolet spectrum

1 Introduction

Molecular modeling is a method which combines computational chemistry techniques with graphics visualization for simulating and predicting the three-dimensional structure, chemical processes and physicochemical properties of molecules and solids [1]. As such, the object of study are systems that are precursors of materials for nanotechnology [2,3].

The azathiophenes, the molecules which result from the replacement of the carbon atoms in thiophene by nitrogen atoms, are systems of particular interest. They are isoelectronic with thiophene and can be the basis of oligomers and conducting polymers [4,5]. In this way and many others, these heterocycles and its derivatives can be considered as potential nanomaterials.

In order to adequately describe the molecular structures and properties of heterocyclic systems, it is necessary to resort to model chemistries specially suited to accomplish this task. We understand for model chemistry (or theoretical

model chemistry), the implementation of a theoretical model which should be uniformly applicable to molecular systems of any size and type, up to a maximum size determined only by the practical availability of computer resources. This can be accomplished by linking a density functional for exchange and correlation with a particular basis set [6].

The objective of this work is to perform a detailed calculation of the molecular structure of the azathiophenes, as well as to predict their infrared (IR) and ultraviolet (UV-Vis) spectra, by using a new model chemistry within Density Functional Theory (DFT) [7] specially tailored to study heterocyclic systems, which is called CHIH-DFT (Chihuahua Heterocycles-Density Functional Theory) and to validate the calculated results by comparison with the experimental available data for these molecules as well as with the results of other theoretical models. Our approach will be limited to the description of molecules in their equilibrium geometry and, in some sense, it can be regarded as a semiempirical DFT. The CHIH-DFT has been already validated for the case of antiparasitic drugs [8–10], flavonoids [11,12] and organic corrosion inhibitors [13,14].

2 Theory and computational details

All computational studies were performed with the Gaussian 03W [15] series of programs with density functional methods as implemented in the computational package. The equilibrium geometries of the molecules were determined by means of the gradient technique. The force constants and vibrational frequencies were determined by the FREQ calculations on the stationary points obtained after the optimization to check if there were true minima. The basis sets used in this work were 3-21G* and 6-31G(d, p) (for their explanation see Ref. [6]). Additionally, the CBSB2**, CBSB7, CBSB4 and CBSB1 basis sets were used. The CBSB7 has the form 6-311G($2d$, d, p) and has been developed by Petersson and coworkers as a part of the Complete Basis Set CBS-QB3 energy compound method [16]. It was designed for obtaining the best results for optimization of geometries and they found that this basis set

D. Glossman-Mitnik
Grupo NANOCOSMO - Química Computacional de Moléculas y Nanomateriales and PRINATEC - Programa Institucional de Nanotecnología
CIMAV, S.C., Miguel de Cervantes 120, Complejo Industrial Chihuahua, 31109, Chihuahua, México
E-mail: daniel.glossman@cimav.edu.mx
Fax: +52-614-4394852

was necessary for obtaining acceptable results on the full G2 test set [17]. The CBSB2** basis set is esentially the same as 6-31G(d, p), but with the exponents for the d functions taken from the 6-311G basis set, and is also called 6-31G†† [6, 18, 19]. The CBSB4 basis set is identical to 6-31+G(d, p) on H – Si and to 6-31+G(df, p) on P, S and Cl. The CBSB1 basis set is identical to 6-31+g(d, p) on H and He, to 6-311+G(2df) on Li – Ne, and to 6-311+g(3$d2f$) on Na – Ar. The CBSB2**, CBSB4 and CBSB1 basis sets are also part of the CBS-QB3 method [16].

Density functionals used in this study are a modification of those incorporated in the Gaussian 03W computational package [15]. To this end, we have defined a new model chemistry that we have found empirically that works well with heterocyclic molecules. The model was found by trial and error determination of the molecular structure of several heterocycles and a comparison with the experimental results. The implementation is a slight different version of the PBE0 hybrid density functional [20, 21]. In the PBE0 (or PBE1PBE one-parameter) functional, there is only one coefficient which is theoretically adjusted to 0.25, reflecting the mix of Hartree-Fock (HF) or exact exchange and the DFT exchange which is represented by the PBE density functional [22]. The correlation part is also represented by the PBE correlation functional [22] with coefficient equal to one. Our proposed density functional model, which we have called PBEg, is the same as PBE0, but with the mixing coefficient g which adopts different values depending on the number of heteroatoms in the studied molecule, or, in turn, of its molecular structure. The value of g can be calculated through the following empirical formula: $g = 0.02 + 0.14 \times FHA \times FV + 0.03 \times AHA$, where FHA is the first heteroatom chosen as the one less electronegative, FV is valence factor which represents the oxidation state of the FHA (i.e., 1 for the first oxidation state, two for the second, and so on), and AHA are the number of additional heteroatoms besides the FHA. FHA is always equal to one. This formula has been empirically found by studying a large number of heterocyclic compounds with different number of heteroatoms and oxidation states. For example, for the 1,2,5-thiadiazole molecule, the g coefficient will be $g = 0.02 + 0.14 \times 1 + 0.03 \times 2 = 0.22$, thus implying that 22% of HF exchange will be mixed with 78% of PBE exchange. Similarly, for 1,2,5-thiadiazole 1,1-dioxide, the g coefficient will be $g = 0.02 + 0.14 \times 3 + 0.03 \times 2 = 0.50$, reflecting 50% of HF exchange and 50% of PBE exchange. For those cases in which the molecule has several heterocyclic rings, we will calculate the coefficient g by averaging the coefficient for each heterocycle. As it is evident, the bounds to the empirical formula are 0 and 1 meaning no mixing of HF exchange in the first case and a purely HF model in the last case. The reasons for the dependence of the mix of HF and DFT exchange with the number of heteroatoms and their oxidation state are not apparent, but the validity of the empirical formula have been computationally assessed for several different molecular systems [8–14]. Based on these results it is clear that our choice of this particular functional has been done because its performance is superior to other methods both in accuracy and computational cost.

In order to define our model chemistry, we have to couple the proposed density functional with one or more basis sets. In this way, the new model chemistry that we have called CHIH-DFT can be represented by the expression CHIH = PBEg/basis sets. There are three different CHIH-DFT model chemistries: CHIH(small) that uses the 3-21G* basis set for geometry optimizations and frequency calculations, and the CBSB2** basis set for the calculation of the electronic properties; CHIH(medium) that uses the CBSB2** basis set for geometry optimizations and frequency calculations and the CBSB4 basis set for the electronic properties; and CHIH (large) the which uses the CBSB7 basis set for geometry optimizations and frequency calculations and the CBSB1 basis set for the electronic properties. In this way, by considering a compromise between accuracy and CPU time, the CHIH(large) will be used for small heterocyclic molecules, the CHIH(medium) for medium-sized molecules and the CHIH(small) for large heterocyclic molecules. We understand that a molecule is small when the number of atoms within the cycle is five or six. When the number of atoms in the cycle is more that six, we considered it a medium-sized molecule. If there is more than one cycle, or if there are a large number of side-chain radical substituents, we say that the molecule is large.

The calculation of the UV-Vis spectrum of the azathiophenes has been performed by solving the time dependent Kohn-Sham equations according to the method implemented in Gaussian 03W [23–26]. The equations have been solved for 10 excited states.

The IR and UV-Vis spectra were calculated and visualized using the Swizard program [27]. In all cases the displayed spectra show the calculated frequencies. The performance of the CHIH-DFT model for the prediction of infrared spectra is evaluated in the sections devoted to each molecule by calculating the corresponding averaged scaling factor.

3 Results and discussion

3.1 Thiophene

The results for the equilibrium conformation of the neutral molecule of thiophene calculated with the CHIH(large) model chemistry are reported in Table 1, and the representation of the molecular structure of this molecule showing

Table 1 Interatomic bond distances (Å) and bond angles (°) for thiophene

	Bond distance				Bond angle	
	CHIH-DFT	Exp.[a]			CHIH-DFT	Exp.[a]
S–C1	1.717	1.714	C1–S–C4		92.1	92.2
C1–C2	1.369	1.370	S–C1–C2		111.4	111.5
C2–C3	1.422	1.423	C1–C2–C3		112.6	112.5
C1–H	1.082	1.078	H–C1–S		120.0	119.9
C2–H	1.085	1.081	H–C2–C3		124.2	124.3

[a]Reference [28]

the atomic labeling and numbering are presented in Fig. 1a. For this heterocycle, the g coefficient will be $g = 0.02 + 0.14 \times 1 = 0.16$, thus implying that 16% of HF exchange will be mixed with 84% of PBE exchange. The results are compared with the experimental microwave spectroscopy determination of the molecular structure of thiophene [28]. The agreement is excellent: the standard error of the differences

between the experimental and the calculated bond lengths and bond angles being very low. Although not shown in the table, an analysis of the torsional angles confirms that this heterocycle is planar.

The IR spectra for the thiophene molecule calculated with the CHIH(large) model chemistry is displayed in Fig. 1b where the numbers correspond to the calculated frequencies. The results are compared with the experimental vibrational assignments [29]. The vibrations of A_1 symmetry are (in cm^{-1}) (the experimental results in parenthesis): 616 (606), 851 (833), 1059 (1033), 1090 (1081), 1388 (1360), 1453 (1408), 3242 (3110). For the A_2 symmetry, the results are: 573 (565), 676 (686), 907 (900). For the B_1 symmetry are: 762 (750), 878 (871), 1092 (1081), 1261 (1250), 3192 (3073), 3240 (3110). Finally, for the B_2 symmetry are: 460 (453), 718 (712), 865 (864). The scaling factors are 0.9768 for A_1, 0.9931 for A_2, 0.9800 for B_1 and 0.9917 for B_2, while the average scaling factor is 0.9854.

The UV-Vis spectra of the thiophene molecule calculated with the CHIH(large) model chemistry is displayed in Fig. 1c. The wavelength belonging to the HOMO–LUMO transition will take place at 216 nm, while the experimental spectrum shows a peak at 215 nm [30].
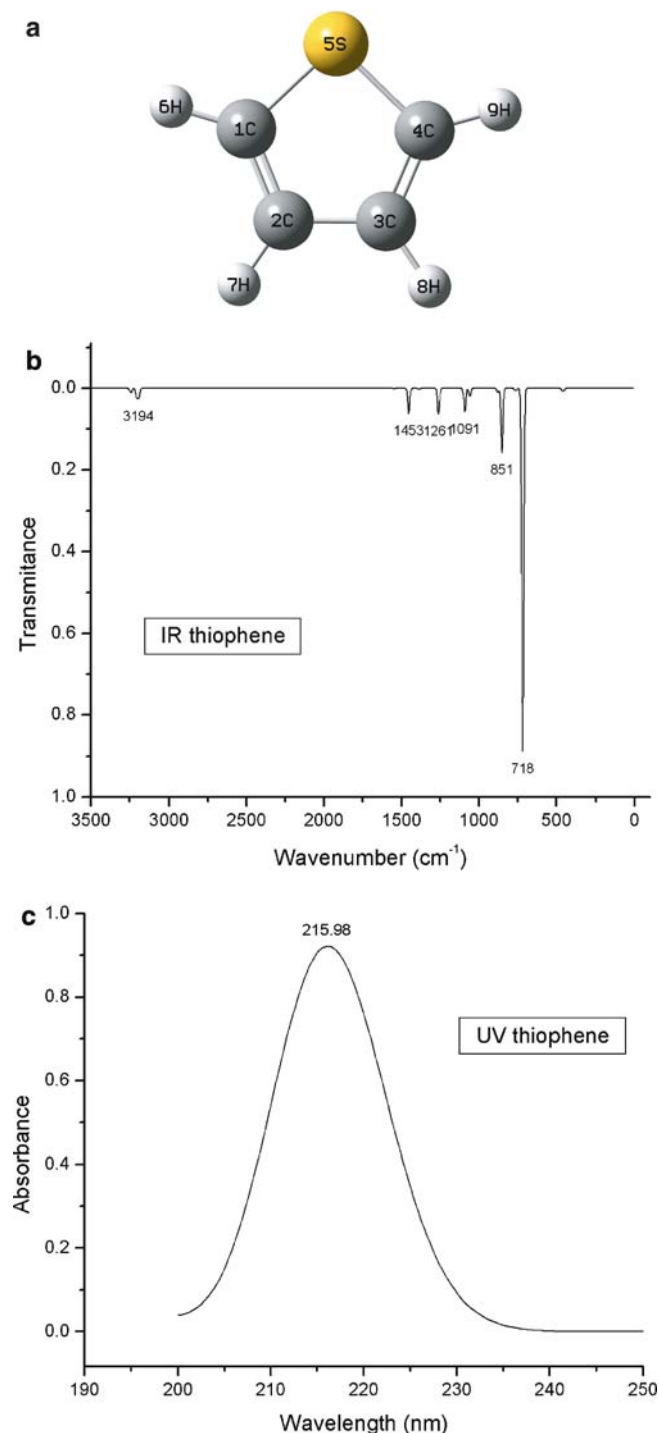
3.2 Thiazole and isothiazole

The results for the equilibrium conformation of the neutral molecules of thiazole and isothiazole calculated with the CHIH(large) model chemistry are reported in Tables 2 and 3,

Fig. 1 Molecular structure (**a**), IR spectrum (**b**) and UV spectrum (**c**) of thiophene calculated with the CHIH(large) model chemistry

Table 2 Interatomic bond distances (Å) and bond angles (°) for thiazole

	Bond distance			Bond angle	
	CHIH-DFT	Exp.[a]		CHIH-DFT	Exp.[a]
S–C3	1.728	1.724	C1–S–C3	89.2	89.3
S–C1	1.714	1.713	S–C3–N	115.1	115.2
C3–N	1.300	1.304	S–C1–C2	109.5	109.6
C1–C2	1.366	1.367	C1–C2–N	116.0	115.8
C2–N	1.367	1.372	C2–N–C3	110.3	110.1
C3–H	1.082	–	S–C3–H	120.6	–
C1–H	1.081	–	C1–C2–H	124.8	–
C2–H	1.084	–	N–C2–H	119.3	–

[a]Reference [31]

Table 3 Interatomic bond distances (Å) and bond angles (°) for isothiazole

	Bond distance			Bond angle	
	CHIH-DFT	Exp.[a]		CHIH-DFT	Exp.[a]
S–N2	1.649	1.642	C1–S–N	95.7	96.1
S–C1	1.703	1.712	S–N–C3	108.7	112.2
N–C	1.318	1.319	S–C1–C2	108.8	106.2
C1–C2	1.372	1.388	C1–C2–C3	110.0	111.8
C2–C3	1.417	1.436	N–C3–C2	116.9	113.8
C1–H	1.083	–	C3–N–H7	118.2	120.6
C2–H	1.083	–	C2–C3–H	125.0	127.6
C3–H	1.087	–			

[a]Reference [32]

while the representation of the molecular structure of these molecules showing the atomic labeling and numbering are presented in Figs. 2a and 3a. For these heterocycles, the *g* coefficient will be $g = 0.02 + 0.14 \times 1 + 0.03 \times 1 = 0.19$, thus implying that 19% of HF exchange will be mixed with
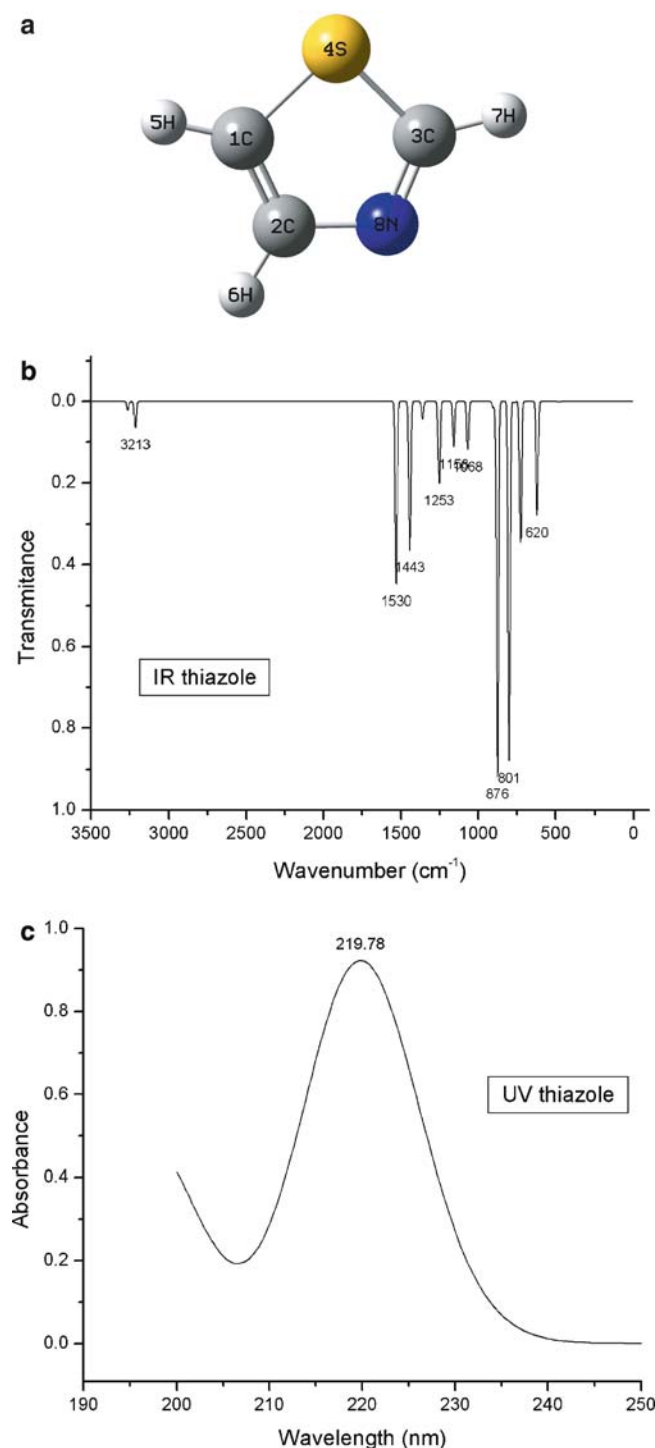

Fig. 2 Molecular structure (**a**), IR spectrum (**b**) and UV spectrum (**c**) of thiazole calculated with the CHIH(large) model chemistry

81% of PBE exchange. The results are compared with the experimental microwave spectroscopy determination of the molecular structures of thiazole [31] and isothiazole [32]. As in the case of thiophene the agreement is excellent, and also an analysis of the torsional angles reveals that these heterocycles are planar.

The IR spectra for the thiazole and isothiazole molecules calculated with the CHIH(large) model chemistry are displayed in Figs. 2b and 3b. The results are compared with the experimental vibrational assignments [33,34]. For thiazole, the vibrations of A′ symmetry are (in cm^{-1}) (the experimental results in parenthesis): 621 (612), 766 (750), 890 (862), 904 (889), 1068 (1039), 1158 (1119), 1253 (1237), 1360 (1317), 1443 (1378), 1530 (1477), 3213 (3067), 3222 (3083), 3262 (3115). For the A″ symmetry, the results are: 479 (470), 620 (605), 727 (722), 801 (799), 876 (849). The scaling factors are 0.9691 for A′ and 0.9834 for A″, while the average scaling factor is 0.9763. Both in Figs. 2b and 3b, the numbers correspond to the calculated frequencies. For isothiazole, the vibrations of A′ symmetry are (in cm^{-1}) (the experimental results in parenthesis): 656 (639), 774 (758), 833 (815), 880 (869), 1065 (1040), 1077 (1066), 1261 (1236), 1340 (1296), 1439 (1390), 1540 (1484), 3186 (3056), 3224 (3086), 3247 (3105). For the A″ symmetry, the results are: 489 (474), 605 (587), 737 (728), 870 (858), 924 (908). The scaling factors are 0.9738 for A′ and 0.9793 for A″, while the average scaling factor is 0.9766.

The UV-Vis spectra of the thiazole and isothiazole molecules calculated with the CHIH(large) model chemistry are displayed in Figs. 2c and 3c. The wavelength belonging to the HOMO–LUMO transition in the spectrum of thiazole will take place at 229 nm, while the experimental spectrum shows a peak at 207.5 nm [30]. For isothiazole, the corresponding values are 219 and 244 nm [30]. The agreement between the calculated and experimental values is not so good as in the case of thiophene probably because the solvent effect is more important when heterocyclic nitrogen atoms are involved and this also explains while in some cases the theoretical value overestimates the experimental one, and in others is the other way around.

3.3 The thiadiazoles

The results for the equilibrium conformation of the neutral molecules of 1,2,3-thiadiazole (23T), 1,2,4-thiadiazole (24T), 1,2,5-thiadiazole (25T) and 1,3,4-thiadiazole (34T) calculated with the CHIH(large) model chemistry are reported in Tables 4, 5, 6 and 7, while the representation of the molecular structure of these molecules showing the atomic labeling and numbering are presented in Figs. 4a, 5a, 6a and 7a, respectively. For these heterocycles, the *g* coefficient will be $g = 0.02 + 0.14 \times 1 + 0.03 \times 2 = 0.22$, thus implying that 22% of HF exchange will be mixed with 78% of PBE exchange. The results are compared with the experimental microwave spectroscopy determination of the molecular structures of 23T [35], 24T [36], 25T [37,38] and 34T
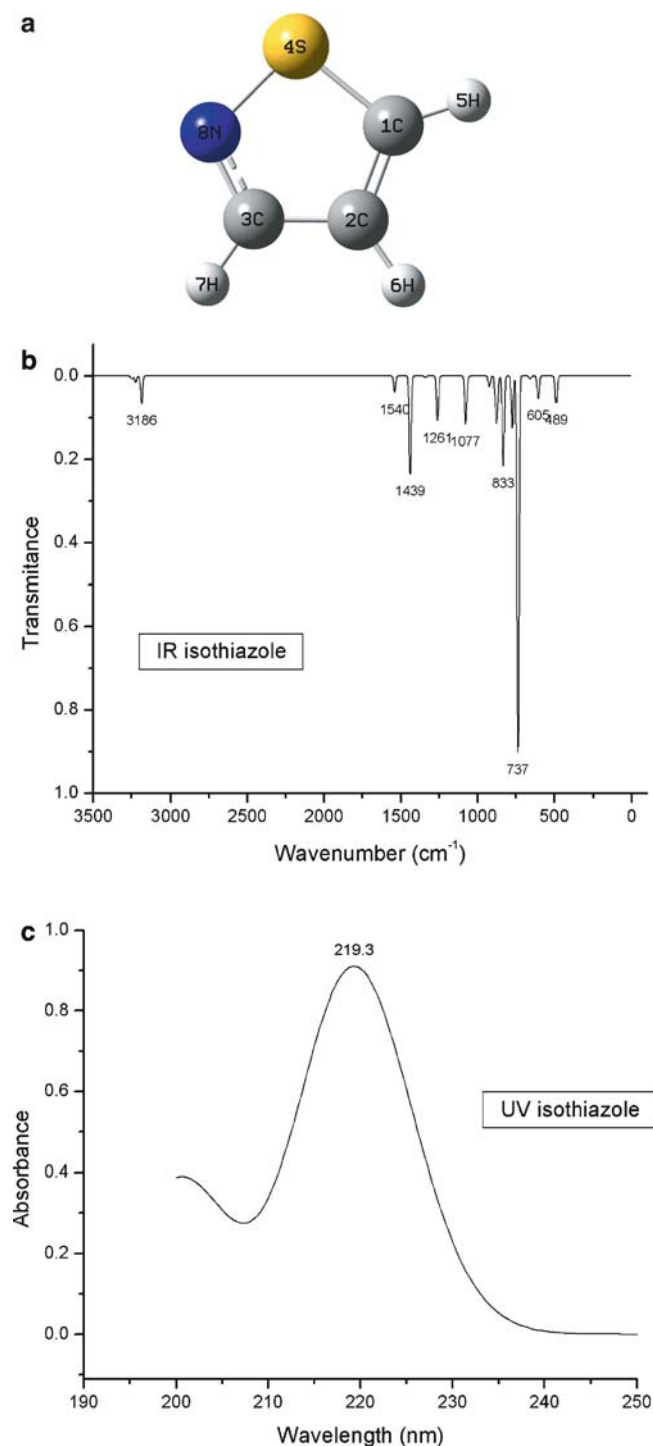
Fig. 3 Molecular structure (**a**), IR spectrum (**b**) and UV spectrum (**c**) of isothiazole calculated with the CHIH(large) model chemistry

Table 4 Interatomic bond distances (Å) and bond angles (°) for 1,2,3-thiadiazole

	Bond distance			Bond angle	
	CHIH-DFT	Exp.[a]		CHIH-DFT	Exp.[a]
S–C	1.686	1.689	C–S–N	92.6	92.9
S–N	1.706	1.692	S–N–N	110.8	111.2
N–N	1.273	1.290	N–N–C	114.8	114.0
C–C	1.370	1.369	C–C–S	107.8	107.8
N–C	1.361	1.366	N–C–C	113.9	114.2
C(5)–H(7)	1.082	1.078	S–C–H	123.8	122.9
			N–C–H	119.4	119.2

[a]Reference [35]

Table 5 Interatomic bond distances (Å) and bond angles (°) for 1,2,4-thiadiazole

	Bond distance			Bond angle	
	CHIH-DFT	Exp.[a]		CHIH-DFT	Exp.[a]
S–N	1.649	1.649	C–S–N	92.6	92.8
S–C	1.709	1.707	S–N–C	107.0	107.1
N(6)–C(1)	1.312	1.317	N–C–N	120.3	120.1
N(7)–C(2)	1.362	1.366	C–N–C	108.0	107.7
N(7)–C(1)	1.306	1.313	S–C–N	112.2	112.3
C(1)–H(4)	1.084	1.079	N(7)–C(2)–H(5)	119.7	119.9
C(2)–H(5)	1.085	1.078	S–C(2)–H(5)	123.6	123.9

[a]Reference [36]

Table 6 Interatomic bond distances (Å) and bond angles (°) for 1,2,5-thiadiazole

	Bond distance			Bond angle	
	CHIH-DFT	Exp.[a]		CHIH-DFT	Exp.[a]
S–N	1.629	1.630	N–S–N	99.2	99.4
C–N	1.320	1.327	S–N–C	106.6	106.5
C–C	1.419	1.417	N–C–C	113.8	113.8
C–H	1.084	1.081	C–C–H	126.3	126.3
			N–C–H	120.0	120.0

[a]Reference [37,38]

Table 7 Interatomic bond distances (Å) and bond angles (°) for 1,3,4-thiadiazole

	Bond distance			Bond angle	
	CHIH-DFT	Exp.[a]		CHIH-DFT	Exp.[a]
S–C	1.722	1.721	C–S–C	86.2	86.4
C–N	1.297	1.302	S–C–N	114.3	114.6
N–N	1.355	1.371	N–C–H	123.3	122.9
C–H	1.082	1.079	S–C–H	122.3	121.9
			C–N–N	112.6	112.2

[a]Reference [39–42]

[39–42]. An analysis of the torsional angles (not shown) reveals that these heterocycles are also planar. The computational molecular structures of the isomeric thiadiazoles and its derivatives have been extensively studied by our group [8, 9,43–58]. It can be concluded that there is an excellent agreement between the CHIH-DFT model chemistry prediction of the molecular structures of the thiadiazoles and their experimental counterparts. The only exceptions to this finding are in the S–N and N–N bond lengths of 23T which are 0.014 Å longer and 0.017 Å shorter than the experimental values. However, these results are closer to the experimental values than those obtained using MP2/6-31G** [63].

The IR spectrum for the 23T molecule calculated with the CHIH(large) model chemistry is displayed in Fig. 4b. The results are compared with the experimental vibrational
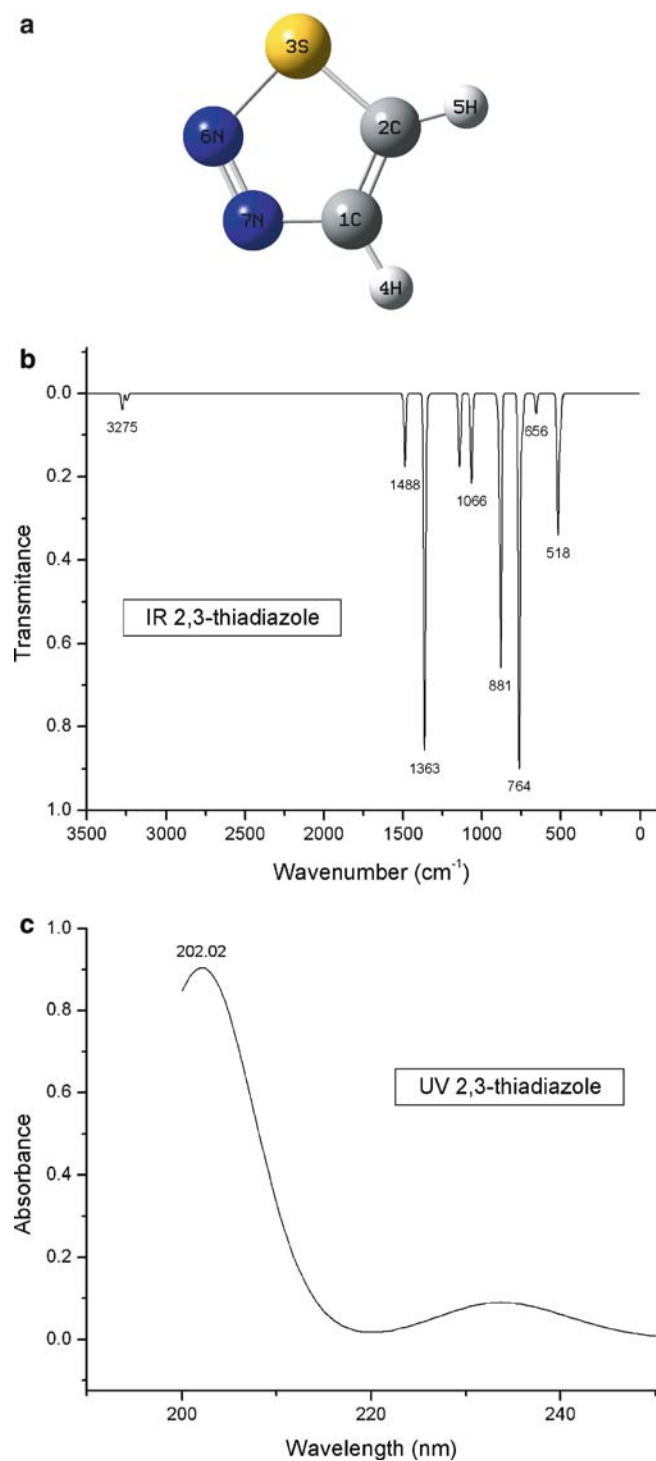
Fig. 4 Molecular structure (**a**), IR spectrum (**b**) and UV spectrum (**c**) of 1,2,3-thiadiazole calculated with the CHIH(large) model chemistry
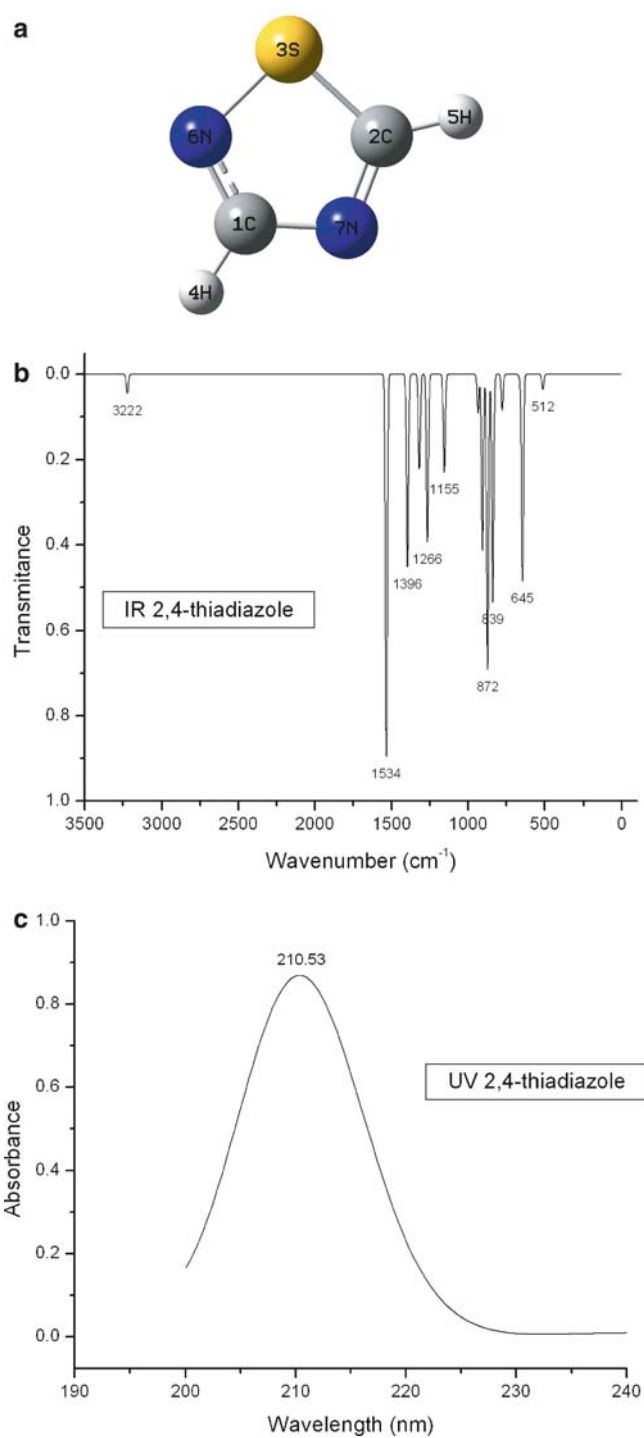

Fig. 5 Molecular structure (**a**), IR spectrum (**b**) and UV spectrum (**c**) of 1,2,4-thiadiazole calculated with the CHIH(large) model chemistry

assignments [59]. The experimental assignment have been done on the basis of the spectra of a series of 1,2,3-thiadiazoles and not on the parent molecule. For this reason, they should be considered as averaged results. The vibrations are (in cm^{-1}) (the experimental results in parenthesis): 656 (670), 704 (705), 881 (890), 1066 (950), 1363 (1280), 1488 (1475).

The scaling factor is 0.9758. The IR spectrum for the 24T molecule calculated with the CHIH(large) model chemistry is displayed in Fig. 5b. The results are compared with the experimental vibrational assignments [59]. The vibrations of A′ symmetry are (in cm^{-1}) (the experimental results in parenthesis): 645 (727), 839 (795), 872 (860), 1155 (1160), 1266
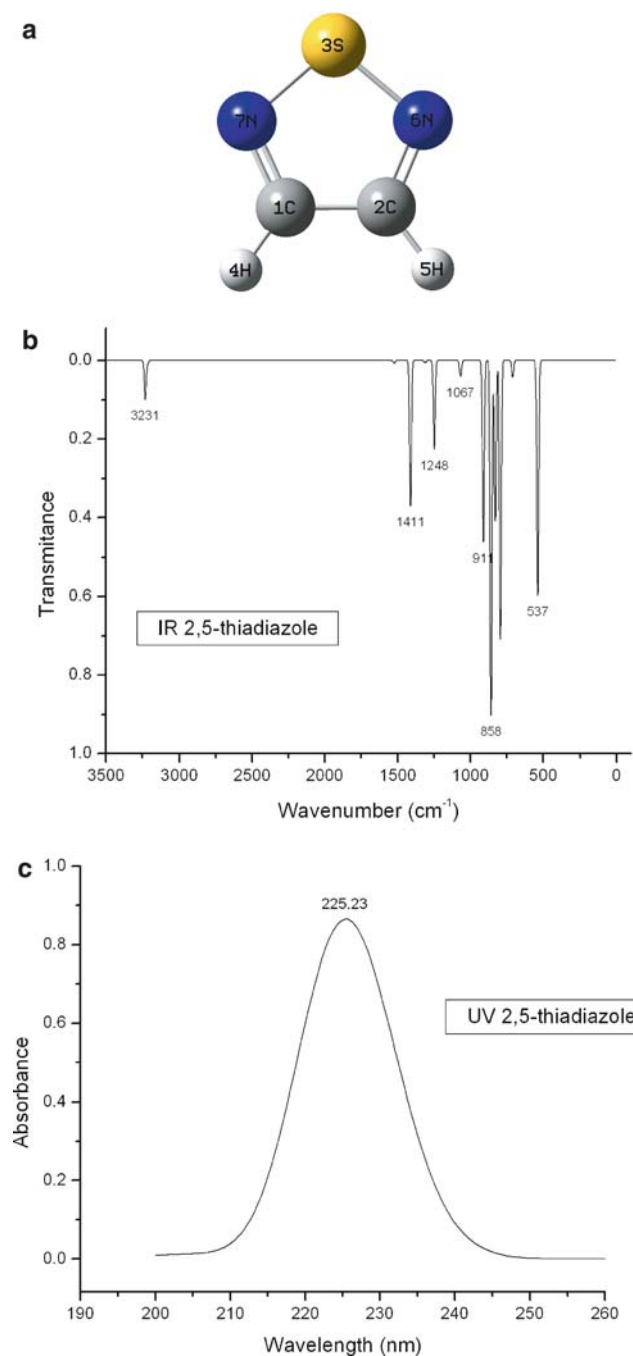
Fig. 6 Molecular structure (**a**), IR spectrum (**b**) and UV spectrum (**c**) of 1,2,5-thiadiazole calculated with the CHIH(large) model chemistry

Fig. 7 Molecular structure (**a**), IR spectrum (**b**) and UV spectrum (**c**) of 1,3,4-thiadiazole calculated with the CHIH(large) model chemistry

(1270), 1534 (1529). The scaling factor is 1.011. The IR spectrum for the 25T molecule calculated with the CHIH(large) model chemistry is displayed in Fig. 6b. The results are compared with the experimental vibrational assignments [60]. The vibrations of A_1 symmetry are (in cm^{-1}) (the experimental results in parenthesis): 709 (688), 828 (806), 1067 (1041), 1310 (1251), 1411 (1350), 3215 (3106). For the A_2 symmetry, the results are: 631 (612), 926 (908). For B_1: 3231 (3108), 1523 (1461), 1248 (1227), 911 (895), 794 (780). For
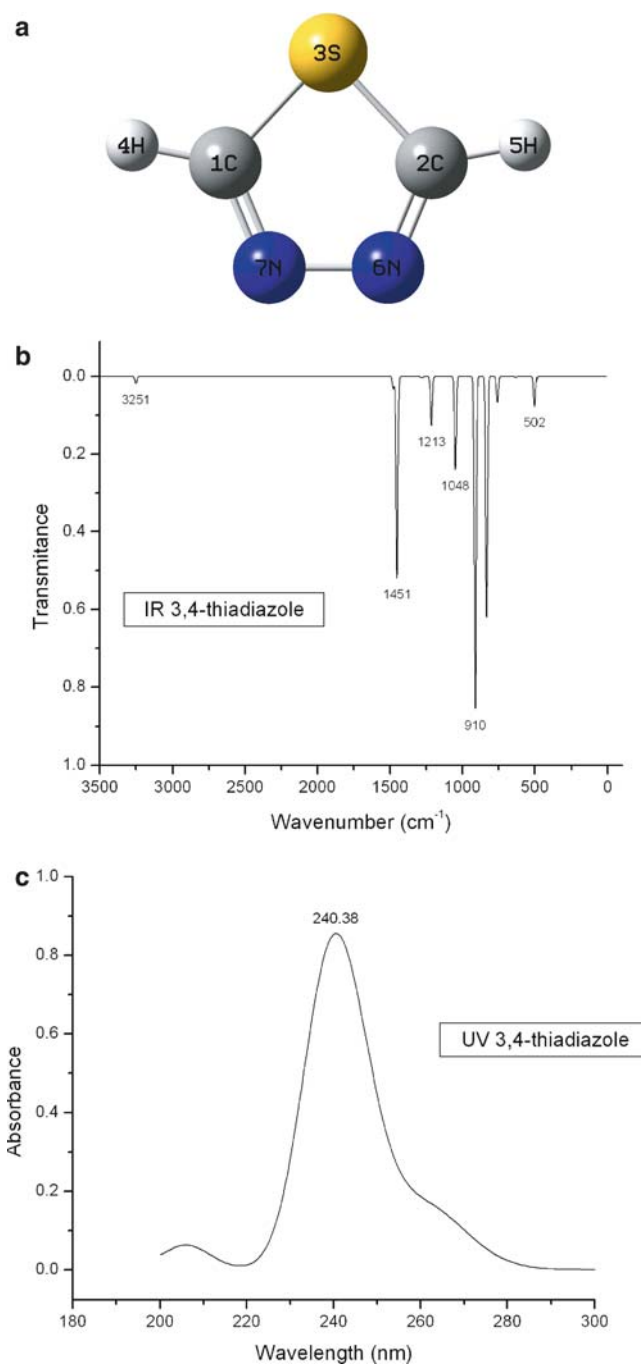
B_2: 537 (520), 858 (838). The scaling factors are 0.9662 for A_1, 0.9752 for A_2, 0.9519 for B_1 and 0.9725 for B_2, while the average scaling factor is 0.9665. The IR spectrum for the 34T molecule calculated with the CHIH(large) model chemistry is displayed in Fig. 7b. The results are compared with the experimental vibrational assignments [61]. The vibrations of A_1 symmetry are (in cm^{-1}) (the experimental results in parenthesis): 643 (636), 894 (810), 962 (1048), 1229 (1278), 1399 (1451), 3115 (3253). For the A_2 symmetry, the results are:

616 (631), 796 (806). For B_1: 743 (758), 897 (913), 1193 (1213), 1403 (1476), 3112 (3249). For B_2: 483 (502), 820 (832). The scaling factors are 0.9610 for A_1, 0.9819 for A_2, 0.9709 for B_1 and 0.9738 for B_2, while the average scaling factor is 0.9719.

The UV-Vis spectra of the isomeric thiadiazole molecules 23T, 24T, 25T and 34T calculated with the CHIH(large) model chemistry are displayed in Figs. 4c, 5c, 6c and 7c. The wavelength belonging to the HOMO–LUMO transitions in the spectrum of 23T, 24T, 25T, and 34T will take place at 202, 211, 225 and 240 nm, while the experimental spectra show peaks at 211, 229, 250 and 220 nm, respectively [30]. The small differences can be attributed to the fact that the experimental spectra have been taken in the presence of solvents while the calculated spectra are in the gas phase as for the other systems included in this paper.

3.4 The thiatriazoles

The thiatriazoles are another interesting group of molecules. There is a recent review on the methods of synthesis of 1,2,3,4-thiatriazole (234T) and 1,2,3,5-thiatriazole (235T) [62]. Recent work from our group has considered these molecules and their derivatives as potentially organic corrosion inhibitors [13,14].

The results for the equilibrium conformation of the neutral molecules of 234T and 235T calculated with the CHIH (large) model chemistry are reported in Tables 8 and 9, while the representation of the molecular structure of these molecules showing the atomic labeling and numbering are presented in Figs. 8a and 9a, respectively. For these heterocycles, the g coefficient will be $g = 0.02 + 0.14 \times 1 + 0.03 \times 3 = 0.25$, thus implying that 25% of HF exchange will be mixed

Table 8 Interatomic bond distances (Å) and bond angles (°) for 1,2,3,4-thiatriazole

	Bond distance			Bond angle	
	CHIH-DFT	MP2[a]		CHIH-DFT	MP2[a]
S–C1	1.689	1.691	C1–S–N4	89.6	90.2
S–N4	1.691	1.698	S–N4–N5	110.5	110.3
N4–N5	1.266	1.311	N4–N5–N6	116.8	116.0
N5–N6	1.345	1.355	N5–N6–C1	110.8	110.7
N6–C1	1.306	1.328	N6–C1–S	112.2	114.0
C1–H	1.081	1.078	H–C1–S	124.9	124.8

[a]Reference [63]

Table 9 Interatomic bond distances (Å) and bond angles (°) for 1,2,3,5-thiatriazole

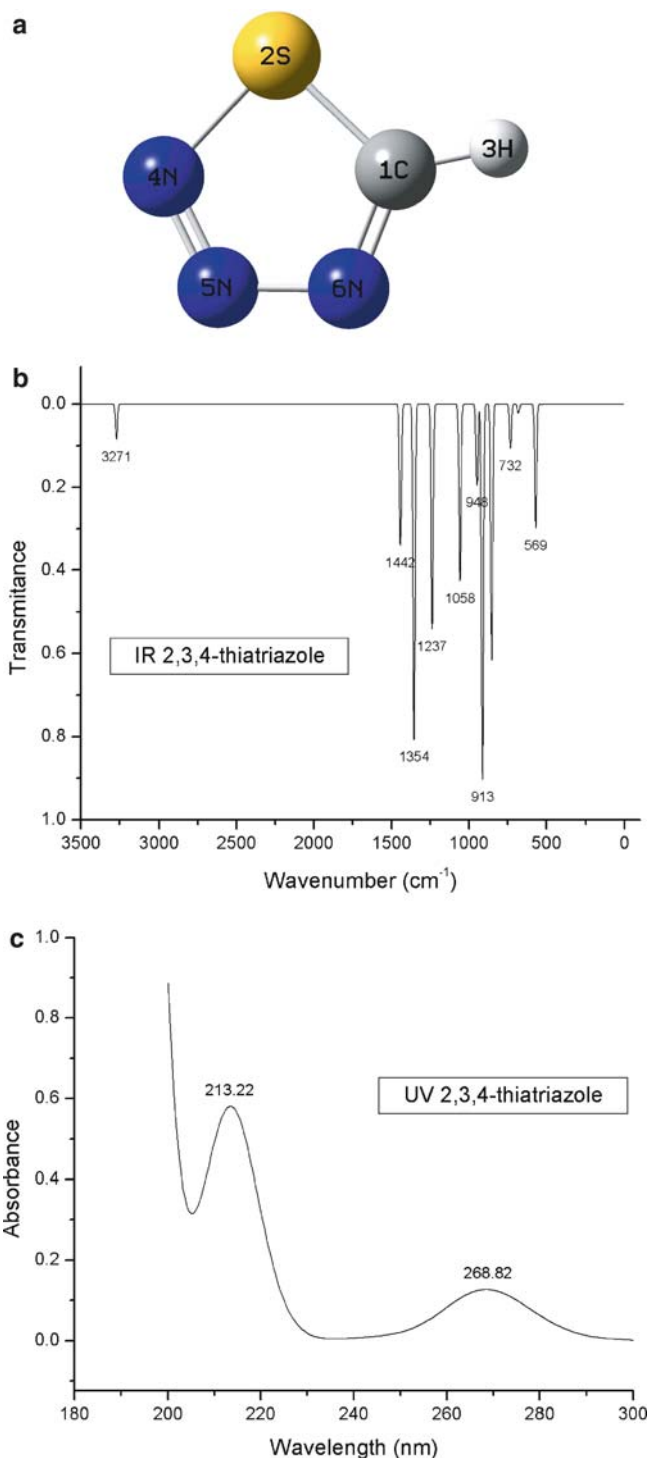|	Bond distance			Bond angle	
	CHIH-DFT	MP2[a]		CHIH-DFT	MP2[a]
S–N4	1.662	1.680	N6–S–N4	96.3	97.1
N4–N5	1.283	1.327	S–N4–N5	108.9	108.1
N5–C1	1.363	1.357	N4–N5–C1	111.5	111.3
C1–N5	1.313	1.343	N5–C1–N6	117.6	118.6
N6–S	1.617	1.631	C1–N6–S	105.6	105.0
C1–H	1.082	1.078	H–C1–N6	122.0	120.8

[a]Reference [63]

Fig. 8 Molecular structure (**a**), IR spectrum (**b**) and UV spectrum (**c**) of 1,2,3,4-thiatriazole calculated with the CHIH(large) model chemistry

with 75% of PBE exchange. Thus, for these heterocycles the CHIH-DFT chemistry model will be equal to the original PBE0 [20,21]. To the best of our knowledge, the experimental molecular structures of the parent heterocycles have never been reported and for this reason, we chose to compare our
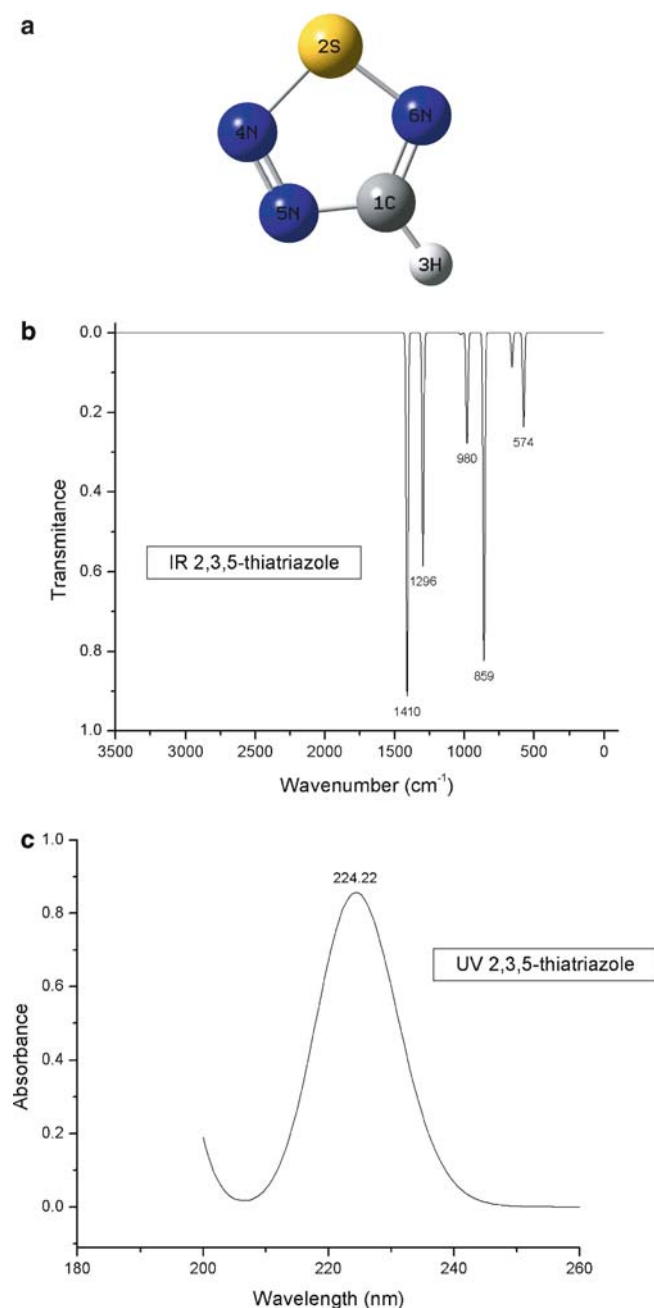
Fig. 9 Molecular structure (**a**), IR spectrum (**b**) and UV spectrum (**c**) of 1,2,3,5-thiatriazole calculated with the CHIH(large) model chemistry

results with that reported in a previous computational work [63] in the context of MP2 calculations. There are some differences: all the bonds involving nitrogen atoms are shorter than the MP2 counterparts. The bond angles are pretty much the same. These molecules are planar.

The IR spectrum for the 234T and 235T molecules calculated with the CHIH(large) model chemistry are displayed in Figs. 8b and 9b. As the experimental spectra have not been reported in the literature, we present the results only in a graphical form without any comparison.

The UV-Vis spectra of the isomeric thiatriazole molecules 234T and 235T calculated with the CHIH(large) model chemistry are displayed in Figs. 8c and 9c. The wavelength peaks of 213 and 269 nm in the spectrum of 234T can be attributed to the HOMO–LUMO+1 and HOMO-2–LUMO transitions, and to the HOMO–LUMO transition, respectively. For the 235T, the spectrum shows one peak at 224 nm, that can be attributed to the HOMO-1–LUMO and HOMO–LUMO+1 transitions.

3.5 Thiatetrazole

The thiatetrazole is the thiophene derivative where all the carbon atoms have been replaced by nitrogens. This molecule seems to have not been prepared already. The only references to it are theoretical studies in relation with the possible aromatic character [64,65] and as a molecule which could served as a storage of chemical energy [66,67]. For this heterocycle, the g coefficient will be $g = 0.02 + 0.14 \times 1 + 0.03 \times 4 = 0.28$, thus implying that 28% of HF exchange will be mixed with 72% of PBE exchange. The results for the equilibrium conformation of the neutral molecule of thiophene calculated with the CHIH(large) model chemistry are reported in Table 10, and the representation of the molecular structure of this molecule showing the atomic labeling and numbering are presented in Fig. 10a. As there are no experimental results, the structure can be compared with other theoretical values at the HF/6-31G*, B3LYP/6-31G*, MP2-631G* and B3LYP/6-311+G* [66]. The results for the bond lengths are (in Å): S–N2 = 1.641 (1.648, 1.690, 1.655, 1.687), N2–N3 = 1.273 (1.234, 1.270, 1.327, 1.265) and N3–N4 = 1.355 (1.377, 1.395, 1.347, 1.396). The bond angles are (in degrees): N2–S–N5 = 93.6 (91.6, 92.1, 94.9, 91.8) and S–N2–N3 = 109.2 (110.6, 109.9, 108.3, 110.1).

The predicted IR spectrum of thiatetrazole is shown in Fig. 10b. The transitions can be assigned as follows: 574 cm^{-1} : out-of-plane deformation; 859 cm^{-1} : in-plane deformation; 980 cm^{-1} : N3–N4 stretching; 1296 cm^{-1} : N2–N3 and N4–N5 symmetric stretching; 1410 cm^{-1} : asymmetric stretching.

The predicted UV spectrum of thiatetrazole is shown in Fig. 10c. There is a strong peak at 212 nm belonging to the HOMO-2–LUMO and HOMO-1–LUMO+1 transitions, and a small peak at 288 nm corresponding to the HOMO–LUMO transition.

3.6 Other molecules

In order to further validate our proposed model chemistry, we are presenting here the results of the calculations of the

Table 10 Interatomic bond distances (Å) and bond angles (°) for thiatetrazole

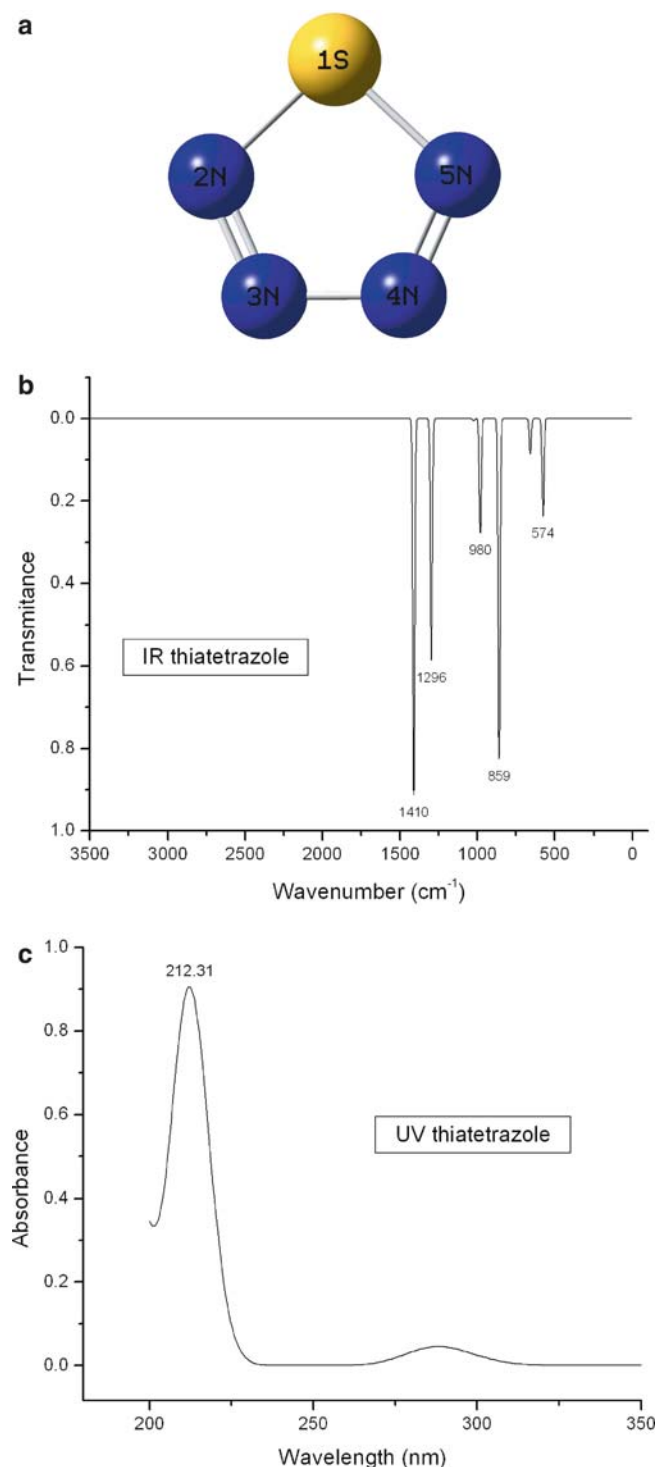|	Bond distance CHIH-DFT		Bond angle CHIH-DFT
S–N2	1.641	N2–S–N5	93.6
N2–N3	1.273	S–N2–N3	109.2
N3–N4	1.355	N2–N3–N4	114.0

Fig. 10 Molecular structure (**a**), IR spectrum (**b**) and UV spectrum (**c**) of thiatetrazole calculated with the CHIH(large) model chemistry

molecular structure of two other systems. The first is antiparasitic drug megazol (2-amino-5-(1-methyl-5-nitroimidazole-2-yl)-1,3,4-thiadiazole). This molecule has two heterocyclic rings, one with $g = 0.22$ and the other with $g = 0.19$. Thus the value of the mixing coefficient g for the entire molecule will be $g = 0.205$, implying the mix of 20.5% of HF exchange

and 79.5% of PBE exchange. The results of the calculation of the molecular structure of megazol with the CHIH(small), CHIH(medium) and CHIH(large) models as well as using the PBE0 functional with a 3-21G* or a CBSB2** basis sets have already been published [8] and a comparison has been made with the experimental X-ray crystallographic values. The standard deviation for the comparison of the calculated versus the experimental results was 0.01556 for the CHIH(large) model, 0.01728 for the CHIH(medium) model, 0.0368 for the CHIH(small) model, 0.01637 for PBE0/CBSB2** and 0.02839 for PBE0/3-21G*, in all cases for the interatomic distances. For the interatomic angles, there was only a small difference between the models where the standard deviations were about 0.94. The representation of the molecular structure of the megazol molecule showing the atomic labeling and numbering is presented in Fig. 11.

The second system is 4-ethoxy-5-methyl-1,2,5-thiadiazoline 1,1-dioxide. This molecule has been previously studied at the HF/3-21G* level and the experimental X-ray molecular structure were reported [54]. The representation of the molecular structure of the molecule showing the atomic labeling and numbering is presented in Fig. 12. This system is different because is a larger molecule, and it should be studied with the CHIH(small) model chemistry, and the first heteroatom (the S) is in an oxidized state, so the g factor will be very different than that from the original PBE0 model. For this heterocycle, the g coefficient will be $g = 0.02 + 0.14 \times 3 + 0.03 \times 2 = 0.50$, thus implying that 50% of HF exchange will be mixed with 50% of PBE exchange. In the present work we have determined the structure using both the CHIH(small) model chemistry and the PBEO/3-21G*. The standard deviation for the comparison of the calculated versus the experimental results was 0.01936 for the CHIH(small) model and 0.02970 for PBE0/3-21G*, in all cases for the interatomic distances. For the interatomic angles, the standard deviation for the comparison of the calculated versus the experimental results was 1.3398 for the CHIH(small) model and 1.7875 for PBE0/3-21G*. Thus, the CHIH-DFT model chemistry represents an improvement over the original PBE0 model in describing the molecular structure when a comparison with the experimental results is made.

4 Conclusions

In this work, a new model chemistry within DFT (the CHIH-DFT chemistry model) has been presented and the methodology has been applied to the study of the molecular structure and IR and UV spectra of the azathiophenes, which are potential precursors of nanotechnology materials. The molecular structures of the azathiophenes have been determined by using the CHIH(large) model chemistry. A comparison has been made with the results from the experimental microwave spectroscopy determinations of the structure of these molecules. The agreement is excellent.

The IR and UV-Vis spectra for the azathiophenes have been predicted according to the CHIH(large) model
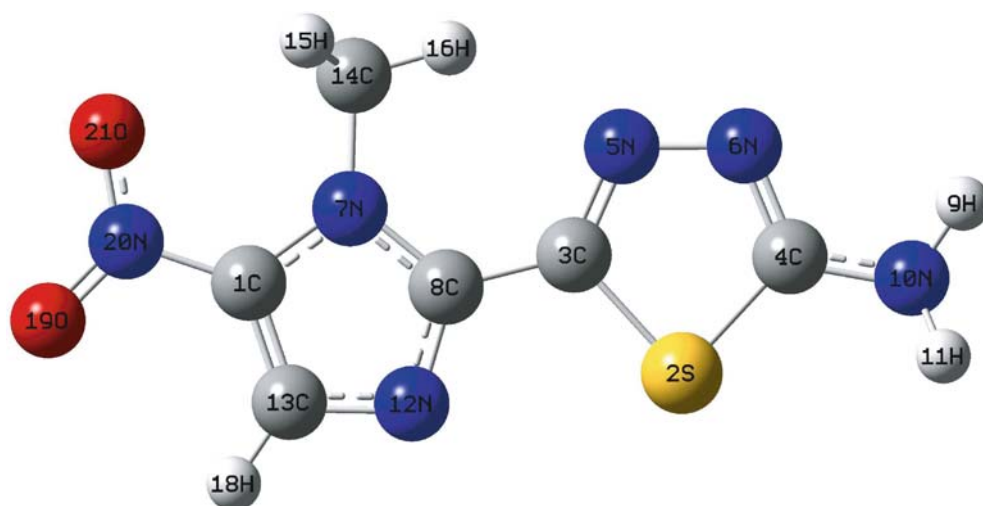
Fig. 11 Molecular structure of megazol calculated with the CHIH(large) model chemistry
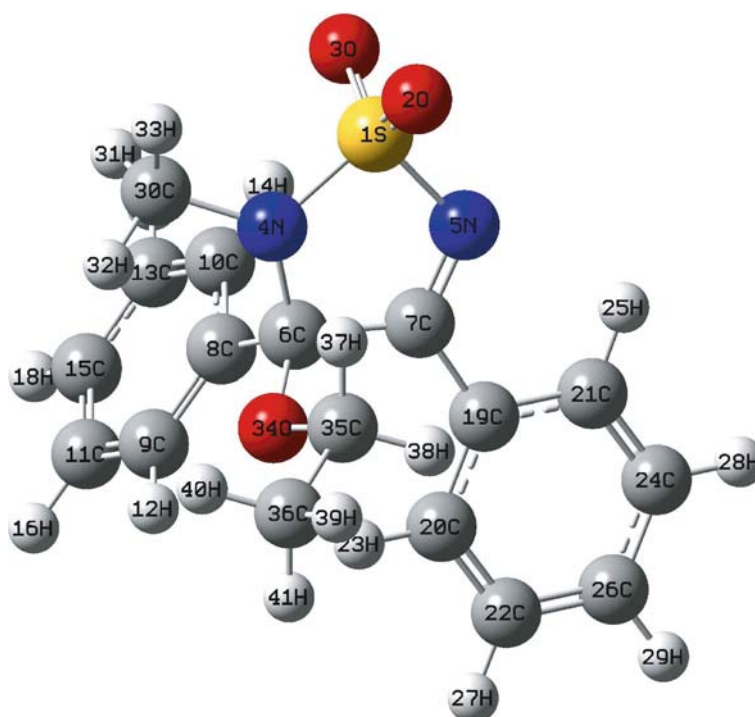

Fig. 12 Molecular structure of 4-ethoxy-5-methyl-3,4-diphenyl-1,2,5-thiadiazoline 1,1-dioxide calculated with the CHIH(small) model chemistry

chemistry, and an assignment of the principal peaks have been achieved. The results were compared with the experimental results to take note of similarities and differences. The overall scaling factor is very close to 1. The shape of the UV-Vis spectra and the maximum absorption wavelength belonging to these molecules have also been presented and compared with available experimental data.

To further validate our proposed model chemistry, a comparison has been made with the predicted molecular structure of two larger heterocyclic systems: megazol(2-amino-5-(1-methyl-5-nitroimidazole-2-yl)-1,3,4-thiadiazole) and

4-ethoxy-5-methyl-1,2,5-thiadiazoline 1,1-dioxide, and their experimental counterparts and the original PBE0 model with the same basis set. The results indicate that the standard deviation of bond lengths and angles has lower values for the CHIH-DFT model than for the PBE0. This is considered an indication of the goodness of the new model chemistry.

The CHIH-DFT model chemistry appears to be a useful tool for the study of the molecular structure and electronic properties of heterocycles, and further applications to several molecular systems are being pursued in our laboratory.

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