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## A DFT investigation of conformational geometries and interconversion equilibria of phenylthiosemicarbazone and its complexation with zinc

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**Abstract** The geometrical structures of phenylthiosemicarbazone (HAPhTSC) conformers have been obtained by geometry optimizations using density functional theory (DFT) calculations at the B3LYP/6-31G(d) and B3LYP/6-311G(d,p) levels of theory. Six thioamino and 24 thioimino tautomers of HAPhTSC have been found. Six tautomerization reactions between thioamino and thioimino tautomers occurring via transition states and their corresponding activation energies have been obtained. Conformational pathways for tautomerizations and interconversions of HAPhTSC conformers have been presented. Tautomerization between the most stable species of thioamino (Atttc) and its thioimino (Itttct) tautomer is an endothermic reaction,  $\Delta H^0 = 18.17 \text{ kcal mol}^{-1}$  and its  $\log K = -13.74$ , at 298.15 K. Thermodynamic quantities of tautomerizations, interconversions of HAPhTSC conformers and their equilibrium constants are reported. The geometry of the zinc complex with HAPhTSC, found as a  $\text{Zn}(\text{HAPhTSC})_2\text{Cl}_2$  structure, has been obtained using B3LYP/6-31G(d) calculations. Binding of the  $\text{Zn}(\text{HAPhTSC})_2\text{Cl}_2$  complex is an exothermic and spontaneous reaction.

**Keywords** HAPhTSC · Phenylthiosemicarbazone · Tautomerization · Interconversion · Zinc complex · DFT method

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### Introduction

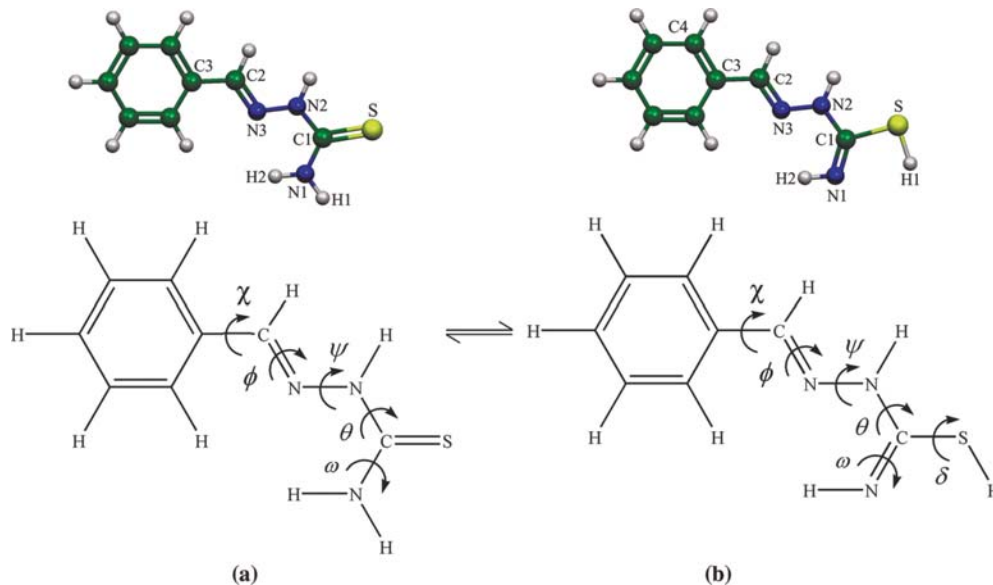
Many carbazones of variously substituted benzaldehydes and acetophenones have been studied with respect to their IR spectroscopic properties [1]. Crystal structures of metal complexes of thiosemicarbazone derivatives have been obtained and the compounds spectroscopically characterized [2, 3]. Coordination of thiosemicarbazone derivatives to form complexes with ruthenium, [4–6] osmium, [7] rhodium [8] and tin [9] have been observed. The molecular structures of nickel complexes with thiosemicarbazone and semicarbazone ligands were measured and the complexes characterized by IR spectroscopic and other measurements [10]. Single crystals of semicarbazone were grown and identified by X-ray diffraction and functional groups were identified using FT-IR spectra [11].

In the present work, conformational structures of HAPhTSC conformers, thermodynamic properties of their interconversions and tautomerizations have been investigated theoretically using DFT calculations. The geometrical structure of a HAPhTSC/zinc complex and thermodynamic quantities of complexation have been determined. A similar methodology to that used for the HMPAO/Zinc [12] and BHAM/technetium complexes [13] has been employed in this study.

### Computational method

Conformational geometries of phenylthiosemicarbazone (HAPhTSC) conformers were determined using hybrid density functional theory (DFT) at the B3LYP [14, 15] level of theory with the standard 6-31G(d) [16] and 6-311G(d,p) [17–19, 20] basis sets. All DFT calculations were performed with zero-point energy corrections. Vibrational analyses have been carried out on minima and transition states (TS). All computations were performed using the Gaussian 03 program package [21]. The Molekel 4.3 program [22] was used to visualize the molecular geometries and generate the electrostatic potential surface of the most stable HAPhTSC tautomer from the Gaussian output file. The reaction energies  $\Delta E^0$ , standard enthalpies  $\Delta H^0$  and Gibbs free energies  $\Delta G^0$  of interconversion reactions between the HAPhTSC conformers were derived from frequency calculations at the B3LYP/6-31G(d) and B3LYP/6-

**Fig. 1** Conformational notation defined as a name consisting of a letter “A” for a thioamino tautomer followed by “c” for *cis* or “t” for *trans* isomerism of five dihedral angles of  $\chi(C4-C3-C2-N3)$ ,  $\varphi(C3-C2-N3-N2)$ ,  $\psi(C2-N3-N2-C1)$ ,  $\theta(N3-N2-C1-N1)$  and  $\omega(N2-C1-N1-H2)$ , serially, or a letter “I” for b thioimino tautomer followed by “c” for *cis* or “t” for *trans* isomerism of six dihedral angles of  $\chi(C4-C3-C2-N3)$ ,  $\varphi(C3-C2-N3-N2)$ ,  $\psi(C2-N3-N2-C1)$ ,  $\theta(N3-N2-C1-N1)$ ,  $\omega(N2-C1-N1-H2)$  and  $\delta(N2-C1-S-H1)$ , serially.



**Table 1** Structures of HAPhTSC tautomers optimized at B3LYP/6-311G(d,p) and (in parenthesis) B3LYP/6-31G(d) levels, specified by dihedral angles of  $\chi(C3-C2-N3-N2)$ ,  $\varphi(C3-C2-N3-N2)$ ,  $\psi(C2-N3-N2-C1)$ ,  $\theta(N3-N2-C1-N1)$ ,  $\omega(N2-C1-N1-H2)$  and  $\delta(N2-C1-S-H1)$ , in degrees

Conformers	$\chi$	$\varphi$	$\psi$	$\theta$	$\omega$	$\delta$
<b>Thioamino tautomers</b>						
Attccc	180.0 (180.0)	180.0 (180.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	–
Attcc <sup>a</sup>	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)	0.0 (0.0)	0.0 (0.0)	–
Attctc	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)	0.0 (0.0)	–
Attctc	180.0 (180.0)	180.0 (180.0)	0.0 (0.0)	180.0 (180.0)	0.0 (0.0)	–
Atctcc	180.0 (180.0)	0.0 (0.0)	180.0 (180.0)	0.0 (0.0)	0.0 (0.0)	–
Atcttc	–138.5 (–141.1)	1.5 (1.4)	174.1 (173.0)	–175.4 (–174.9)	–27.4 (–29.6)	–
<b>Thioimino tautomers</b>						
Ittccct	180.0 (180.0)	180.0 (180.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	180.0 (180.0)
Ittcccc	180.0 (180.0)	180.0 (180.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
Ittctct	180.0 (180.0)	180.0 (180.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
Ittctct	180.0 (180.0)	180.0 (180.0)	0.0 (0.0)	0.0 (0.0)	180.0 (180.0)	0.0 (0.0)
Itttcct	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)	0.0 (0.0)	0.0 (0.0)	180.0 (180.0)
Itttccc	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
Itttctc	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)	0.0 (0.0)	180.0 (180.0)	0.0 (0.0)
Itttctt	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)	0.0 (0.0)	180.0 (180.0)	180.0 (180.0)
Itttctt	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)	0.0 (0.0)	180.0 (180.0)
Itttctc	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)	0.0 (0.0)	0.0 (0.0)
Itttttc <sup>b</sup>	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)	0.0 (0.0)
Itttttt	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)
Itttctt	180.0 (180.0)	180.0 (180.0)	0.0 (0.0)	180.0 (180.0)	0.0 (0.0)	180.0 (180.0)
Itttctc	180.0 (180.0)	180.0 (180.0)	0.0 (0.0)	180.0 (180.0)	0.0 (0.0)	0.0 (0.0)
Itttctc	180.0 (180.0)	180.0 (180.0)	0.0 (0.0)	180.0 (180.0)	180.0 (180.0)	0.0 (0.0)
Itttctt	180.0 (180.0)	180.0 (180.0)	0.0 (0.0)	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)
Itctcct	147.2 (148.5)	–1.1 (–1.0)	–171.4 (–170.2)	–7.0 (–8.5)	3.4 (3.7)	–171.9 (–173.2)
Itctccc	146.9 (148.5)	–0.9 (–0.8)	–169.0 (–167.6)	–5.4 (–6.4)	4.7 (5.2)	29.5 (30.3)
Itctctc	143.1 (144.6)	–0.4 (–0.2)	–168.4 (–167.2)	0.2 (–0.3)	–173.9 (–173.5)	48.5 (44.1)
Itctctt	143.2 (144.8)	–0.7 (–0.7)	–170.4 (–169.8)	1.9 (1.3)	–172.7 (–172.5)	–145.8 (–148.5)
Itctctt	143.1 (144.6)	–1.1 (–1.0)	–173.3 (–171.6)	173.0 (171.9)	–1.0 (–1.1)	–177.3 (–176.6)
Itctctc	143.9 (145.2)	–1.1 (–1.0)	–172.6 (–171.0)	170.9 (169.6)	–1.4 (–1.4)	4.8 (5.4)
Itctctc	147.4 (148.1)	–1.0 (–1.0)	–173.2 (–171.7)	169.8 (168.0)	178.6 (178.2)	5.7 (6.6)
Itctttt	146.1 (146.9)	–1.1 (–1.0)	–174.2 (–172.9)	172.1 (170.9)	179.0 (178.8)	–176.9 (–176.0)

<sup>a</sup> The most stable tautomer

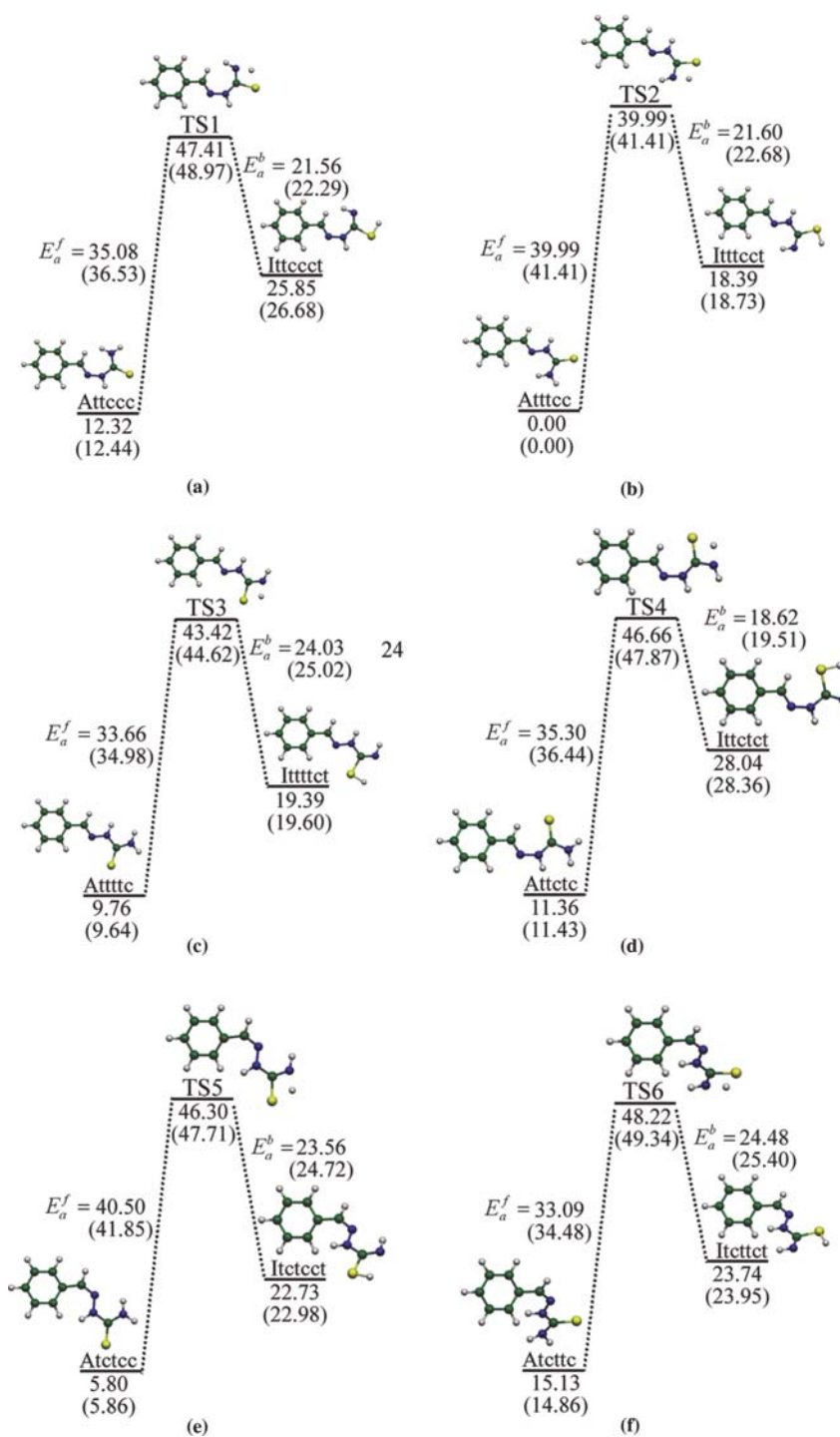
<sup>b</sup> The most stable species of thioimino tautomer

311G(d,p) levels of theory. The reaction entropies ( $\Delta S^\ddagger$ ) of interconversions were evaluated using a thermodynamic equation  $\Delta S^\ddagger = (\Delta H^\ddagger - \Delta G^\ddagger)/T$ . The rate constant  $k(T)$  derived from transition state theory was computed from the Gibbs free energy of activation

$\Delta^\ddagger G^0$ , using  $k(T) = (k_B T/hc^0) e^{-\Delta^\ddagger G^0/RT}$  where the factor  $c^0$  is assigned to unity [23]. The equilibrium constant  $K$  at 298.15 K and 1 atm is computed using the equation  $\Delta G^0 = -RT \ln K$ .

**Table 2** Thermodynamic quantities of interconversion reactions between thioamino tautomers of HAPhTSC, derived from B3LYP/6-311G(d,p) and (in parenthesis) B3LYP/6-31G(d) calculations

Reactions	$\Delta E_{\text{rel}}^0$ (kcal mol <sup>-1</sup> )	$\Delta H^0$ (kcal mol <sup>-1</sup> )	$\Delta G^0$ (kcal mol <sup>-1</sup> )	$\Delta S^0$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	Log <i>K</i>
Attccc $\rightleftharpoons$ Atttcc <sup>a</sup>	-12.32 (-12.44)	-11.58 (-11.64)	-13.46 (-13.62)	-6.33 (-6.64)	9.87 (9.99)
Attccc $\rightleftharpoons$ Attttc	9.76 (9.64)	9.59 (9.40)	9.81 (9.81)	0.73 (1.35)	-7.19 (-7.19)
Attctc $\rightleftharpoons$ Attttc	-1.60 (-1.79)	-1.59 (-1.81)	-1.35 (-1.37)	0.81 (1.48)	0.99 (1.00)
Attccc $\rightleftharpoons$ Attctc	-0.97 (-1.01)	-0.39 (-0.43)	-2.30 (-2.45)	6.41 (6.77)	1.69 (1.79)
Atctcc $\rightleftharpoons$ Atcttc <sup>b</sup>	9.33 (9.01)	9.81 (9.37)	8.14 (8.03)	-5.60 (-4.50)	-5.97 (-5.89)

<sup>a</sup> The most stable tautomer<sup>b</sup> The least stable species of thioamino tautomer**Fig. 2** Relative energetic profiles for tautomerization reactions between **a** Attccc and Ittccct, **b** Atttcc and Itttct, **c** Attttc and Itttct, **d** Attctc and Ittctc, **e** Atctcc and Itctct and **f** Atcttc and Itctct. Relative and activation energies derived from B3LYP/6-311G(d,p) and (in parenthesis) B3LYP/6-31G(d) calculations, in kcal mol<sup>-1</sup>. All relative energies are related to the most stable (Attttc) conformer.

**Table 3** Activation energies of tautomerizations of HAPhTSC tautomers derived from their total energies at B3LYP/6-311G(d,p) and (in parenthesis) B3LYP/6-31G(d) levels

Tautomerization	$E_a^f$ <sup>a</sup>	$E_a^b$ <sup>a</sup>	$\Delta E_{rel}^{0\ a,b}$	Log $k_f^c$	Log $k_b^d$	Log $K^e$
Attccc → TS1 → Ittcct	35.08 (36.53)	21.56 (22.29)	13.52 (14.24)	-12.59 (-13.69)	-2.55 (-3.08)	-10.05 (-10.61)
Attccc → TS2 → Itttcct	39.99 (41.41)	21.60 (22.68)	18.39 (18.73)	-16.61 (-17.71)	-2.87 (-3.70)	-13.74 (-14.01)
Attccc → TS3 → Ittttct	33.66 (34.98)	24.03 (25.02)	9.63 (9.96)	-11.94 (-12.90)	-4.99 (-5.75)	-6.95 (-7.15)
Attccc → TS4 → Itttctct	35.30 (36.44)	18.62 (19.51)	16.68 (16.93)	-14.10 (-15.02)	-1.15 (-1.81)	-12.95 (-13.21)
Attccc → TS5 → Ittctct	40.50 (41.85)	23.56 (24.72)	16.93 (17.13)	-16.84 (-17.87)	-5.34 (-6.10)	-11.50 (-11.77)
Attccc → TS6 → Itcttct	33.09 (34.48)	24.48 (25.40)	8.61 (9.09)	-11.60 (-12.60)	-5.14 (-5.81)	-6.46 (-6.79)

<sup>a</sup> Relative energies compared to energy of the most stable tautomer, all energies have been corrected for ZPE at B3LYP/6-311G(d,p) and (in parenthesis) B3LYP/6-31G(d) levels, in kcal mol<sup>-1</sup>

<sup>b</sup>  $\Delta E_{rel} = E_a^f - E_a^b$

<sup>c</sup> Forward kinetic constant

<sup>d</sup> Backward kinetic constant

<sup>e</sup> Equilibrium constant ( $K = k_f/k_b$ )

**Table 4** Thermodynamic quantities of tautomerizations of HAPhTSC tautomers derived from their frequency calculations at B3LYP/6-311G(d,p) and (in parenthesis) B3LYP/6-31G(d) levels

Tautomerization	$\Delta H^0$ (kcal mol <sup>-1</sup> )	$\Delta G^0$ (kcal mol <sup>-1</sup> )	$\Delta S^0$ (cal mol <sup>-1</sup> K <sup>-1</sup> )
Attccc → TS1 → Ittcct	13.56(14.27)	13.71(14.47)	-0.51(-0.68)
Attccc → TS2 → Itttcct	18.17(18.46)	18.74(19.11)	-1.91(-2.17)
Attccc → TS3 → Ittttct	9.83(10.18)	9.48(9.75)	1.20(1.44)
Attccc → TS4 → Itttctct	16.41(16.65)	17.66(18.02)	-4.18(-4.59)
Attccc → TS5 → Ittctct	17.52(17.62)	15.68(16.05)	6.18(5.27)
Attccc → TS6 → Itcttct	8.57(9.07)	8.82(9.26)	-0.81(-0.63)

The conformational notation of HAPhTSC is defined as a name consisting of a letter “A” for the thioamino tautomer followed by “c” for *cis* or “t” for *trans* isomerism of five dihedral angles of  $\chi(C4-C3-C2-N3)$ ,  $\phi(C3-C2-N3-N2)$ ,  $\psi(C2-N3-N2-C1)$ ,  $\theta(N3-N2-C1-N1)$  and  $\omega(N2-C1-N1-H2)$ , serially, or the letter “I” for thioimino tautomer followed by “c” for *cis* or “t” for *trans* isomerism of six dihedral angles of  $\chi(C4-C3-C2-N3)$ ,  $\phi(C3-C2-N3-N2)$ ,  $\psi(C2-N3-N2-C1)$ ,  $\theta(N3-N2-C1-N1)$ ,  $\omega(N2-C1-N1-H2)$  and  $\delta(N2-C1-S-H1)$ , serially, as shown in Fig. 1.

## Results and discussion

### Structural conformers of HAPhTSC and their interconversions

Geometry optimizations of phenylthiosemicarbazone (HAPhTSC) tautomers were performed with DFT calculations at the B3LYP/6-31G(d) and B3LYP/6-311G(d,p) levels of theory. Structural data for the optimized geometries of HAPhTSC tautomers, specified by dihedral angles of  $\chi(C4-C3-C2-N3)$ ,  $\phi(C3-C2-N3-N2)$ ,  $\psi(C2-N3-N2-C1)$ ,  $\theta(N3-N2-C1-N1)$ ,  $\omega(N2-C1-N1-H2)$  and  $\delta(N2-C1-S-H1)$  are listed in Table 1. Reaction energies, standard enthalpies, Gibbs free energies, entropy changes and equilibrium constants of interconversion reactions of HAPhTSC thioamino tautomers obtained from B3LYP/6-311G(d,p) and B3LYP/6-31G(d) calculations are listed in Table 2. For the HAPhTSC thioamino conformers, Attccc was found to be the most stable species. As rotational change of the  $\pi$  bond ( $\phi$  dihedral angle) was not allowed, interconversion of Atctcc and Attccc, and Atcttc and Attttc also did not occur. The reaction energies, standard enthalpies, Gibbs free energies, entropy changes and

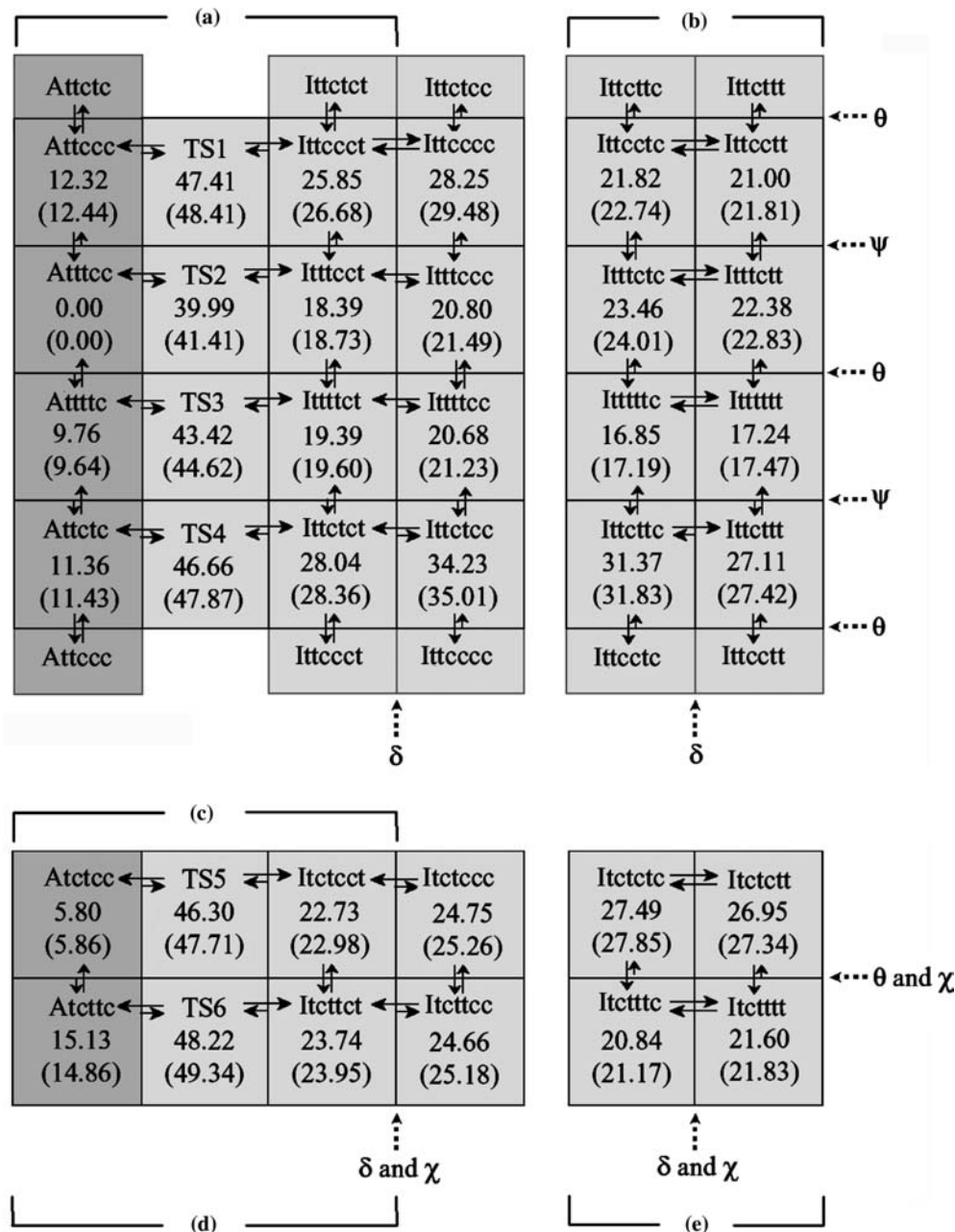
equilibrium constants of interconversion reactions of all HAPhTSC thioimino conformers were obtained (Table S1 of the Supplementary Material). As Ittctcc and Ittttcc are the least and the most stable tautomers of the thioimino form of HAPhTSC, respectively, reaction numbers 19 and 20, as listed in Table S1, show large equilibrium constants as log  $K = -10.66$  and  $-10.74$ .

### HAPhTSC Tautomers and their tautomerizations

Six thioamino and 24 thioimino tautomers of HAPhTSC are shown in the first and the third to sixth columns of Fig. S1 (Supplementary Material), respectively. Six tautomerizations between thioamino and thioimino tautomers occur via transition states TS1, TS2, TS3, TS4, TS5 and TS6, as shown in the second column of Fig. S1. Relative energetic profiles for tautomerization reactions between Attccc and Ittcct, Attccc and Itttcct, Attttc and Ittttct, Attctc and Itttctct, Atctcc and Ittctct and Atcttc and Itcttct are shown in Fig. 2. Considering the molecular symmetries of the conformers, the tautomerizations can be separated into two types, one of the same (see Fig. 2a-d and f) and another of different (Fig. 2e) molecular point groups. Activation energies and thermodynamic quantities of HAPhTSC tautomers are listed in Tables 3 and 4, respectively. The transition structures of TS1, TS2, TS3, TS4, TS5 and TS6 were confirmed by imaginary frequencies of  $-1656.5$ ,  $-1644.3$ ,  $-1666.8$ ,  $-1625.4$ ,  $-1648.1$  and  $-1669.5$  cm<sup>-1</sup> obtained from frequency calculations at the B3LYP/6-311G(d,p) level, respectively. Forward rate coefficients of tautomerizations evaluated from Gibbs free energies of activation according to TS1, TS2, TS3,



**Fig. 3** Integrated pathways of interconversions of two thioamino conformers (*dark grey boxes*), two thioimino conformers (*grey boxes*) and tautomerizations (via transition states TS1, TS2, TS3, TS4, TS5 and TS6) are composed of **a** tautomerizations of  $C_s$ -symmetrical, **b** conversions of  $C_s$ -symmetrical, **c** tautomerization of  $C_1$ -symmetrical, **d** tautomerization between  $C_s$ - and  $C_1$ -symmetrical and **e** conversions of  $C_1$ -symmetrical tautomers. These rotational interconversions according to the changes of  $\chi$ ,  $\psi$ ,  $\theta$  and  $\delta$  dihedral angles are pointed by the *arrows*. The *numbers in boxes* are relative energies derived from B3LYP/6-311G(d,p) and (in parentheses) B3LYP/6-31G(d) calculations, in kcal mol<sup>-1</sup>.

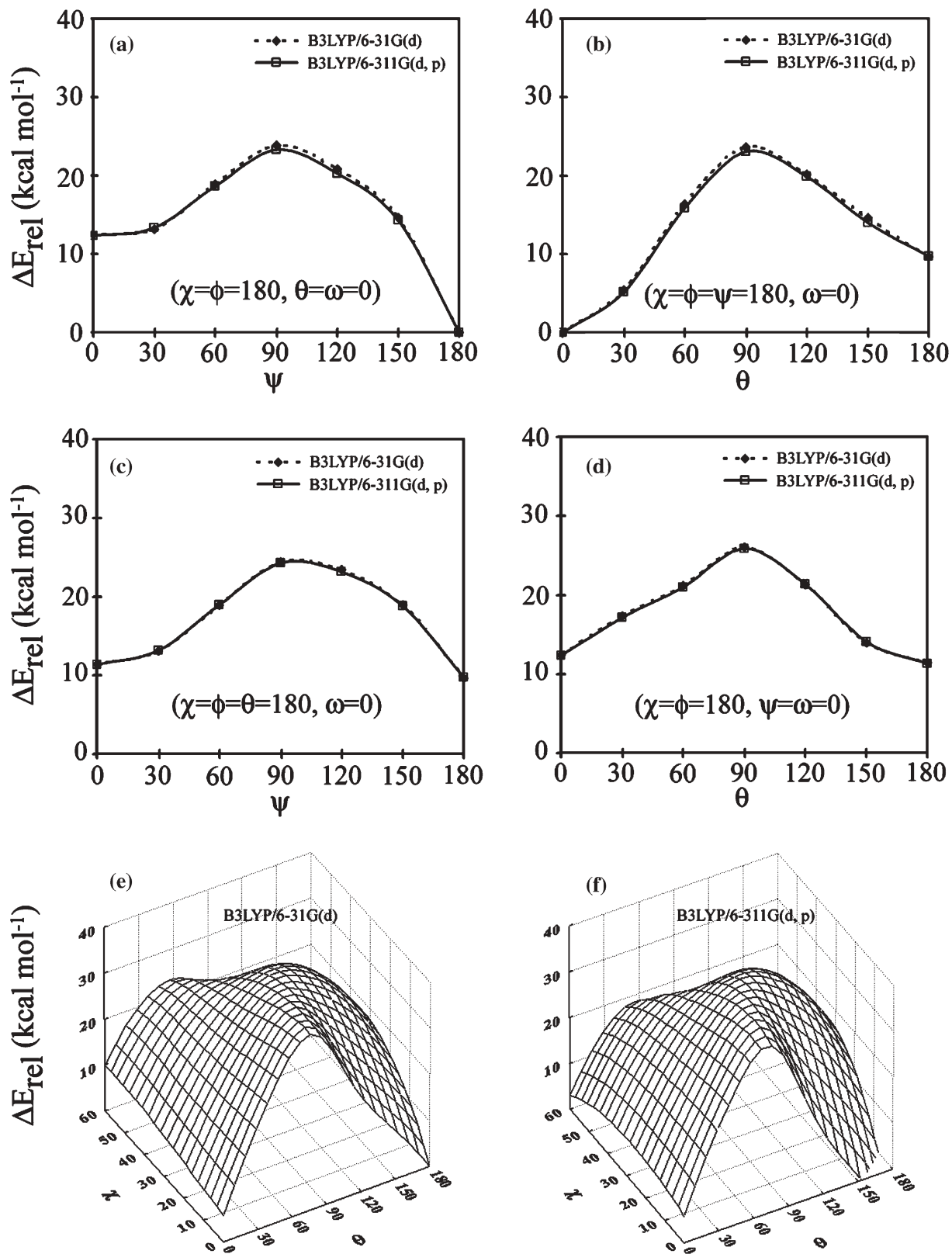


TS4, TS5 and TS6, expressed as  $\log k_f$  are  $-12.59$ ,  $-16.61$ ,  $-11.94$ ,  $-14.10$ ,  $-16.84$  and  $-11.60$ , respectively. For tautomerization between the most stable HAPhTSC thioamino (Attccc) and thioimino (Itttct) tautomers, reaction enthalpy and  $\log K$  are  $18.17$  kcal mol<sup>-1</sup> and  $-13.74$ , respectively.

#### Interconversion pathways and rotational energy barriers

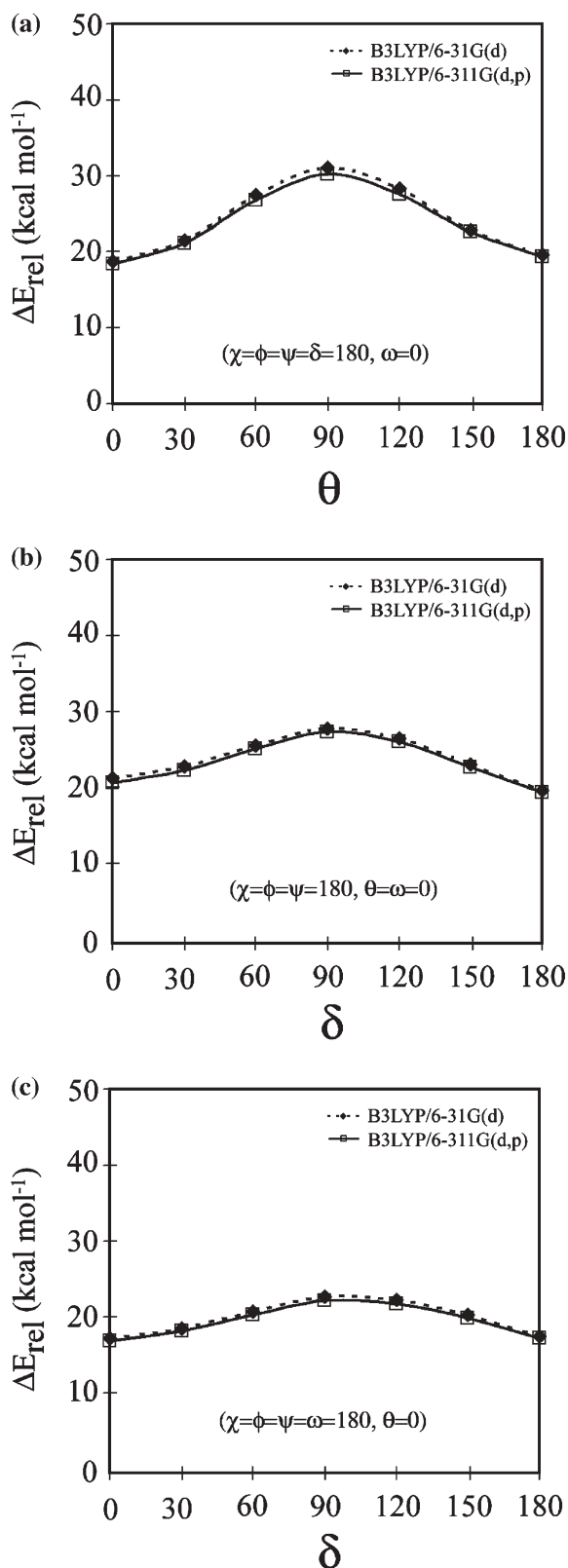
Integrated pathways of tautomerizations and interconversions of HAPhTSC tautomers are shown in Fig. 3, which shows that Attccc and Itttct are the most stable species of the HAPhTSC thioamino and thioimino tautomers, respectively. The interconversions between the

$C_s$ -symmetrical tautomers and between the  $C_1$ -symmetrical tautomers take place via rotational barriers according to dihedral angles of  $\psi$ ,  $\theta$  (see Fig. 4a–d) and  $\psi$ ,  $\theta$  and  $\delta$  (see Fig. 4e–f), respectively. Rotational energy barriers of interconversions between Attccc and Attccc, Attccc and Attttc, Attctc and Attttc, Attccc and Attctc, and Attctc and Attctc, evaluated from the rotational potential curves shown in Fig. 4a–f are  $11.00$  ( $11.46$ ),  $23.03$  ( $23.66$ ),  $12.89$  ( $12.98$ ),  $13.57$  ( $13.61$ ) and  $28.77$  ( $28.89$ ) kcal mol<sup>-1</sup>, respectively. The energies were derived from the B3LYP/6-311G(d,p) and (in parentheses) B3LYP/6-31G(d) calculations. Rotational energy barriers of interconversion between Itttct and Itttct, Itttcc and Itttct, Itttcc and Ittttt, and Ittttc and Ittttt, evaluated from their rotational potentials shown in Fig. 5a–c are  $11.84$  ( $12.37$ ),  $6.62$  ( $6.57$ )



**Fig. 4** Rotational potential curves for interconversions between thioamino conformers **a** Atctcc and Attctc, **b** Attctc and Attttc, **c** Attctc and Attttc, and **d** Atctcc and Attctc. Rotational potential

surfaces for interconversions between **e** Atctcc and Attctc at B3LYP/6-31G(d) level and **f** at B3LYP/6-311G(d,p) level. Dihedral angles of  $\chi$ ,  $\psi$ ,  $\theta$  and  $\delta$  are in degrees.



**Fig. 5** Rotational potential curves for interconversion between thioimino conformers **a** Itttct and Itttctt, **b** Itttcc and Itttct, and **c** Ittttc and Ittttt. Dihedral angles of  $\chi$ ,  $\psi$ ,  $\theta$  and  $\delta$  are in degrees.

and 5.30 (5.53) kcal mol<sup>-1</sup>, respectively. Relative energetic profiles for the tautomerizations and interconversions of the most stable thioamino and thioimino tautomers (in kcal mol<sup>-1</sup>) are shown in Fig. 6. This interconversion pathway composed of the reactions between Attcc and Itttcc, Itttcc and Itttct, Itttct and Itttctt, and Itttcc and Itttct were therefore investigated. TS2 is a transition state of tautomerization between the most stable thioamino and its thioimino tautomers. EB1, EB2 and EB3 are rotational energy barriers according to dihedral angles of  $\theta$ ,  $\delta$  and  $\delta$ , respectively.

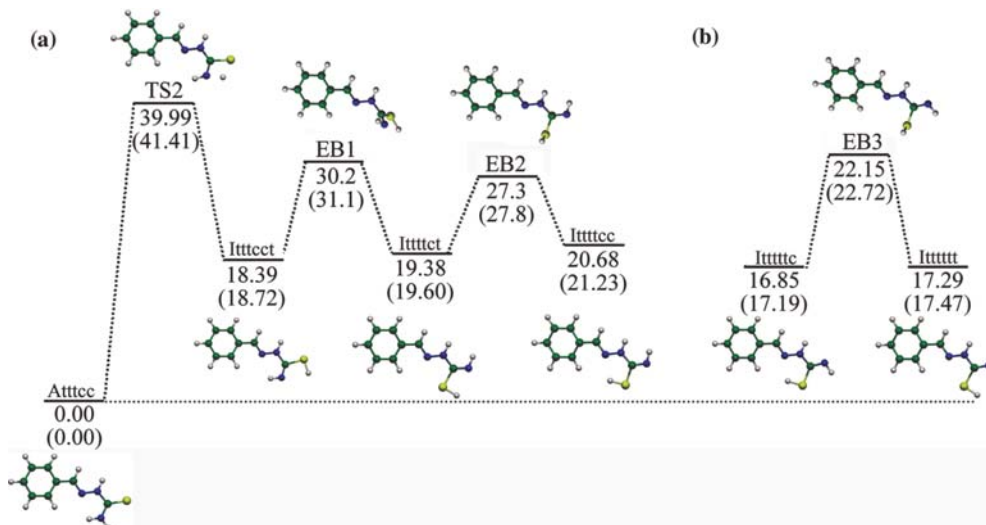
#### Zinc complex with HAPhTSC (Attcc) tautomer

The electrostatic potential of the most stable HAPhTSC (Attcc) tautomer was computed at the B3LYP/6-311(d,p) level. Its electrostatic potential surface at an isodensity ( $\rho=0.015$  e Å<sup>-3</sup>) surface of volume,  $V_s=92.22$  Å<sup>3</sup>, with minimum ( $\psi_-$ ) and maximum ( $\psi_+$ ) potentials of  $\psi_-=-0.10326$  and  $\psi_+=0.13021$  is shown in Fig. 7, which shows high negative electronic potential distributing around the thiosulfur atom. This means that this sulfur atom could coordinate with appropriate transition metal cations such as the zinc(II) ion.

The B3LYP/6-31G(d)-optimized structure of the Zn(HAPhTSC)<sub>2</sub>Cl<sub>2</sub> complex is a C<sub>2</sub>-symmetrical geometry, as shown in Fig. 8. Complexation of Zn(HAPhTSC)<sub>2</sub>Cl<sub>2</sub> is an exothermic and spontaneous reaction. The entropy change of this complexation,  $\Delta S^0=-122.66$  cal mol<sup>-1</sup> K<sup>-1</sup> is computed from the equation  $\Delta S^0=(\Delta H^0 - \Delta G^0)/T$ . Thermodynamic quantities for complexation of HAPhTSC Attcc tautomer, Zn<sup>2+</sup> and Cl<sup>-</sup> derived from the B3LYP/6-31G(d) level calculations are listed in Table 5. The B3LYP/6-31G(d) optimized geometry of Zn(HAPhTSC)<sub>2</sub>Cl<sub>2</sub> complex is in good agreement with X-ray crystallographic data, [24] as listed in Table 6.

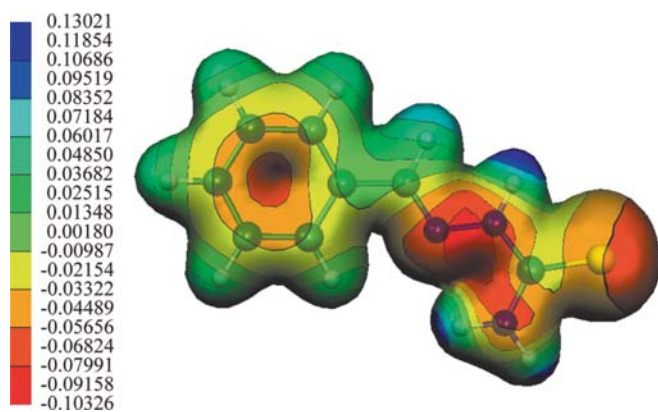
#### Conclusions

The potential energy surface (PES) for the phenylthiosemicarbazone (HAPhTSC) conformers was explored using calculations at the B3LYP/6-31G(d) and B3LYP/6-311G(d,p) levels. Six thioamino and twenty four thioimino tautomers of HAPhTSC have been found. Six tautomerization reactions between thioamino and thioimino tautomers have occurred via TS. Tautomerization between the most stable species (Attcc) of thioamino and its thioimino tautomer is an endothermic reaction,  $\Delta H^0=18.17$  kcal mol<sup>-1</sup> and its log  $K=-13.74$ , at 298.15 K. Thermodynamic quantities of tautomerization, interconversion of HAPhTSC conformers and their equilibrium constants are reported. Vibrational frequencies of the most stable tautomer of HAPhTSC computed at B3LYP/6-31G(d) and B3LYP/6-311G(d,p) levels have been carried out. The geometry of the zinc complex with HAPhTSC, Zn(HAPhTSC)<sub>2</sub>Cl<sub>2</sub> was obtained using



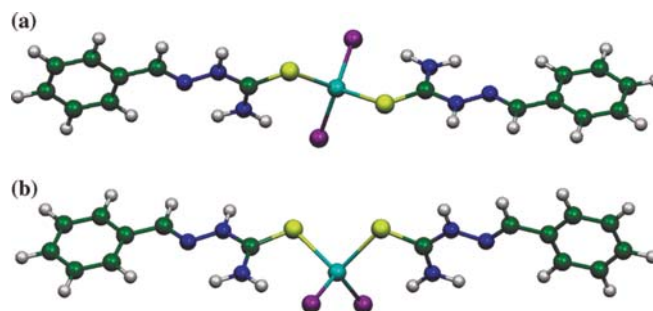
**Fig. 6** Relative energetic profiles (in kcal mol<sup>-1</sup>) for interconversion pathways of **a** the most stable thioamino tautomer and **b** the most stable of thioimino tautomer. TS2 is a transition state of tautomerization between the most stable thioamino and its thioimino tautomers. EB1, EB2 and EB3 are rotational energy barriers according to dihedral angles of  $\theta$ ,  $\delta$ , and  $\delta$ , respectively.

Relative energies derived from B3LYP/6-311G(d,p) and (in parenthesis) B3LYP/6-31G(d) calculations of the most stable (Atttcc) tautomer of which total energies are  $-872.689832$  au at B3LYP/6-311G(d,p) and  $-872.535998$  au at B3LYP/6-31G(d) levels.



**Fig. 7** Electrostatic potential (in au) presented over electronic isodensity ( $\rho=0.015$  e Å<sup>-3</sup>) surface of volume,  $V_s=92.22$  Å<sup>3</sup>, minimum,  $\psi_-$  and maximum,  $\psi_+$  potentials of  $\psi_-=-0.09085$  and  $\psi_+=0.11657$  for HAPhTSC Attctc tautomer.

B3LYP/6-31G(d). Binding of the Zn(HAPhTSC)<sub>2</sub>Cl<sub>2</sub> complex is an exothermic ( $\Delta H^0=-672.77$  kcal mol<sup>-1</sup>) and spontaneous reaction ( $\Delta G^0=-636.20$  kcal mol<sup>-1</sup>).



**Fig. 8** Top **a** and side **b** views of B3LYP/6-31G(d) optimized geometry of Zn(HAPhTSC)<sub>2</sub>Cl<sub>2</sub> complex of C<sub>2</sub> symmetry.

**Table 6** Bond distances (Å) of Zn(HAPhTSC)<sub>2</sub>Cl<sub>2</sub> complex optimized at B3LYP/6-31G(d) level of theory

Bond types	Exp <sup>a</sup>	B3LYP/6-31G(d)
Zn-Cl	2.26	2.26
Zn-S	2.36	2.45
N1-C1	1.32	1.32
N2-C1	1.33	1.36
N2-N3	1.38	1.36
N3-C2	1.27	1.28

<sup>a</sup>X-ray data from Ref. [24]

**Table 5** Thermodynamic quantities for complexation of HAPhTSC Attctc tautomer, Zn<sup>2+</sup> and Cl<sup>-</sup>, derived from the B3LYP/6-311G(d,p) calculations

Reaction	$\Delta E^0$ (kcal mol <sup>-1</sup> )	$\Delta H^0$ (kcal mol <sup>-1</sup> )	$\Delta G^0$ (kcal mol <sup>-1</sup> )	$\Delta S^0$ (cal mol <sup>-1</sup> K <sup>-1</sup> )
2 L + Zn <sup>2+</sup> + 2Cl <sup>-</sup> → ZnL <sub>2</sub> Cl <sub>2</sub>	-671.60	-672.77	-636.20	-122.66



## Electronic Supplementary Material

The list of optimized structures coordinates, a Fig. S1 of optimized structures and a table of thermodynamic quantities is available as Supplementary Material.

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