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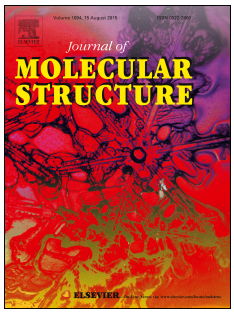

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Tautomerism in 4-chlorophenyl benzoylcarbamodithioate: Experimental and DFT study

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Abstract

The title dithiocarbamate compound was synthesised, and characterised by means of spectroscopic and single-crystal X-ray diffraction methods. Density functional theory method with the 6−311++G(d,p) basis set was employed to affirm the spectroscopic and structural properties and also to study the tautomerism in the compound. The obtained theoretical parameters clearly support the experimental findings. Among the six structural forms of the title compound, the *syn*-keto-amine-thione is found to be the most stable one, and the stability sequence is as the followings: *syn*-keto-amine-thione > *anti*-enol-imine-thione > *anti*-keto-amine-thione > *anti*-keto-imine-thiol > *syn*-keto-imine-thiol > *syn*-enol-imine-thione. The energy difference between the *anti* and *syn* forms changes from ca. 8 to 59 kJ mol^{-1} with or without barriers. The energetic and thermodynamic findings of the *syn*-keto-amine-thione ⇄ *syn*-keto-imine-thiol reaction display that the single proton exchange is unfavoured in both directions. Although the reverse barrier energy of the *anti*-enol-imine-thione ⇄ *anti*-keto-imine-thiol tautomeric transformation is found to be small, neither the forward nor the reverse reaction appears to happen from the thermodynamic point of view.

Keywords: crystal structure; spectroscopy; density functional theory; rotamerism; tautomerism

1. Introduction

Tautomerism is the ability of certain organic molecules to exist in isomeric structures, which are related by the movement of an atom, usually a hydrogen atom, with simultaneous rearrangement of a double bond [**1**]. It is known as keto/enole [**2**], nitroso/oxime [**3**] thioketo/thioenol [**4**], azo/hydrazone [**5**], thioamide/iminothiol [**6**,**7**] etc. One of the most commonly encountered examples is keto-enol tautomerism resulting from the migration of a hydrogen atom from carbon to oxygen [O=C-CH3 ⇄ HO-C=CH2].

In biology, tautomers of some molecules play very important role in hydrogen bonding interactions and stabilize the structure of molecules [**8**]. Mutations in DNA are thought to arise from tautomeric alterations and unusual base pairing [**9**]. Considering the importance of tautomerism in the pharmaceutical industry, identification of the correct tautomer is recognized as one of the important tasks in pharmacophore-based virtual screening and drug discovery programs [**10**]. Therefore, tautomeric structure stability of the synthesized molecule may determine their activity [**11**]. Organic dithiocarbamates are organosulfur compounds and they can also consist of the tautomeric structure. At the same time, they can act as ligands for transition metals because of these properties [**12**].

On the other hand, organic dithiocarbamates are valuable synthetic intermediates, which are ubiquitously found in a variety of biologically active compounds [**13**,**14**], whereas they are used as accelerators in vulcanisation, as high-pressure lubricants [**15**] and as fungicides and pesticides [**16**].

In this work, 4-chlorophenyl benzoylcarbamodithioate was synthesized and characterised with elemental analysis and spectroscopic techniques such as IR and NMR, and single-crystal X-ray crystallography. We focus our attention on the tautomerism in the compound and report the results from both theoretical and experimental points of view. The effect of solvents with different polarity on the tautomerism was examined by applying the integral equation formalism polarizable continuum model (IEF-PCM). Chloroform, methanol and water were chosen as solvent.

2. Materials and methods

2.1. *General remarks*

Reagents such as potassium thiocyanate, benzoyl chloride, 4-chlorothiophenol and solvents from Sigma-Aldrich were used without purification. The melting point was measured on an Electro Thermal IA 9100 apparatus using a capillary tube and is uncorrected. Reactions were monitored by thin-layer chromatography (TLC) on silica-gel 60 F254 plates (Merck) and an UV lamp. The IR spectrum of the title compound was recorded in the range 4000-650 cm^{-1} with a Perkin Elmer

Spectrum 100 FT-IR spectrometer using KBr pellets. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE DPX NMR spectrometer operating at 400 and 101.6 MHz, respectively, using TMS as an internal standard and DMSO-d_6 as solvent.

2.2. *Synthesis*

The mixture of benzoyl chloride **(1)** (2.32 ml, 20 mmol) in 20 mL acetone with the equimolar amount of potassium thiocyanate (1.94 g, 20 mmol) in 20 mL acetone was refluxed with stirring for 1 h to obtain white colour benzoyl isothiocyanate and then cooled to room temperature. A solution of the appropriate of 4-chlorothiophenol **(2)** (2.89 g, 20 mmol) in 20mL acetone was added dropwise to the benzoyl isothiocyanate within 15 min and was stirred for ca. 3 h at room temperature (Scheme 1). The progress of reaction was controlled by TLC. As the reaction was completed, yellow solution was filtered and organic solvent was concentrated with a rotary evaporator under reduced pressure. After then, raw product was chromatographed over silica gel using ethyl acetate-hexane (4:1) as the eluent to separate the product. After evaporation the solvent, the fairly pure, brilliant yellow product (4-chlorophenyl benzoylcarbamodithioate, **(3)**) was crystallized out, mp. 109-110 °C, yield 90%, anal. calc. for $C_{14}H_{10}ClNO_2S_2$: C, 54.63; H, 3.27; Cl, 11.52; N, 4.55; S, 20.83 Found: C, 53.97; H, 3.19; Cl, 11.66; N, 4.49; S, 20.64 [**17**].

<Scheme 1>

2.3. *X-ray crystallography*

Intensity data of the compound were collected on a STOE diffractometer with an IPDS II image plate detector. The diffraction measurements were performed at room temperature (296 K) using graphite monochromated Mo Kα radiation (λ=0.71073 Å) by applying the ω-scan method. Data collection and cell refinement were carried out using X-AREA [**18**] while data reduction was applied using X-RED32 [**18**]. The structure was solved by direct methods using SHELXS-2013 [**19**] and refined with full-matrix least-squares calculations on F^2 using SHELXL-2016 [**20**] implemented in WinGX [**21**] program suit. All H atoms bonded to C atoms were positioned geometrically and refined as a riding model with C─H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C), while the H atom bonded to the N atom was located in a difference Fourier map and refined isotropically [N─H = 0.818(18) Å]. Details of the data collection conditions and the parameters of refinement process are given in Table 1. The general-purpose crystallographic tool PLATON [**22**] was used for the structure analysis and presentation of the results. The molecular graphics were generated using ORTEP-3 [**21**].

<Table 1>

2.4. *Computational procedure*

The stationary structures were optimized using the three-parameter hybrid density functional (B3LYP) [**23**, **24**] and 6−311++G(d,p) [**25**, **26**] basis set. The vibrational frequencies were obtained at the same level to characterize the local minimum and the transition state (TS). The stable structures exhibited all positive frequencies, whereas the TSs possessed one imaginary frequency. The recommended scale factor of 0.9679 [**27**] has been applied to correct the theoretical harmonic vibrational frequencies. The ^{1}H and ^{13}C NMR chemical shifts were calculated within the gauge-independent atomic orbital (GIAO) approach [**28**, **29**] at the same level, in which solvent effects were included by means of the IEF-PCM method [**30**]. All the calculations in the current paper were performed via the GaussView molecular visualisation program [**31**] and Gaussian 03W package [**32**].

3. Results and discussion

3.1. *Experimental and theoretical structures*

The structure of the compound was established by X-ray diffraction, which crystallizes in the monoclinic space group *C*2/*c* with *Z* = 8, and is depicted in Figure 1(a).

<Figure 1>

The structure contains three essentially planar fragments; a chlorobenzene ring (Cl1/C1-C6), a *N*-carbonylcarbamodithioate group (S1/C7/S2/N1/C8/O1) and a benzene ring (C9-C14). The central *N*-carbonylcarbamodithioate moiety makes dihedral angles of 56.17(6) and 13.76(8)° with the chlorobenzene and benzene rings, respectively, while the chlorobenzene and benzene rings are inclined to one another at 44.78(9)°. The bond lengths of the carbonyl and thiocarbonyl groups have usual double-bond character with distances of 1.210(2) and 1.649(17) Å, respectively. The C─N bonds [1.379(2) and 1.383(2) Å] are intermediate between 1.48 Å for a normal C─N single bond and 1.25 Å for a normal C═N double bond [**33**]. These results agree with expected delocalisation in this part of the molecule, and indicate that the compound has a keto-amine-thione form. All other bond lengths and angles present no unusual features.

The molecular structure does not include any intramolecular hydrogen bonds, and there are no important interactions in the crystal structure of the compound, other than van der Waals contacts.

<Table 2>

The corresponding DFT structure is shown in Figure 1(b), while the experimental and computed structural parameters are tabulated in Table 2. As can be seen in the table, the biggest deviation of the bond lengths is 0.19 Å at N1─H1 and the biggest deviation of the bond angles is 2.92° at N1─C8─C9. Theoretically, the *N*-carbonylcarbamodithioate moiety makes dihedral angles of 89.37 and 24.82° with the chlorobenzene and benzene rings, respectively, while the chlorobenzene and benzene rings are tilted at an angle of 65.53°.

When the experimental and computed structures are fitted by PLATON as shown in Figure 1(c), the obtained root mean square (RMS) bond fit and angle fit values of 0.019 Å and 1.493° emphasize the close relationship between them. As a result, the theoretical structure sufficiently resembles to the experimental one, and the level of theory can be applied to obtain the other properties.

3.2. *Spectroscopic characterisation*

The FT-IR spectrum of the compound is shown in Fig. 2 while the observed and calculated frequencies with their proposed assignments are given in Table 3.

<Figure 2>

<Table 3>

A series of absorptions appearing in the high-energy region (3500-2500 cm^{-1}) of the infrared spectrum are associated with the N─H and C─H stretching modes [**34**]. The experimental band at 3286 cm^{-1} corresponds to the stretching vibration of the N─H group, which has been calculated at 3472 cm^{-1}. The C─H aromatic stretching modes were observed at 3078 and 3060 cm^{-1} experimentally and were calculated at 3091 and 3082 cm^{-1}. We assigned the absorption band at 1689 cm^{-1} due to the C═O stretching vibrations [**35**], which is in coincidence with its theoretical value of 1693 cm^{-1}. The thiocarbonyl C═S stretching mode recorded at 1078 cm^{-1} [**36**] is in good agreement with theoretical result of 1056 cm^{-1}. The bands at 1598 and 1573 cm^{-1} in the FT-IR

spectrum of the compound, which can be attributed to the ring C═C stretching vibrations, were calculated at 1588 and 1561 cm^{-1}. The infrared spectrum shows a very strong absorption at 1459 cm^{-1}, which is tentatively assigned to the rocking deformation mode on the N─H group and has been calculated at 1449 cm^{-1}. The C─N and C─S stretching modes recorded at 1196 and 679 cm^{-1} is in good agreement with theoretical results of 1188 and 669 cm^{-1}, respectively. The stretching of the C─Cl bond was confirmed at 744 cm^{-1} [**37**] while this band appeared at 730 cm^{-1} in the theoretical spectrum.

As a result, the IR spectrum of the compound do not exhibit the S─H and O─H vibration modes indicating that in the solid state this compound exists in the keto-amine-thione form.

The NMR spectra of the compound is given in Fig. S1 in the supplementary material while the experimental and calculated chemical shifts are tabulated in Table 4. The proposed structure of the compound was confirmed by use of ^{1}H and ^{13}C NMR spectroscopy. The N─H proton is an amid proton rather than imide due to the resonance with the carbonyl (C═O) and thiocarbonyl (C═S) groups. The compound shows a peak at 10.17 ppm corresponding to the proton of the N─H group, which has been calculated at 10.29 ppm. The aromatic protons were observed at 7.96-7.28 ppm that have been appeared at 8.59-7.70 ppm in the theoretical spectrum. In the ^{13}C NMR spectrum, the signals of the characteristic thiocarbonyl and carbonyl carbons were monitored at 204.55 and 166.53 ppm, while these peaks were calculated at 224.67 and 170.78 ppm, respectively.

<Table 4>

3.3. *Molecular conformation and tautomerism*

The three tautomeric forms can be expected for the compound; namely keto-amine-thione **(I)**, keto-imine-thiol **(II)** and enol-imine-thione **(III)** (Scheme 2). Besides, the conformational flexibility over the central C7─N1 bond permits the structure to possess various rotameric forms. So, possible rotamers of the three tautomers were searched at the same level by changing the φ(S1─C7─N1─C8) torsion angle from −180° to 180° in steps of 5°. The potential energy curves are shown in Fig. 3. The results show that the molecule may be found in six structural forms, namely *syn*-keto-amine-thione, *anti*-keto-amine-thione, *syn*-keto-imine-thiol, *anti*-keto-imine-thiol, *syn*-enol-imine-thione and *anti*-enol-imine-thione (Scheme 2).

<Scheme 2>

The energy trend of the six conformers was obtained as *syn*-keto-amine-thione < *anti*-enol-imine-thione < *anti*-keto-amine-thione < *anti*-keto-imine-thiol < *syn*-keto-imine-thiol < *syn*-enol-imine-thione. Especially, the *syn*-keto-amine-thione conformer was demonstrated as the most stable

one. The relative energy of the *anti* and *syn* conformers was determined as ca. 21 kJ mol^{-1} for the keto-amine-thione tautomer and ca. 8 kJ mol^{-1} for the keto-imine-thiol tautomer. The energy barriers for *syn* → *anti* isomerisation were calculated as ca. 42 and 37 kJ mol^{-1} for the keto-amine-thione and keto-imine-thiol tautomers, while these barriers were found to be 20 and 45 kJ mol^{-1} for *anti* → *syn* isomerisation, respectively. The *anti* form of the enol-imine-thione tautomer is more stable than its *syn* form by ca. 59 kJ mol^{-1} without barrier (Table 5).

<Figure 3>

<(Table 5).>

As shown in Scheme 2, two possible tautomeric transformations can occur. The structural parameters belonging to these two transformations are also listed in Table 2, while their energetic and thermodynamic parameters are given in Table 6. During the discussion of these reactions, the forward direction is chosen as the proton transfer from the more stable tautomer to the less stable one, and the reverse is the opposite one.

<Table 6>

In the *syn*-keto-amine-thione ⇄ *syn*-keto-imine-thiol tautomerisation, the imaginary wavenumber at the TS is calculated at 1641i, 1666i, 1678i and 1679i cm^{-1} for the gas phase, chloroform, methanol and water, respectively. During the *syn*-keto-amine-thione → TS → *syn*-keto-imine-thiol single proton transfer reaction, the N1─H1 (1.011 Å) bond breaks and the S2─H1 bond (1.349 Å) forms simultaneously. The N1···H1 and S2··H1 distances in the TS structure are found as 1.402 and 1.633 Å, respectively. When going from the *syn*-keto-amine-thione to *syn*-keto-imine-thiol form, the N1─C7 bond length is reduced from 1.387 to 1.285 Å, which shows corresponding N─C single bond is transformed into N=C double bond after the hydrogen transfer. In adition, the S2─C7 distance increases from 1.655 to 1.780 Å indicating that the π bond in this S═C bond is broken down and the S═C double bond is transformed into an S─C single bond. The other bond distances remain almost unchanged. In the bond angles, the C7─N1─C8 and S2─C7─S1 angles decrease while the N1─C7─S1 angle increases.

< Figure 4>

Fig. 4 displays the relative energy curve for the *syn*-keto-amine-thione ⇄ *syn*-keto-imine-thiol isomerisation. The energy difference between them is obtained as −45.24, −49.55, −51.28 and −51.49 kJ mol^{-1} in going from the gas phase to water, respectively. The reaction barrier is high and in the range 143.50-151.46 kJ mol^{-1} for the forward reaction and in the range 98.26-99.97 kJ mol^{-1} for the reverse reaction. Consequently, it is obvious that the proton transfer for both directions requires very high energy to happen. This fact is also verified by the standard enthalpy and free energy changes since these are obtained as large positive values implying its endothermicity

In the *anti*-enol-imine-thione ⇄ *anti*-keto-imine-thiol tautomerisation, the imaginary wavenumber at the TS is calculated at 736i, 791i, 810i and 812i cm^{-1} for the gas phase, chloroform, methanol and water, respectively. The *anti*-enol-imine-thione → TS → *anti*-keto-imine-thiol transition happens in a concerted way with the breaking of the O1─H1 (1.008 Å) bond and the formation of the S2─H1 bond (1.374 Å). The O1···H1 and S2···H1 distances in the TS structure are found as 1.379 and 1.490 Å, respectively. On going from the *anti*-enol-imine-thione to *anti*-keto-imine-thiol form, the O1─C8 bond length is reduced from 1.318 to 1.234 Å, while the S2─C7 distance increases from 1.682 to 1.767 Å. This corresponds to the breaking of the S═C double bond and the formation of a O═C double bond. A shortening in the N1─C7 bond and a lengthening in the N1─C8 and C8─C9 bonds are also noteworthy. In the bond angles, the S2─C7─S1 and N1─C8─C9 angles decrease as the N1─C7─S1 and O1─C8─C9 angles increase.

< Figure 5>

Fig. 5 exhibits the relative energy curve for the *anti*-enol-imine-thione ⇄ *anti*-keto-imine-thiol isomerisation. The energy difference between them is computed as −21.44, −20.32, −20.10 and −20.09 kJ mol^{-1}, while the energy of the TS is higher than the *anti*-enol-imine-thione tautomer by 25.23, 25.17, 25.33 and 25.37 kJ mol^{-1} in going from the gas phase to water, respectively. These energies together with the positive standard enthalpy and free energy changes make the forward reaction a disfavoured process. In the case of the reverse reaction, very low energy barriers are found as 3.79, 4.85, 5.23 and 5.27 kJ mol^{-1} in going from the gas phase to water, respectively. The values of the standard enthalpies for the reverse reaction show that all the proton transfers are enthalpically favoured (exothermic). However, the proton transfer reaction needs larger entropy change rather than energy change to occur ($|T\Delta S_{298}|>|\Delta H_{298}|$). Therefore, the reverse reaction is thermodynamically disfavoured for all phases ($\Delta G_{298} > 0$) [**38**].

4. Conclusions

In this study, the title dithiocarbamate molecule was obtained and characterised by IR and NMR spectroscopies. The structure of the molecule was confirmed by single-crystal X-ray diffraction technique. To support spectroscopic and structural characterisation and also to investigate the tautomerisation of the compound, theoretical computations have been fulfilled by DFT/B3LYP method with the 6−311++G(d,p) basis set, in which the IEF-PCM method is further used to expose the solvent effects on the tautomerisation. Experimental and quantum chemical calculations show that the keto-amine-thione form is the predominant one among the three possible tautomers. According to the predicted relative energies of the six conformers of the title compound, *syn*-keto-amine-thione conformer is again obtained to be the most stable one. The barrier energy for *anti* ↔ *syn* conformational interconversion for the keto-amine-thione and keto-imine-thiol tautomers is very high and above ca. 42 kJ mol^{-1}, while the two conformations are separated from each other by 59 kJ mol^{-1} without barrier for the enol-imine-thione tautomer. When the two possible tautomeric transitions within the six conformers are considered, the corresponding energy barriers for the *syn*-keto-amine-thione ⇄ *syn*-keto-imine-thiol tautomerisation are bigger than ca. 98 kJ mol^{-1} in both directions. In the case of the *anti*-enol-imine-thione ⇄ *anti*-keto-imine-thiol tautomerisation, it seems impossible to happen thermodynamically for both directions even if the reverse reaction barrier energy is small.

Acknowledgments

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Appendix A. Supplementary data

Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC) with quotation number CCDC 1041602 and can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk/getstructures].

References

[1] M.B. Smith and J. March, Advanced Organic Chemistry (John Wiley & Sons, New York, (2001).

[2] T.A. Gadosy and R.A. McClelland, J. Mol. Struct. Theochem 369 (1996) 1-8.

[3] V. Enchev, G. Ivanova, A. Ugrinov, G.D. Neykov, S. Minchev and N. Stoyanov, J. Mol. Struct. 440 (1998) 227-235.

[4] F. Aydın, H. Ünver, D. Aykaç and N.O. İskeleli, J. Chem. Crystallogr. 40 (2010) 1082-1086.

[5] A.S. Shawali, M.A. Abdallah, M.A. Mosselhi and Y.F. Mohamed, Z. Naturforsch. B 57 (2002) 552-556.

[6] M.J. Cook, A.R. Katritzky, P. Linda and R.D. Tack, J. Chem. Soc. Perkin Trans. 2 (10) (1972) 1295-1301.

[7] N.T. Kochev, V.H. Paskaleva and N. Jeliazkova, Mol. Inf. 32 (2013) 481-504.

[8] V.L. Golo and Y.S. Volkov, Int. J. Mod. Phys. 14 (2003) 133-156.

[9] M. Orozco, B. Hernández and F.J. Luque, J. Phys. Chem. B. 102 (1998) 5228-5233.

[10] D. Venkateswarlu and J. Leszczynski, J. Comput. Aid. Mol. Des. 12 (1998) 373-382.

[11] A.R. Katritzky and A.J. Waring, J. Chem. Soc. (1962) 1540-1544.

[12] M.A. Malik, T. Saeed and P. O'Brien, Polyhedron 12 (1993) 1533-1538.

[13] P. Francis, M. Markman, T. Hakes, B. Reichman, S. Rubin, W. Jones, J.L. Lewis Jr., J. Curtin, R. Barakat, M. Phillips and W. Hoskins, J. Cancer Res. Clin. Oncol. 119 (1993) 360-362.

[14] H. Nabipour, S. Ghammamy, S. Ashuri and Z.S. Aghbolagh, Org. Chem. J. 2 (2010) 75-80.

[15] L. Monser and N. Adhoum, Sep. Purif. Technol. 26 (2002) 137-146.

[16] M.A. Hussein, A.-N. El-Shorbagi, A.-R. Khallil, Arch. Pharm. 334 (2001) 305-308.

[17] F. Aydın, D. Aykac, E. Dagcı, Asian J. Chem. 22 (2010) 3881-3884.

[18] Stoe & Cie, X-AREA (Version 1.18) and X-RED32 (Version 1.04) Stoe & Cie, Darmstadt, Germany 2002.

[19] G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112-122.

[20] G.M. Sheldrick, Acta Crystallogr. C71 (2015) 3-8.

[21] L.J. Farrugia, J. Appl. Crystallogr. 45 (2012) 849-854.

[22] A.L. Spek, Acta Crystallogr. D65 (2009) 148-155.

[23] A.D. Becke, J. Chem. Phys. 98 (1993) 5648-5652.

[24] C. Lee, W. Yang and R.G. Parr, Phys. Rev. B 37 (1988) 785-789.

[25] R. Krishnan, J.S. Binkley, R. Seeger and J.A. Pople, J. Chem. Phys. 72 (1980) 650-654.

[26] M.J. Frisch, J.A. Pople and J.S. Binkley, J. Chem. Phys. 80 (1984) 3265-3269.

[27] M.P. Andersson and P. Uvdal, J. Phys. Chem. A 109 (2005) 2937-2941.

[28] R. Ditchfield, J. Chem. Phys. 56 (1972) 5688-5691.

[29] K. Wolinski, J.F. Hinton and P. Pulay, J. Am. Chem. Soc. 112 (1990) 8251-8260.

[30] J. Tomasi, B. Mennucci and R. Cammi, Chem. Rev. 105 (2005) 2999-3094.

[31] R. Dennington II, T. Keith and J. Millam, GaussView, Version 4.1.2 Semichem, Inc., Shawnee Mission, KS, 2007.

[32] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez and J.A. Pople, Gaussian 03W, Revision E.01,Gaussian, Inc., Wallingford, CT, 2004.

[33] G. Binzet, U. Flörke, N. Külcü and H. Arslan, Z. Kristallogr. NCS 219 (2004) 395-397.

[34] R.M. Silverstein, F.X. Webster and D.J. Kiemle, Spectrometric Identification of Organic Compounds, John Wiley and Sons, New York, 2005.

[35] A. Saeed, A. Khurshid, M. Bolte, A.C. Fantoni and M.F. Erben, Spectrochim. Acta A 143 (2015) 59-66.

[36] H. Arslan, U. Flörke, N. Külcü and G. Binzet, Spectrochim. Acta A 68 (2007) 1347-1355.

[37] A. Saeed, M.F. Erben and U. Flörke, J. Mol. Struct. 982 (2010) 91-99.

[38] V.B. Delchev, I.G. Shterev, H. Mikosch and N.T. Kochev, J. Mol. Model. 13 (2007) 1001-1008.

Table 1. Crystal data and structure refinement parameters for 4-chlorophenyl benzoylcarbamodithioate.

CCDC deposition no.	1041602
Colour/shape	Yellow/prism
Chemical formula	$C_{14}H_{10}ClNOS_2$
Formula weight	307.80
Temperature (K)	296
Wavelength (Å)	0.71073 Mo Kα
Crystal system	Monoclinic
Space group	*C*2/*c* (No. 15)
Unit cell parameters	
a, *b*, *c* (Å)	28.9120(12), 4.1382(2), 24.0699(11)
α, β, γ (°)	90, 107.043(3), 90
Volume (Å^3)	2753.3(2)
Z	8
D_{calc} (g/cm^3)	1.485
μ (mm^{-1})	0.570
Absorption correction	Integration
T_{min}, T_{max}	0.7039, 0.8930
F_{000}	1264
Crystal size (mm^3)	0.76 × 0.43 × 0.19
Diffractometer/measurement method	STOE IPDS II/ω scan
Index ranges	$-36 \le h \le 36$, $-5 \le k \le 5$, $-30 \le l \le 30$
θ range for data collection (°)	$1.473 \le \theta \le 27.155$
Reflections collected	17554
Independent/observed reflections	3052/2141
R_{int}	0.1294
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3052/0/176
Goodness-of-fit on F^2	1.008
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0339$, $wR_2 = 0.0775$
R indices (all data)	$R_1 = 0.0584$, $wR_2 = 0.0833$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e/Å^3)	0.25, −0.12

Table 2. Experimental and optimized structural parameters in the gas phase for the tautomeric transformation of 4-chlorophenyl benzoylcarbamodithioate.

Parameters	X-ray	B3LYP/6−311++G(d,p)					
		syn-keto-amine-thione	TS	syn-keto-imine-thiol	anti-enol-imine-thione	TS	anti-keto-imine-thiol
Bond lengths (Å)							
Cl1─C4	1.743(2)	1.757	1.755	1.755	1.756	1.755	1.754
S1─C1	1.770(2)	1.796	1.805	1.805	1.790	1.794	1.795
S1─C7	1.741(2)	1.787	1.743	1.789	1.787	1.780	1.785
S2─C7	1.649(2)	1.655	1.726	1.780	1.682	1.737	1.767
S2─H1	-	-	-	1.349	-	-	1.374
O1─C8	1.210(2)	1.215	1.223	1.223	1.318	1.259	1.234
O1─H1	-	-	-	-	1.008	-	-
N1─C7	1.379(2)	1.387	1.339	1.285	1.355	1.310	1.289
N1─C8	1.383(2)	1.396	1.395	1.403	1.312	1.365	1.391
N1─H1	0.818(18)	1.011	-	-	-	-	-
C8─C9	1.485(2)	1.498	1.492	1.492	1.475	1.483	1.490
Bond angles (°)							
C1─S1─C7	104.12(8)	101.29	101.14	102.10	104.50	104.31	104.70
C7─N1─C8	127.72(17)	130.11	124.36	121.04	124.38	122.66	125.07
C7─N1─H1	112.7(12)	112.10	-	-	-	-	-
C8─N1─H1	119.6(12)	117.71	-	-	-	-	-
C8─O1─H1	-	-	-	-	108.47	-	-
N1─C7─S2	118.82(13)	118.73	106.54	118.14	129.63	127.68	129.68
N1─C7─S1	115.79(13)	115.34	125.10	125.38	106.96	111.52	112.49
S1─C7─S2	125.38(10)	125.93	128.36	116.48	123.41	120.81	117.83
C7─S2─H1	-	-	-	92.62	-	-	90.04
O1─C8─N1	120.36(17)	122.17	121.70	123.46	125.91	124.98	125.28

O1─C8─C9	121.59(16)	122.70	122.63	121.94	114.90	118.95	120.44
N1─C8─C9	118.04(16)	115.12	115.67	114.60	119.19	116.07	114.28
Dihedral angles (°)							
C8─N1─C7─S2	178.54(14)	178.55	−180.00	180.00	−0.01	0.00	0.00
C8─N1─C7─S1	−2.5(2)	−1.62	0.00	0.00	180.00	−180.00	180.00
C1─S1─C7─N1	−176.32(12)	−178.08	180.00	−179.99	−180.00	180.00	−180.00
C1─S1─C7─S2	2.55(13)	1.74	0.00	0.02	0.01	0.00	0.00
C7─N1─C8─O1	−5.6(3)	−3.73	0.00	−0.01	−0.00	0.00	−0.00
C7─N1─C8─C9	173.94(15)	177.08	−180.00	180.00	180.00	−180.00	−180.00

Table 3. Experimental and calculated vibrational frequencies (cm^{-1}) for 4-chlorophenyl benzoylcarbamodithioate.

Assignments	Experimental	Calculated
v N—H	3286	3472
v C—H	3078	3091
v C—H	3060	3082
v C=O	1689	1693
v C=C	1598	1588
v C=C	1573	1561
γ N—H	1459	1449
v C—N	1196	1188
v C=S	1078	1056
v C—Cl	744	730
v C—S	679	669

v, stretching; *γ*, rocking.

Table 4. Experimental and theoretical ^{1}H and ^{13}C NMR chemical shifts from TMS for 4-chlorophenyl benzoylcarbamodithioate.

Atom	Experimental	Calculated	Atom	Experimental	Calculated
H1	10.17	10.29	C3	129.52	137.15
H2	7.28	7.75	C4	132.07	153.56
H3	7.48	7.72	C5	129.52	137.38
H5	7.48	7.84	C6	131.26	144.41
H6	7.28	7.70	C7	204.55	224.67
H10	7.96	8.01	C8	166.53	170.78
H11	7.57	7.83	C9	138.22	139.89
H12	7.67	7.99	C10	129.08	133.35
H13	7.57	7.95	C11	130.11	136.10
H14	7.96	8.59	C12	133.90	142.07
C1	135.86	143.08	C13	130.11	136.84
C2	131.26	145.06	C14	129.08	137.93

Notes: The atom numbering according to Fig. 1(a) used in the assignment of chemical shifts.

Table 5. Energies of the tautomers in hartree, and the relative energy between the *anti* and *syn* conformers of the tautomers in kJ mol^{-1}.

tautomers	***E***	**Δ*E***
syn-keto-amine-thione	−1926.33199085	21.93
anti-keto-amine-thione	−1926.32363827	
syn-keto-imine-thiol	−1926.31476043	8.36
anti-keto-imine-thiol	−1926.31794323	
syn-enol-imine-thione	−1926.30360050	59.10
anti-enol-imine-thione	−1926.32610911	

Table 6. Energies of the tautomers in Hartree, and energy differences, activation energies and thermodynamic parameters in kJ mol^{-1}.

	E_1	E_2	ΔE	E_a(f)	E_a(r)	ΔH_{298}(f)	ΔG_{298}(f)	$T\Delta S_{298}$(f)	ΔH_{298}(r)	ΔG_{298}(r)	$T\Delta S_{298}$(r)
	syn-keto-amine-thione	*syn*-keto-imine-thiol									
gas phase	−1926.33199085	−1926.31476043	−45.24	143.50	98.26	126.00	126.99	−0.99	90.00	90.79	−0.78
chloroform	−1926.34071439	−1926.32184233	−49.55	148.97	99.42	131.30	131.17	0.14	91.22	93.13	−1.92
methanol	−1926.34428320	−1926.32475166	−51.28	151.19	99.91	133.51	133.93	−0.41	91.72	93.54	−1.82
water	−1926.34470047	−1926.32508936	−51.49	151.46	99.97	133.78	134.33	−0.55	91.77	93.60	−1.82
	anti-enol-imine-thione	*anti*-keto-imine-thiol									
gas phase	−1926.32610911	−1926.31794323	−21.44	25.23	3.79	11.10	13.94	−2.85	−3.37	1.38	−4.75
chloroform	−1926.33121266	−1926.32347318	−20.32	25.17	4.85	10.92	14.71	−3.78	−2.59	2.40	−5.00
methanol	−1926.33333080	−1926.32567508	−20.10	25.33	5.23	11.06	14.33	−3.27	−2.28	3.29	−5.57
water	−1926.33358081	−1926.32592782	−20.09	25.37	5.27	11.09	14.19	−3.10	−2.24	3.41	−5.65

$\Delta E = E_1 - E_2$, E_a(f) = forward activation energy, E_a(r) = reverse activation energy.

Figure Captions

Scheme 1. Synthesis pathway of 4-chlorophenyl benzoylcarbamodithioate.

Scheme 2. Tautomerism in 4-chlorophenyl benzoylcarbamodithioate.

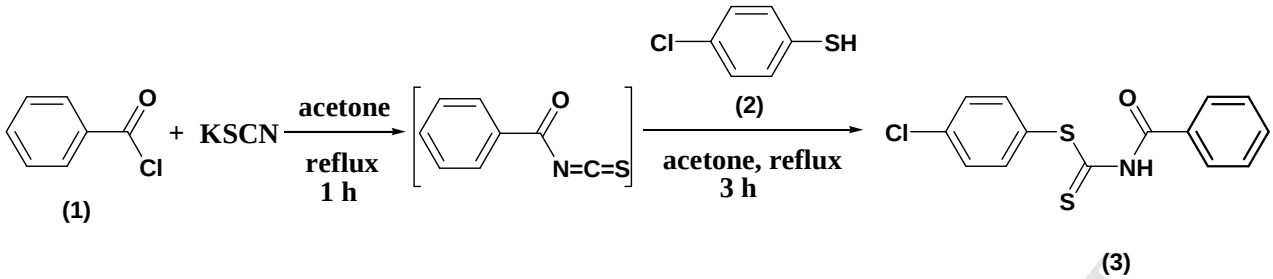
Figure 1. (a) The molecular structure of 4-chlorophenyl benzoylcarbamodithioate showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. (b) The theoretical geometric structure of 4-chlorophenyl benzoylcarbamodithioate. (c) A molecular fit of the experimental and calculated structures shown in red and black, respectively.

Figure 2. (a) FT-IR spectrum of 4-chlorophenyl benzoylcarbamodithioate.
(b) Simulated IR spectrum of 4-chlorophenyl benzoylcarbamodithioate.

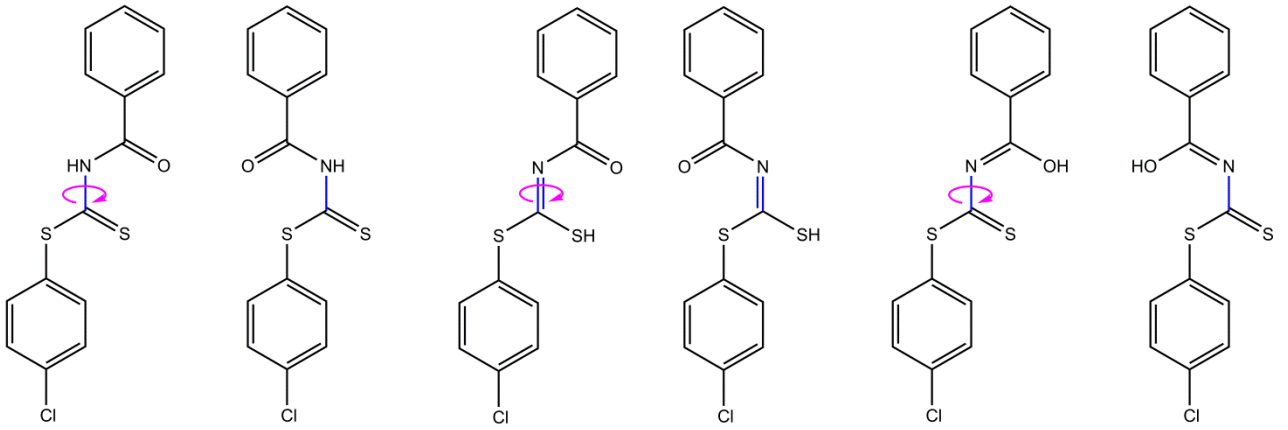
Figure 3. The potential energy profiles for interconversion between two low energy forms of the keto-amine-thione (a), keto-imine-thiol (b) and enol-imine-thione (c) tautomers of 4-chlorophenyl benzoylcarbamodithioate.

Figure 4. Relative energy profile of the *syn*-keto-amine-thione ⇄ *syn*-keto-imine-thiol tautomerism in the gas phase and various solvents.

Figure 5. Relative energy profile of the *anti*-enol-imine-thione ⇄ *anti*-keto-imine-thiol tautomerism in the gas phase and various solvents.



Scheme 1



Scheme 2

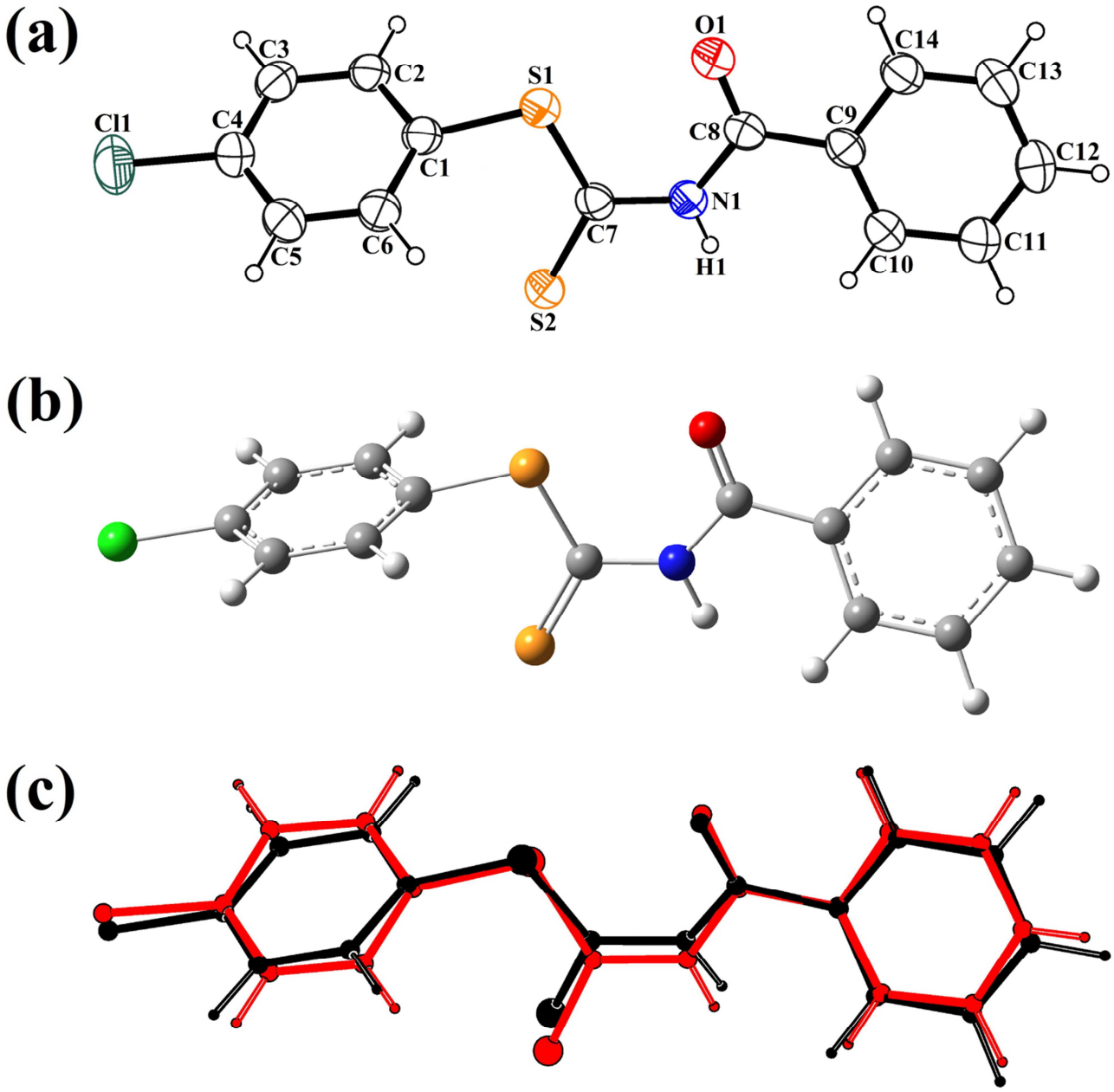


Figure 1

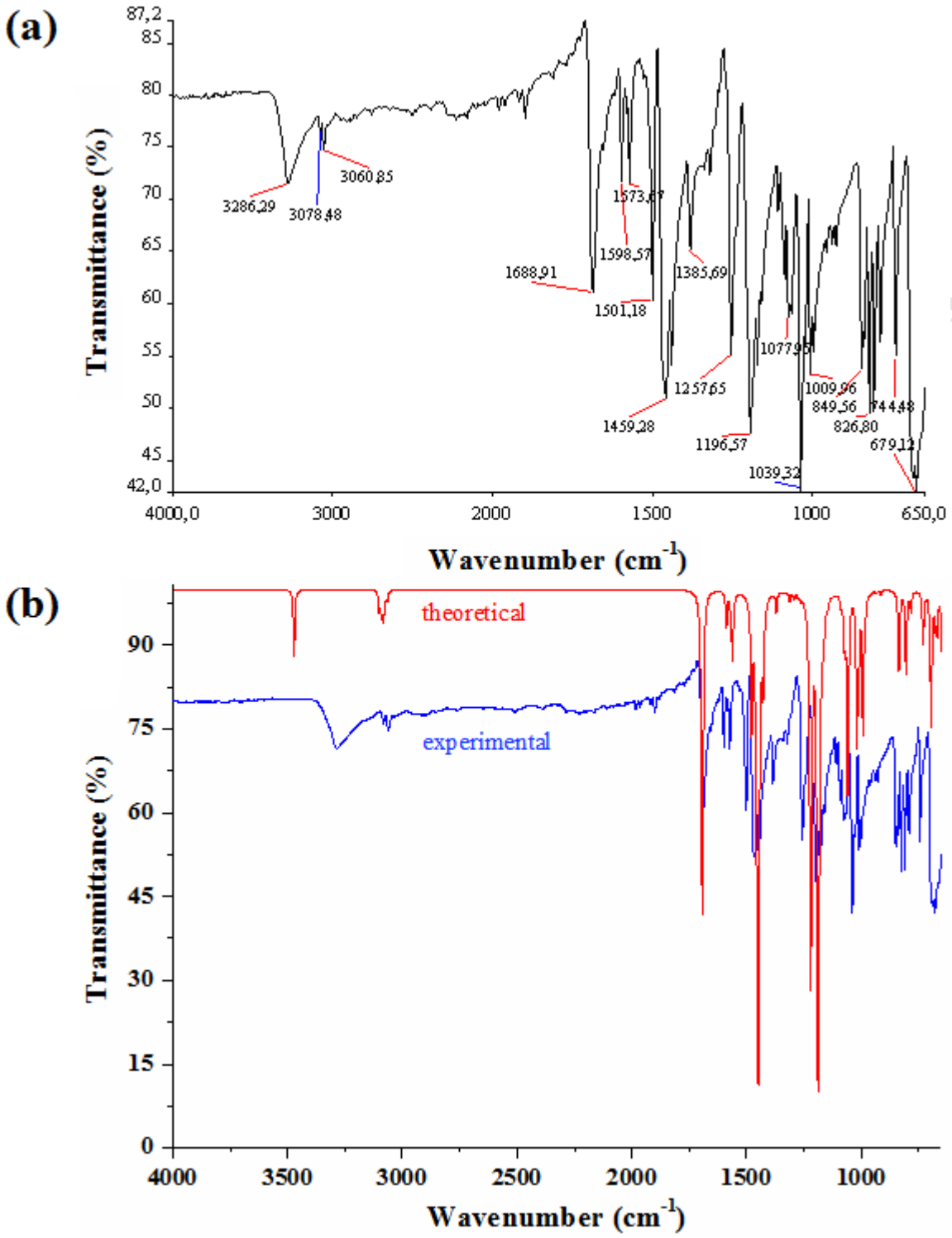


Figure 2

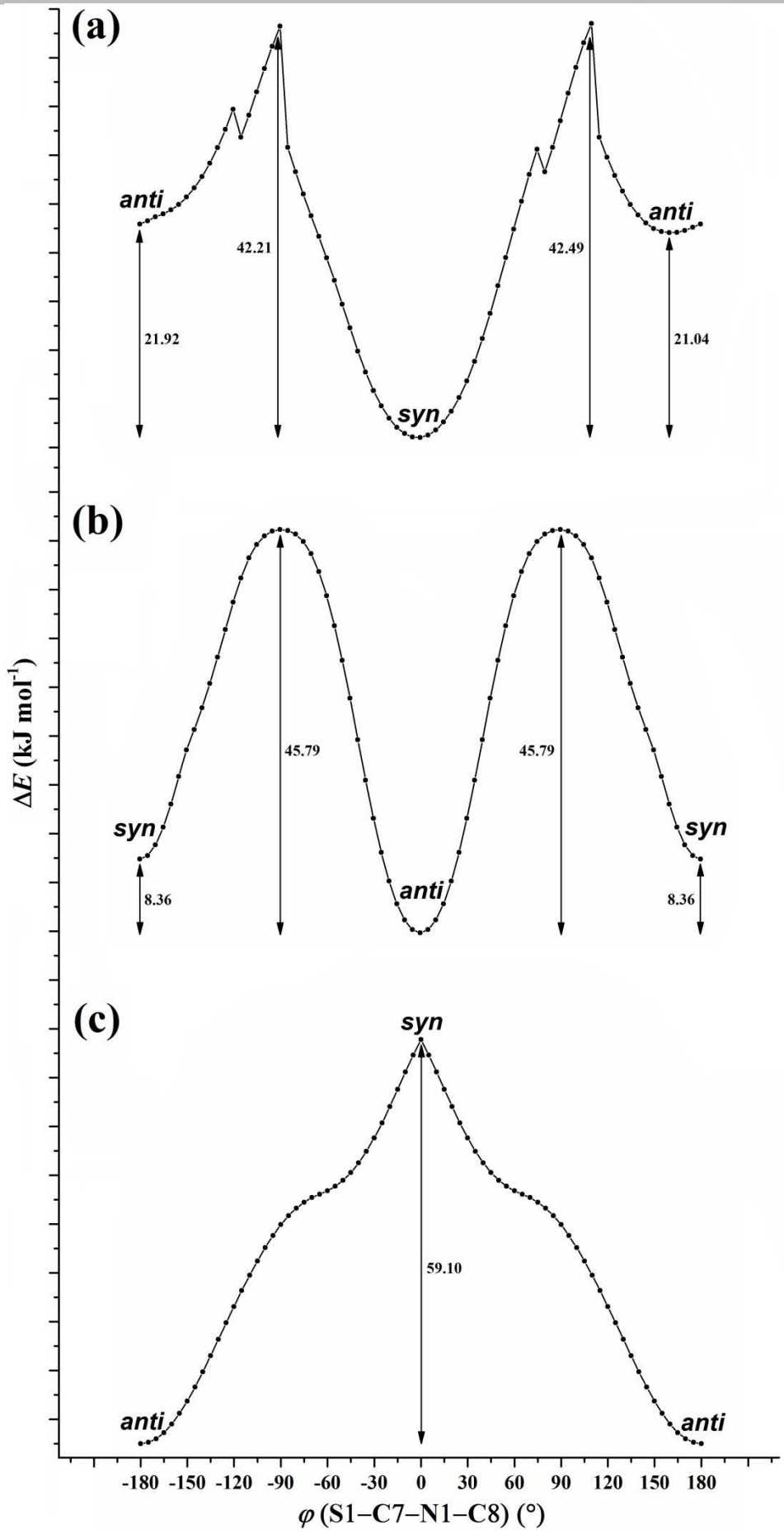


Figure 3

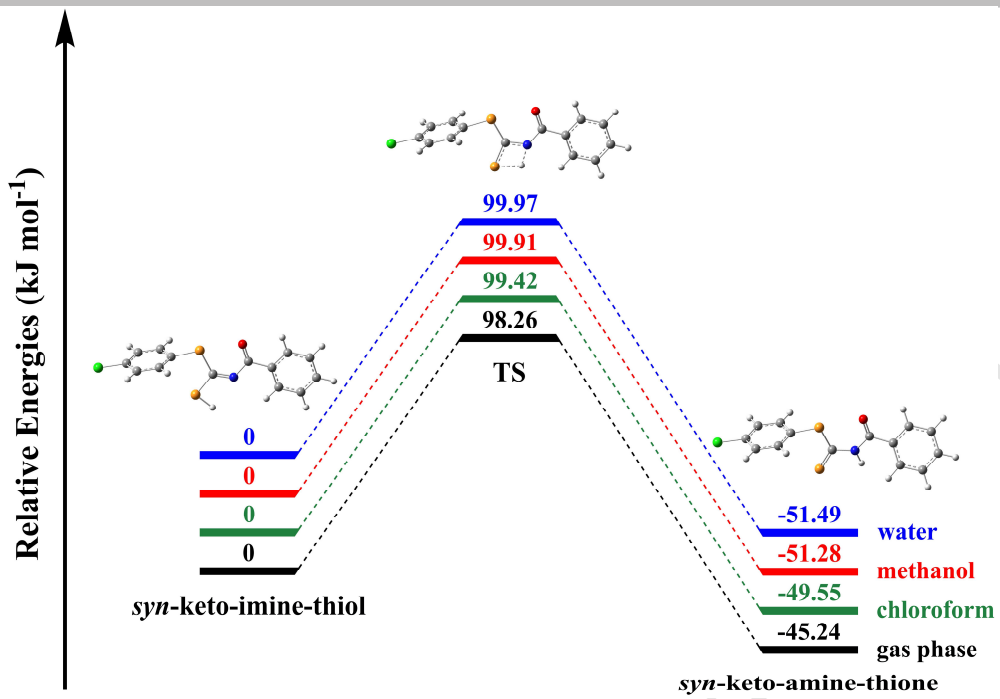


Figure 4

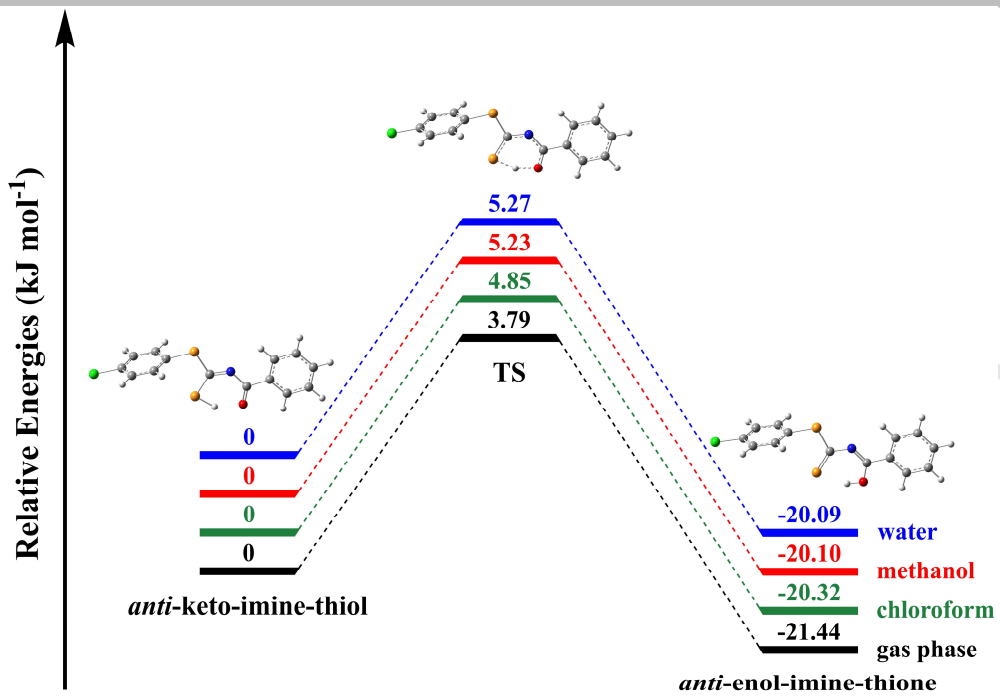


Figure 5

Research Highlights

- In this work, 4-chlorophenyl benzoylcarbamodithioate was synthesized and characterised with elemental analysis and spectroscopic techniques such as IR and NMR, and single-crystal X-ray crystallography.
- We focus our attention on the tautomerism in the compound and report the results from both theoretical and experimental points of view.
- The effect of solvents with different polarity on the tautomerism was examined by applying the integral equation formalism polarizable continuum model (IEF-PCM). Chloroform, methanol and water were chosen as solvent.