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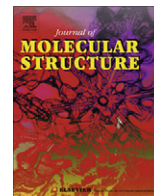


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Synthesis and structure of dithiocarbonimidates derived from aromatic heterocycles: Role of weak interactions in the preferred conformation

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ABSTRACT

The synthesis and the structure of four dimethyldithiocarbonimidates: 1-methyl-2-dimethyldithiocarbonimidate-benzimidazole (**1**), 5-chloro-2-[dimethyldithiocarbonimidate]-benzoxazole (**2**), 1-methyl-2-[dimethyldithiocarbonimidate]-pyrimidinium iodide (**3**) and 1,4-dimethyl-6-oxo-2-[dimethyldithiocarbonimidate]-pyrimidine (**4**), were investigated by TOF mass spectra, NMR and X-ray diffraction analyses. It was found that the molecules were planar with preferred conformations dictated by intramolecular N → S interactions. In the crystals, dimers or polymers were stabilized through S ⋯ S, S ⋯ π and C–H ⋯ Y (Y = S, O, N and π electrons) interactions. Calculations confirmed the weak interactions.

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1. Introduction

The presence of sulfur atoms in organic molecules determines their preferred conformations and macromolecular arrangements due to the sulfur behavior as Lewis base or Lewis acid. The divalent sulfur may act as an electron donor on a perpendicular axis to the plane of the X–S–Z sulfur bonds, or as Lewis acid along the axis of one of the two X–S or S–Z bonds, receiving electronic density from π electrons or lone electron pairs of other atoms [1–7]. The sulfur interactions with electron donor atoms affect the conformation and secondary structure of biological molecules [8]. Interactions also act in molecular recognition and in the architecture of materials [9–17]. Specifically, sulfur–sulfur short contacts can be considered as acceptor donor pairs [18–21]. Sulfur–arene interactions have been less studied, despite the fact that it has been established that contacts between sulfur atoms and aromatic rings of biological substances are common in the distances range of 3.5–4.9 Å [22,23].

Between weak interactions, the C–H ⋯ D (D = electron donor atoms) are the less studied, in spite of their important role in stabilizing conformations and crystalline polymers [24–30]. It has been reported that the distances of highest incidence for C–H ⋯ D bonds are longer than those established [25]. In particular the C–H ⋯ π interactions (12.5 kJ/mol) have influence in the secondary structure of proteins [31].

Polyfunctional nitrogenated aromatic heterocycles are frequently recognized in the structure of numerous naturally and synthetic compounds with interesting biological and pharmacological properties. They form many intra- and inter-molecular weak interactions, leading to secondary and tertiary structures in biological molecules [32]. 2-Aminobenzimidazole derivatives have applications in cancer therapy [33], and in allergic sickness [34], among others. Benzoxazole derivatives are used as analgesics [35], fungicides and insecticides [36], or as models for calcymycin [37]. 2-Amino-1,3-benzoxazole is extensively used in pre-clinical biological modeling studies as a benchmark standard, due to its properties as a potent skeletal muscle relaxant [38]. Derivatives of 2-amino-3H-pyrimidin-4-one or isocytosine have shown significant anticancer [39], antimicrobial [40] and pharmacological properties [41]. Their behavior in nucleobase recognition processes [42] and as self-assembling hydrogen-bonding modules in macromolecular systems have also been studied [43].

Our research is focused on polyfunctional aromatic heterocycles bearing labile protons and atoms with lone pairs as basic sites, which can be used as starting materials for polycyclic molecules or ligands for metal atoms [44–47]. We have studied the role of sulfur atoms in the structure and conformation of aromatic heterocycles, for example, in the nitrogen-sulfur short contacts in 2-(2-benzothiazolylimino)-heterazolidines [48] and the effect of weak sulfur interactions and hydrogen bonds in the folded and unfolded conformations of bis[2-(1H-benzimidazol-2-yl)phenyl]disulfide derivatives [49].

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Aromatic dimethyldithio-carbonimide compounds are particularly interesting due to its reactivity and versatile behavior in substitution reactions, when building more complex molecules. The dimethyldithiocarbonimide group [$-\text{N}=\text{C}(\text{SMe})_2$] adds two sulfur atoms to aromatic planar amines ArNH_2 transforming them in convenient ligands for metal coordination [50].

We have analyzed the structure of the 2-dimethyldithiocarbonimide 2-aminobenzothiazole [44], which in a planar conformation could have two arrangements. The dithiocarbonimide group could be *cis* or *trans* to the endocyclic nitrogen, Scheme 1. The crystals showed that the molecule adopts the conformation with the sulfur atom close to N-3 giving a $\text{N} \cdots \text{S}$ short contact (2.8 Å). The supramolecular association of 2-aminobenzothiazole is noteworthy because a polymer is formed stabilized by $\text{S} \cdots \text{S}$ interactions and $\text{C}-\text{H} \cdots \text{N}$ hydrogen bonds, Fig. 1. The structure of 2-aminobenzothiazole motivated us to analyze carbonimidates **1–4** where sulfur weak interactions and $\text{C}-\text{H}$ hydrogen bonds could induce also preferred conformations and supramolecular associations, Scheme 2.

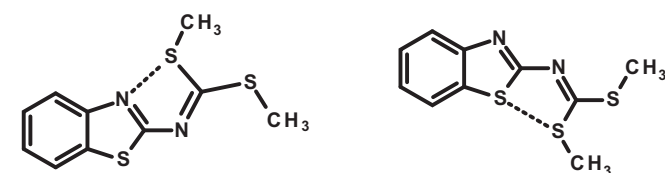
2. Experimental

2.1. General

All reagents and solvents were commercial and used without further purification. The melting points were obtained on a Mel-Temp II apparatus and are uncorrected. High resolution mass spectra were obtained by liquid chromatography–mass spectrometry of time of flight (TOF) on Agilent Technologies instrument model LC/MSD with atmospheric pressure chemical ionization (APCI). Elemental analyses were performed on Eager 300 equipment. IR spectra were recorded in KBr discs, in a Perkin Elmer GX. NMR spectra were obtained on a Jeol GSX-270, Jeol Eclipse 400 MHz and Bruker Avance 300 MHz. Assignment of ^1H and ^{13}C NMR data was based on 2D $^1\text{H}/^1\text{H}$ correlation spectroscopy (COSY), $^1\text{H}/^{13}\text{C}$ 2D heterocorrelation (HETCOR) and $^1\text{H}/^{13}\text{C}$ correlated spectroscopy for long-range coupling (COLOC) experiments.

2.2. Crystallographic study

Suitable single crystals of **1–4** were obtained. Diffraction data were measured on a Nonius Kappa CCD instrument with a charge coupled device (CCD) area detector using graphite-monochromated $\text{Mo K}\alpha$ radiation. Intensities were measured using $\phi + \omega$ scans. Crystals of **1** were collected at 173 K and **2–4** at rt. Crystals of **1** were obtained from MeOH, crystals of **2** from dimethyl sulfoxide (DMSO) and crystals of **3–4** from CHCl_3 . All structures were solved using direct methods with SHELX-97 [51] and the refinement for all structures (based on F^2 of all data) was performed by full matrix least-squares techniques with Crystals 12.84 [52]. All non-hydrogen atoms were refined anisotropically. Selected bond lengths and angles for compounds **1–4** are in Table 1. For structure **1** all hydrogen atoms were located in the difference map and were allowed to ride on their respective atoms, for structure **2** all hydrogen atoms were geometrically placed, and for structures **3–4** all



Scheme 1. Two possible planar geometric isomers for 2-aminobenzothiazole. In one the S atom is close to the N, whereas in the other one, two sulfur atoms are contiguous.

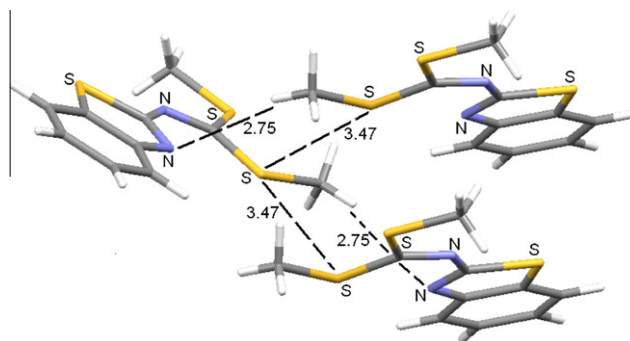
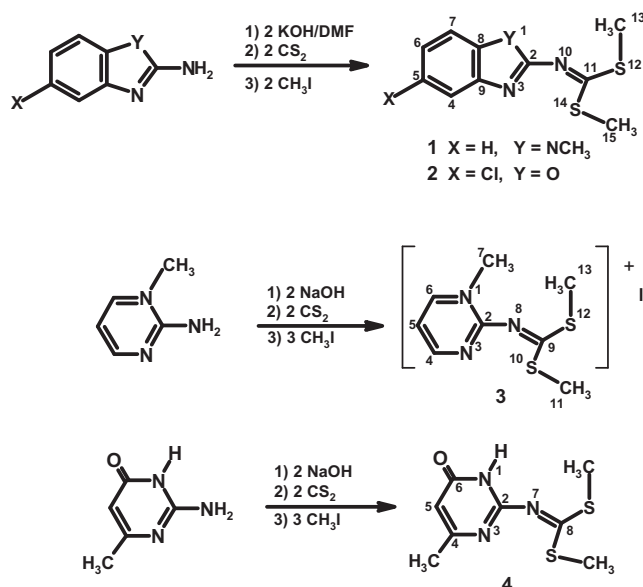


Fig. 1. Zig-zag polymer of 2-aminobenzothiazole found in the solid state. The polymer involves $\text{S} \cdots \text{S}$ (3.47 Å) and $\pi \text{CH} \cdots \text{N}$ (2.75 Å) contacts [44].



Scheme 2. Synthesis of compounds **1–4**.

Table 1
Selected bond lengths and angles for compounds **1–4**.

Compounds	1 X = NMe	2 X = O	3 X = NMe	4 X = NMe
X–C2	1.370(3)	1.376(3)	1.375(5)	1.381(3)
C2–N3	1.323(3)	1.305(4)	1.329(5)	1.304(3)
C2–N4	1.372(3)	1.358(4)	1.349(5)	1.377(3)
N4–C5	1.282(3)	1.291(4)	1.300(5)	1.294(3)
C5–S6	1.752(3)	1.749(3)	1.743(4)	1.749(3)
C5–S8	1.758(3)	1.746(3)	1.751(4)	1.755(3)
S6–C7	1.809(3)	1.807(3)	1.816(5)	1.817(3)
S8–C9	1.793(3)	1.796(3)	1.805(5)	1.783(3)
X–C2–N3	113.0(2)	115.1(3)	120.7(3)	123.0(2)
X–C2–N4	117.1(2)	113.3(2)	113.9(3)	113.6(2)
N3–C2–N4	130.0(2)	131.6(3)	125.5(3)	123.4(2)
C2–N4–C5	122.9(2)	121.8(3)	124.7(3)	122.1(2)
N4–C5–S6	126.0(2)	125.1(2)	126.9(3)	127.5(2)
C5–S6–C7	104.1(1)	104.4(1)	104.0(2)	102.8(1)
N4–C5–S8	117.9(2)	119.1(2)	116.9(3)	117.5(2)
C5–S8–C9	100.8(1)	101.4(2)	101.5(2)	102.2(1)

hydrogen atoms were located in the difference map and their positions were refined. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre as numbers: 635405 (1) 652805 (2) 692376 (3) 692377 (4). Copies can be obtained, free of charge, on applications to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0)1223 336033 or www.ccdc.cam.ac.uk/products/ccsd/request/].

2.3. 1-Methyl-2-dimethylcarbonimide-benzimidazole (1). General method for the preparation of compounds 2–4

To a solution of 1-methyl-2-aminobenzimidazole (600 mg, 3.84 mmol) in dimethylformamide (30 mL), KOH pellets (480 mg, 8.7 mmol) were added. The suspension was stirred for 2 h, then cooled in an ice bath and CS₂ (0.51 mL, 8.4 mmol) were added, followed 2 h later of CH₃I (0.48 mL, 7.68 mmol). The mixture was stirred for other 2 h. The reaction mixture was poured into water (200 mL) and the precipitate filtered. Colorless crystals were isolated by crystallization from MeOH (434 mg, 45% yield). Mp 112–114 °C. IR (KBr, ν cm⁻¹): (C2=N1) 1533, (N1–C2–N3)_{as} 1428; (C–S14) 1005 calc 1025; (CS12) 941, calc 944. TOF Mass: [M+H]⁺ 252.0631, calc 252.0629. NMR (DMSO-d₆, δ ppm). ¹H: 7.54 (H-4), 7.16 (H-5), 7.20 (H-6), 7.46 (H-7), 3.76 (N1–CH₃), 2.64 (SCH₃). ¹³C: 152.0 (C2), 118.9 (C4), 122.1 (C5), 122.2 (C6), 110.2 (C7), 134.8 (C8), 141.6 (C9), 29.4 (N1–CH₃), 174.3 (CS₂), 16.2 (SCH₃). Anal. Calcd. for C₁₁H₁₃N₃S₂: C, 52.56; H, 5.21; N, 16.72. Found: C, 52.32; H, 5.23; N, 16.69.

2.4. 5-Chloro-2-[dimethyldithiocarbonimide]-benzoxazole (2)

2-Amino-5-chloro-benzoxazole (4.2 g, 25 mmol), DMF (15 mL), NaOH (25 mmol, 500 mg), CS₂ (50 mmol, 2.7 mL), CH₃I (3.1 mL 50 mmol). The solid was recrystallized from methanol. (3.48 g, 51% yield). Mp 143–145 °C. IR (KBr, ν cm⁻¹): (C2=N1) 1534, (N1–C2–N3)_{as} 1488; (C–S14) 1015; (C–S12) 918. TOF MS m/z [M+H]⁺ = 272.9919, calc. 272.9923. NMR (DMSO-d₆, δ ppm); ¹³C: 161.2 (C-2); 119.0 (C-4); 128.5 (C-5) 124.3 (C-6); 112.0 (C-7); 146.0 (C-8); 143.0 (C-9); 183.2 (C-11); 16.1 (SCH₃). ¹H: 7.69 (d, ⁴J = 2 Hz, 1 H, 4-H); 7.33 (dd, ⁴J = 2 Hz, ³J = 10 Hz, 1 H, 6-H); 7.61 (d, ³J = 9 Hz, 1 H, 7-H); 2.64 (s, 6 H, SCH₃). Anal. Calcd. for C₁₀H₉ClN₂OS₂: C, 44.12; H, 3.35; N, 10.30. Found: C, 44.49; H, 3.36; N, 10.41. Colorless crystals suitable for X-ray diffraction were obtained from DMSO-d₆ in an NMR tube.

2.5. 1-Methyl-2-[dimethyldithiocarbonimide]-pyrimidinium iodide (3)

2-Amino-pyrimidine (2 g, 21 mmol), DMF (20 mL), KOH (2.4 mg, 85%, 42 mmol), CS₂ (2.54 mL, 42 mmol), CH₃I (3.9 mL, 63 mmol). Pale yellow crystals were obtained from CHCl₃ (2.3 g, 32% yield). Mp. 204–205 °C. IR (KBr, ν cm⁻¹): (C2=N1) 1566, (N1–C2–N3)_{as} 1481; (C–S14) 1008; (C–S12) 939. NMR (CDCl₃, δ ppm); ¹³C: 191.4 (C-8), 164.9 (C-4), 154.8 (C-6), 153.8 (C-3), 40.3 (N–CH₃), 17.6 (S–CH₃). ¹H: 9.21 (5-H), 9.14 (4-H), 7.68 (5-H), 4.07 (N–CH₃), 2.73 (S–CH₃). TOF MS: m/z [M+H]⁺ = 214.0467 calc 214.0473. Anal. Calcd. for C₈H₁₂N₃S₂I: C, 28.16; H, 3.54; N, 12.31. Found: C, 28.08; H, 3.32; N, 12.69.

2.6. 1,4-Dimethyl-6-oxo-2-[dimethyldithiocarbonimide]-pyrimidine (4)

4-Hydroxy-6-methyl-2-aminopyrimidine (2 g, 16 mmol), DMF (20 mL), KOH (1.8 g, 32 mmol), CS₂ (1.0 g., 16 mmol), CH₃I (3 mL, 48 mmol). Colorless crystals of **5** were obtained (1.47 g, 38% yield). Mp 148–149 °C. IR (KBr, ν cm⁻¹): (C2=N1) 1589, (N1–C2–N3)_{as} 1492; (C–S14) 1031; (C–S12) 925. NMR (DMSO-d₆, δ ppm); ¹³C:

178.2 (C-8), 163.1 (C-6), 154.3 (C-2), 107.2 (C-5), 29.1 (N–CH₃), 23.2 (C–CH₃) 15.9 (S–CH₃). ¹H: 5.95 (5-H), 3.38 (N–CH₃), 2.47 (S–CH₃), 2.13 (C–CH₃). TOF MS: m/z [M+H]⁺ = 244.0578, calc 244.0578. Anal. Calcd. for C₉H₁₃N₃S₂O: C, 44.42; H, 5.38; N, 17.27. Found: C, 44.59; H, 5.44; N, 17.55.

3. Results and discussion

Herein we report the synthesis and structural analysis of aromatic dimethyldithio-carbonimides (**1–4**) based on 1-methyl-2-amino-benzimidazole, 2-amino-5-chloro-benzoxazole, 2-amino-pyrimidine and 2-amino-3-methyl-3H-pyrimidin-4-one respectively, Scheme 2.

3.1. Synthesis and structure determination

Compounds **1–4** were prepared by reactions of the corresponding aromatic primary amines with CS₂ in DMF and in the presence of a base, followed by CH₃I addition. The products were isolated and purified by crystallization. In compounds **3** and **4**, the CH₃I reagent also methylated the intracyclic nitrogen atoms. Compound **3** is ionic because of the ammonium iodide formation. Compound **4** is covalent, its N–H proton was substituted by a methyl group. Structures were established in solution by NMR and in the solid state by high resolution TOF mass spectra, IR and X-ray diffraction analyses. The latter confirmed the structures and led to analyze their preferred conformations as well as the weak intramolecular and intermolecular interactions. Calculations performed on compound **1** confirmed the observed weak interactions.

3.2. Compound 1

X-ray diffraction analysis of compound **1** (Fig. 2), performed at –100 °C, showed a planar molecule with an S–CH₃ group close to the imidazole nitrogen (N3), forming an intramolecular N → S short contact {2.851(2) Å, $\sum r_{vdw}$ = 3.4 Å, [53]} which influences the S–C bond lengths: S14–C15 1.809(3) is longer than S12–C13 1.793(3). The planar conformation is strengthened by additional intra molecular weak interactions, such as two hydrogen bonds C–H...S12 (2.79 and 2.85 Å) and three C–H...N10 (2.57, 2.68 and 2.70 Å) each forming five membered rings.

A notable fact was that the molecule forms planar dimers in the solid state, stabilized by two cooperative C15–H...N hydrogen bonds [2.65 Å] and one S14...S14 interaction {3.34 Å; $\sum r_{vdw}$ = 3.6 Å, [53]}.

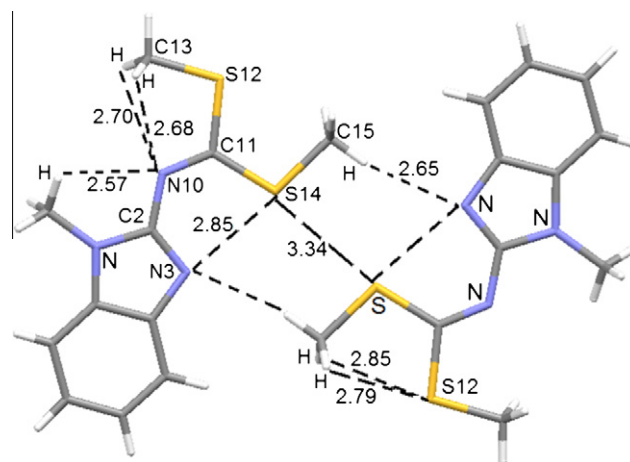


Fig. 2. View of the planar dimer of compound **1**. Intramolecular and cooperative intermolecular short contacts C15–H...N, N...S and S14...S14 are shown.

An important difference has been found in the intermolecular sulfur contacts in compounds **1** and 2-dimethyldithiocarbonimidate 2-aminobenzothiazole. The structure of the dimer **1** (Fig. 2) shows that the two sulfur atoms (S14) approach each other through the C–S bond axis whereas in 2-dimethyldithiocarbonimidate 2-aminobenzothiazole (Fig. 1), sulfur atoms approaches the molecule in diagonal orientation forming a polymer, [44].

From a theoretical study using the *ab initio* Hartree–Fock program (HF/6-31G) [54], two different IR stretching bands for compound **1** were calculated [$\text{C11}–\text{S12} = 1025 \text{ cm}^{-1}$ and $\text{C11}–\text{S14} = 944 \text{ cm}^{-1}$]. These two bands were found in the IR spectrum [1005 and 941 cm^{-1}], confirming the $\text{N} \rightarrow \text{S}$ interaction effect over one of the C–S bonds of the dithiocarbamate group.

In order to evaluate the conformational behavior of compound **1** in solution, ^1H and ^{13}C NMR variable temperature experiments were performed in deuterated tetrahydrofuran (THF- d_8) in a 400 MHz spectrometer. At room temperature the two S–CH₃ groups give only one signal ($^1\text{H} \delta = 2.58$ and $^{13}\text{C} \delta = 15.21$) indicating the fast rotation of the C2–N10 bond. However at -80°C each SCH₃ becomes different [$^1\text{H} \delta = 2.62$ and 2.58 ppm and $^{13}\text{C} \delta = 15.28$ and 15.71 ppm]. The difference was attributed to the $\text{N} \rightarrow \text{S}$ interaction, which affects preferentially one of the S–CH₃ groups, as was observed in the crystal structure. The nitrogen electron donation to the sulfur through the space shifts the chemical shifts of S14-methyl group to lower frequencies. From the variable temperature NMR experiments, the ΔG^\ddagger [-52.67 kJ/mol] for the C2–N10 bond rotation was calculated.

3.3. Compound 2

In compound **2**, two different planar conformations could be expected. In one of them, the S–CH₃ approaches the imidazole nitrogen atom; in the other one, the S–CH₃ group is oriented towards the oxygen atom. The crystal structure of compound **2**, shows that the preferred conformation is the first one, with $\text{N3} \rightarrow \text{S13}$ short contact [2.81 \AA , $\sum r_{\text{vdW}}(\text{N} \cdots \text{S}) 3.85 \text{ \AA}$, [53]] as was found in compounds **1** and 2-dimethyldithiocarbonimidate 2-aminobenzothiazole. Dimers form a ribbon shape polymer by $\text{S} \cdots \text{S}$ short contacts [$\text{S} \cdots \text{S} 3.38 \text{ \AA}$, $\sum r_{\text{vdW}}(\text{S} \cdots \text{S}) = 3.38 \text{ \AA}$] and bifurcated $\text{CH} \cdots \text{N}$ (3.01 \AA) and $\text{CH} \cdots \text{O}$ (2.71 \AA) weak interactions, Fig. 3.

It is noteworthy that the asymmetric unit of compound **2** has seven molecules, Fig. 4. Six are in the *ab* plane forming two groups of three parallel π -stacked molecules, with distances between them close to 4 \AA [$\text{C11} \cdots \text{C11}' (3.98 \text{ \AA})$ and $\text{C8} \cdots \text{C8}' (3.99 \text{ \AA})$], each group is glided with respect to the other. The seventh molecule is perpendicular to the other six and due to the fact that all molecules have the same conformation, only one set of bond lengths and angles are reported, Table 1. The supramolecular array forms channels, where the perpendicular molecules are placed. The asymmetric unit containing seven molecules is not common, as can be seen at the Cambridge Structural Database [55]. In the crystal of

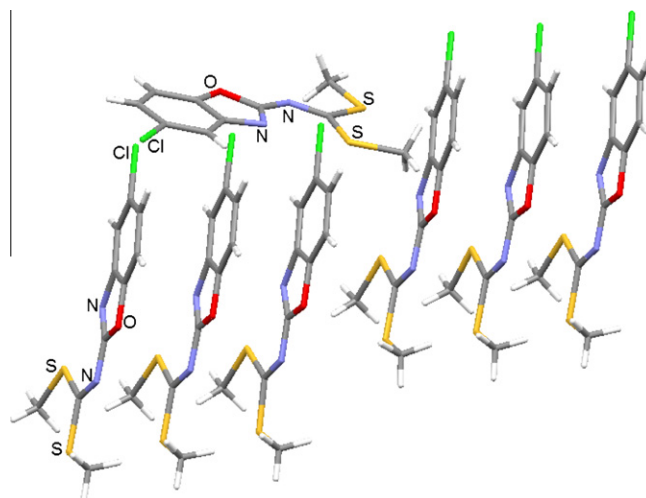


Fig. 4. The asymmetric unit of **2** contains seven molecules, six are stacked and the seventh is located in a perpendicular plane.

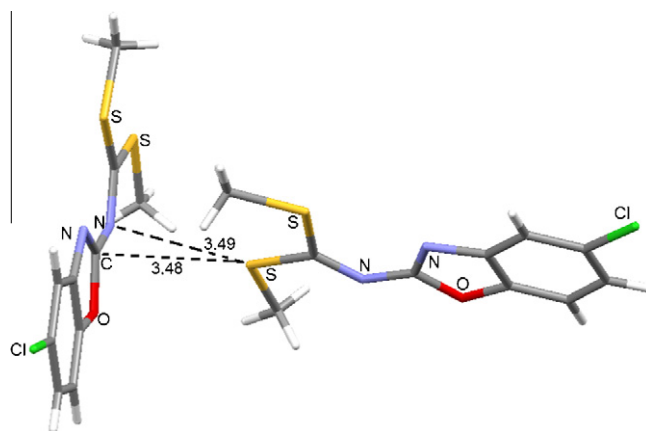


Fig. 5. π -Intermolecular interactions between two perpendicular molecules in the crystal of compound **2**.

compound **2**, there were also found π -intermolecular interaction between two perpendicular molecules through the sulfur atom and the π electrons of the C2–N10 bond, Fig. 5.

3.4. Compound 3

The solid state structure of the ionic compound **3**, shows that the cation is also planar, the S10 atom is close to N3 (2.834 \AA), Fig. 6. Four C–H \cdots S and two C–H \cdots N intramolecular hydrogen

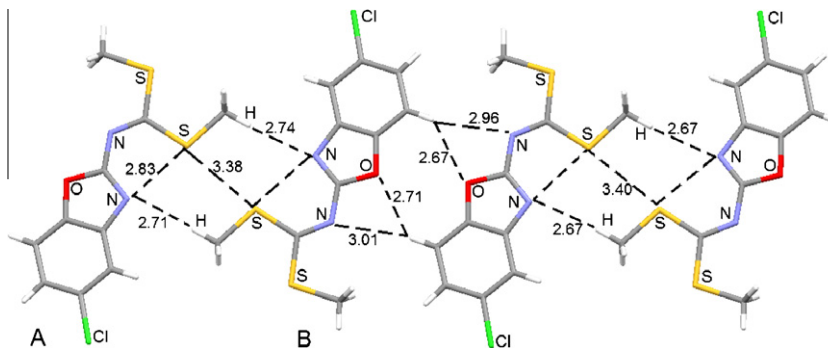


Fig. 3. Cooperative interactions forming the planar polymeric arrangement in **2**. The two molecules bound by sulfur–sulfur interactions the asymmetric unit in the crystal.

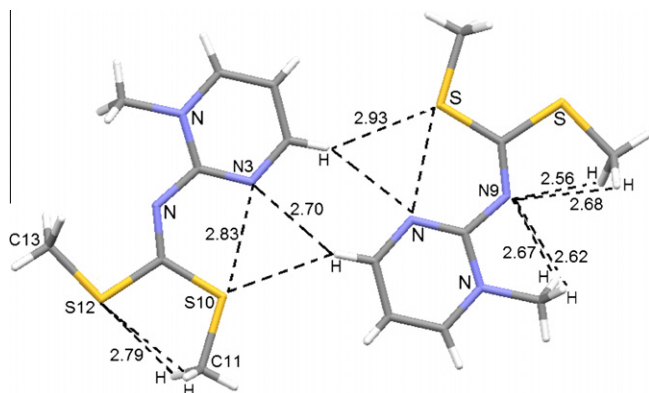


Fig. 6. Dimer of the cation of compound 3.

bonds stabilize the conformation. As a consequence of the N3...S10 contact, the S10–C11 bond becomes slightly longer [1.816(5) Å] than S12–C13 bond [1.805(5) Å]. Compound 3 forms a dimer through two cooperative bifurcated C–H bonds to nitrogen and sulfur. The iodide is stabilized by C–H...I interactions from four pyrimidinium cations, Fig. 7.

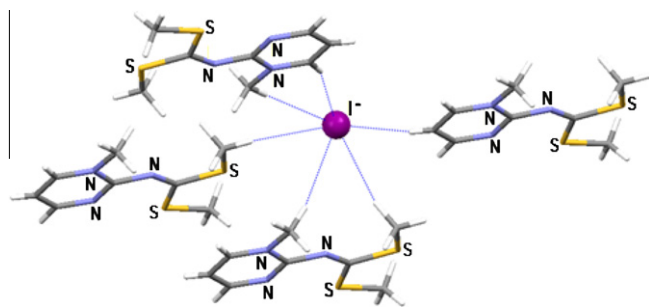


Fig. 7. The iodide in compound 3 is stabilized by six C–H...I interactions, distances 3.02–3.17 Å ($\Sigma \text{vdWr} = 3.4$ Å).

3.5. Compound 4

The crystal structure of compound 4 contains two molecules (A and B) in the asymmetric unit and C–H...S and C–H...N hydrogen bonds contribute to the planar conformation. The two molecules are coplanar. Distances between sulfur and nitrogen are short 2.73 and 2.71 Å. The molecule forms dimers by C–H...O (2.40 Å) and C–H...S (2.06 Å) hydrogen bonds, Fig. 8. There are also inter-molecular sulfur–sulfur contacts (3.55 Å), between molecules lying in two parallel planes, Fig. 9.

3.6. High resolution TOF mass spectra

The stability of the dimers formed by weak interactions in compounds 1–4 allows observing them in their mass spectra. Compounds 1, 2 and 4 showed the dimers (1 $[\text{C}_{22}\text{H}_{27}\text{N}_6\text{S}_4]^+$ m/z 503.1164 calc. 503.1180, 2 $[\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_2\text{S}_4\text{Cl}_2]^+$ m/z 545.9485 calc. 545.9846, and 4 $[\text{C}_{18}\text{H}_{27}\text{N}_6\text{S}_4\text{O}_2]^+$ m/z 487.107832 calc. 487.1078), however due to the cationic nature of the carbonimide in compound 3, the dimer appears together with the monomer. Mass spectrum of compound 1 is found at the [supplementary material](#).

3.7. Theoretical study

Calculations were performed in order to confirm the presence of stabilizing weak interactions in compound 1. The calculations were based on the atomic positions of the monomer and dimer in the crystal of 1 using a Natural Bond Order (NBO) [56] study performed at the B3LYP/cc-PVTZ level of theory (B3LYP/cc-PVTZ: Becke's three-parameter hybrid functional combined with the Lee, Yang, and Parr correlation functional/coupled cluster correlation-consistent with polarized valence triple-zeta) [54]. Detail of calculations are found at the [supplementary material](#).

The calculation of the monomer of compound 1 produces a total energy of -1387.682979 a.u. and the NBO analysis found a structure accounting for 98% of Lewis character and 2% non Lewis. The electrostatic potential isosurface of compound 1 shows the nucleophilic nature of the N16 atom (hard Lewis base) and the acidic

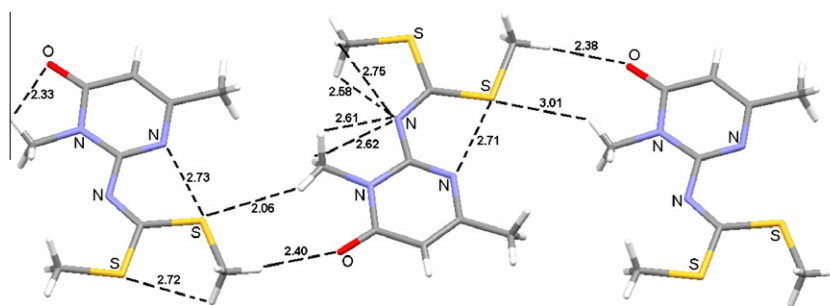


Fig. 8. Planar polymer of compound 4, formed by cooperative C–H...O and C–H...S hydrogen bonds.

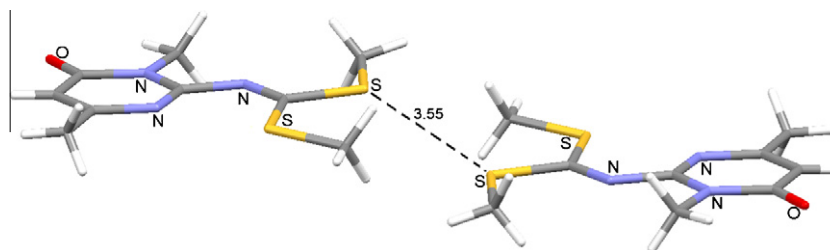


Fig. 9. Sulfur–sulfur contacts between molecules of compound 4, lying in parallel.

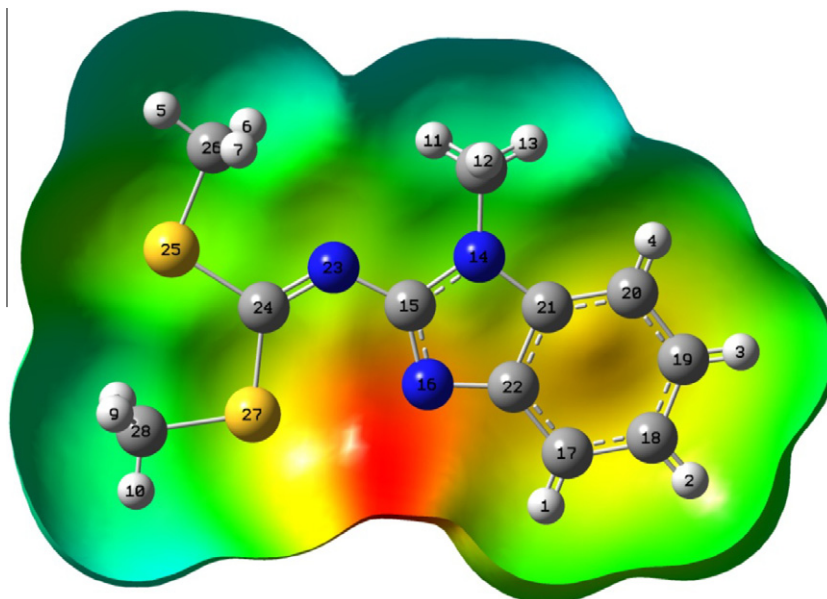


Fig. 10. Isosurface of the electrostatic potential of compound **1**.

character of the S27 atom (soft Lewis acid) which is indicative of the donor–acceptor nature of these two atoms, Fig. 10. These observations were confirmed by means of the natural atomic charges obtained through the natural population analysis [56].

The 2nd-order delocalization energies for all significant donor–acceptor interactions were also obtained along with other significant second order interaction terms of the Fock operator in the NBO basis [56]. Our results show S···N interactions and C–H···S hydrogen bonds accounting for more than 21 kJ/mol. The

$nsp(N16) \rightarrow \sigma^*(S27-C28)$ interaction contributes more significantly to the stabilization of the molecule. This is also in agreement with the reported $p-\sigma^*$ donor–acceptor model of interaction [21].

The B3LYP/cc-PVTZ calculation of the dimer of compound **1** produces a total energy of -2775.369385 a.u. for the solid state geometry of the dimer. The isosurface of the electrostatic potential of the dimer shows the donor–acceptor behavior between the H···S···N non bonding arrangement of each monomer, Fig. 11. Also, it shows

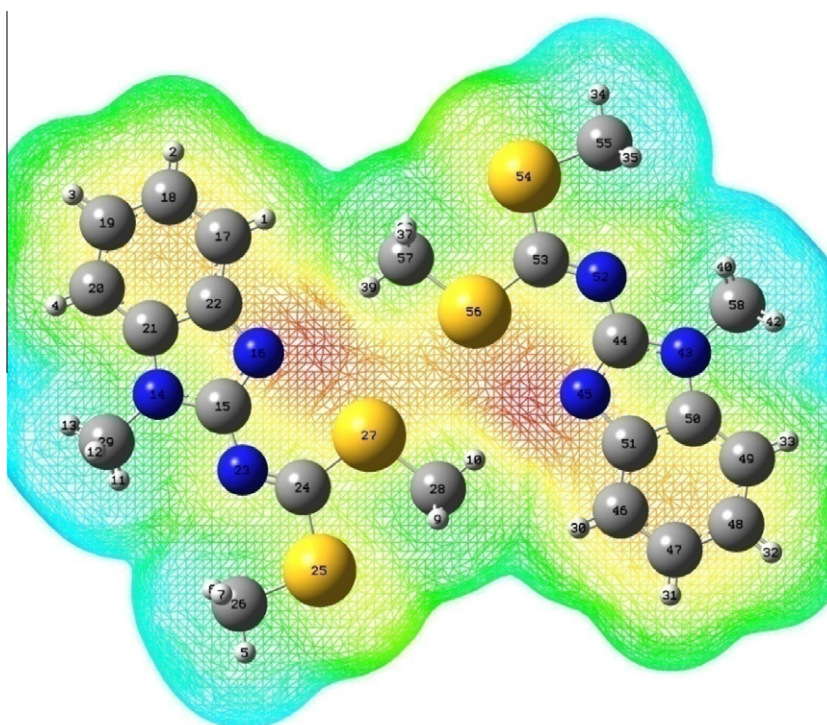


Fig. 11. Isosurface of the electrostatic potential of dimer of compound **1**.

that nitrogen atoms behave like hard Lewis bases, sulfur atoms like soft acids or bases and the hydrogen atoms like hard acids through $S \cdots S$, $S \cdots N$, $CN \cdots H-C$ and $CS \cdots H-C$ weak interactions. The whole structure gets stabilized by means of these weak intramolecular and intermolecular interactions. The values of the relevant non covalent interactions which correspond to $S \cdots N$ weak non bonded atoms and $C-H \cdots N$, $C-H \cdots S$ hydrogen bonds are found in the [supplementary data](#).

4. Conclusions

The structure of four new dithiocarbonimidates derived from aromatic heterocyclic amines was analyzed. The X-ray diffraction analyses showed that all the molecules have a planar conformation, with one of the sulfur atoms close to a nitrogen atom forming an $N \rightarrow S$ intramolecular interaction giving place to a five membered ring. The $N \rightarrow S$ interaction is preferred over $S \rightarrow S$ and $O \rightarrow S$. The relevance of this work is based on the findings of several kinds of intermolecular sulfur weak interactions with electron donor atoms or π -electrons such as $S \cdots S$, $S \cdots N$ and $S \cdots \pi$, where sulfur is acting as a Lewis acid. Several hydrogen bonds $C-H \cdots S$ accounted for the simultaneous basic behavior of the sulfur atoms. Stability of macromolecular frameworks was also provided by π - π interactions and $N-H$ and $C-H$ hydrogen bonds with S , O , N and π electrons. Relatively stable dimers were observed at the +TOF mass spectra of compounds **1**, **2** and **4**. NMR variable temperature experiments in compound **1** showed that the preferred conformer in solution is the one observed in solid state. The theoretical analyses confirmed the experimental evidence, that weak interactions of the $S \cdots S$ and $S \cdots N$ type along with hydrogen bonds, form a cooperative binding system which stabilizes the monomers and dimers of compounds **1–4**.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.molstruc.2010.10.016](https://doi.org/10.1016/j.molstruc.2010.10.016).

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