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Formylation reactions of *N*-protecting 2-Amino-4-phenyl thiazole compounds

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ABSTRACT

The Vilsmeier Haack formylation reactions of 4-phenyl-*N*-*N*'-benzoyl and 4-phenyl-*N*-substituted (*N*-sulphonyl and *N*-phenyl)-2-aminothiazole molecules with $POCl_3$/DMF were studied. The Crystal **(6)** ((E)-*N*'-(5-formyl-4-phenylthiazol-2-yl)-*N,N*-dimethylformimid amide) and crystal **(14)** (*N*-phenyl-*N*-(4-phenylthiazol-2-yl)formamide) molecules were obtained in the formylating reactions of *N,N*'-benzoyl, *N*-sulphonyl protecting group 4-phenyl thiazole molecules. In the *N*-phenyl substituted thiazole compound, an aldehyde functional group is added to the amine group instead of the thiazole ring to form the *N*-phenyl-*N*-(4-phenylthiazol-2-yl)formamide molecule. All compounds have been synthesized and characterized by FT-IR, ^{1}H NMR, ^{13}C NMR techniques, and X-ray structure analysis. These molecules demonstrate O,S-syn conformation.

1. Introduction

The Vilsmeier-Haack reaction is used to obtain iminium species by electrophilic substitution of an activated aromatic ring with a halomethyleneiminium salt [1]. Halomethyleneiminium salt is formed as a result of addition reactions between amides and non-metallic inorganic halides [2]. In addition to the DMF molecule most commonly used as *N,N* disubstituted amide in the formation of Vilsmeier complexes, *N*-methylformamide, *N*-methylpyrrolidone, *N*-methylacetamide, *N*-formylmorpholine, *N,N*-dimethyl acetamide and *N,N*-dimethyl benzamide are used. Besides $POCl_3$ molecule which is the most widely used inorganic halides, $COCl_2$ and $SOCl_2$ and ClOCl are used [1]. Liquid DMF as a reaction solvent, dimethyl acetamide, *N*-methylpyrrolidone, etc. In the case of amides such as amides, excess amide may be used as a solvent. In addition to these, other solvents such as CCl_4, $CHCl_3$, CH_2Cl_2, benzene, toluene, o-dichlorobenzene, dioxane and tetrahydrofuran are also used [1,3].

Gillon group *N,N*-disubstituted-2-aminothiazole-5-carbaldehyde derivatives were synthesized by the Vilsmeier Haack reaction. The rotational properties of functional groups in the 4-substituted *N,N*-disubstituted (*N,N*-dimethyl, *N*-benzyl-*N*-methyl, and *N*-methyl-*N*-phenyl)−2-aminothiazole-5-carbaldehydes was studied (Scheme 1). They examined the effects of substituted groups on the formation of syn or anti-conformation of the aldehyde group. When the crystal structures of 4-*t*-butyl-2-(*N*-methyl-*N*-phenylamino)thiazole-5-carbaldehyde molecule are examined, it is seen that the aldehyde group prefers O,S-syn conformation [4].

When the literature is examined, there are formylation reactions of compounds containing many thiazole rings. Aldehyde derivative (4-(2-oxo-2H-chromen-3-yl)−2-arylthiazole-5-carbaldehyde) was synthesized from the thiazole derivative (3-(2-arylthiazol-4-yl)−2H-chromen-2-one) containing coumarin group by Vilsmeier Haack ($POCl_3$/DMF) reaction [5]. The thiazole derivative (4-phenyl-2-(piperidin-1-yl)thiazole-5-carbaldehyde) containing a formyl group in the 5 position was synthesized from the *N,N*'-protecting thiazole derivative (4-phenyl-2-(-piperidin-1-yl)thiazole) using *n*-BuLi and DMF at −70°C [6]. The aldehyde compound (2-morpholino-4-arylthiazole-5-carbaldehyde) was synthesized from containing *N,N*'-protecting thiazole ring (4-(4-arylthiazol-2-yl)morpholine) using $POCl_3$/DMF [7]. Thumar and Patel obtained the formylation product containing the (E)-*N*'-(5-formyl-4-phenylthiazol-2-yl)-*N,N*-dimethylformimidamide **(6)**) from the 4-pheyl-2-aminothiazole **(5)** with the SDS molecule they used to form the "micellar media" and $POCl_3$/DMF reagents as the Vilsmeier Haack reagent [8].

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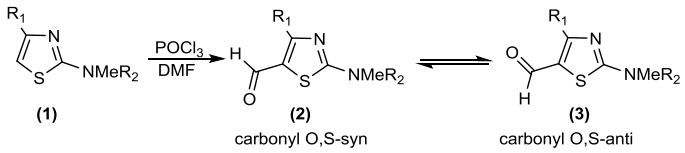


Scheme 1. Conformational isomers.

2. Results and discussion

2.1. Chemistry

In this study, formylation reactions were performed within the scope of the functionalization studies of the aromatic C—H of molecules **(7, 8,** and **12)** [15–19]. Compounds **(6)** and **(9)** containing thiazole structure were obtained instead of the desired product in the reactions performed for the synthesis of compound **(8)** from compound **(11)**. In the reactions performed for the synthesis of compound **(11)** from compound **(7)**, the target product was not obtained, while compounds **(6)** and **(9)** containing thiazole structure were obtained. While the aldehyde product **(13)** was expected from the thiazole compound containing phenyl-amino group **(12)** as a result of the formylation reaction, the compound numbered **(14)** was obtained from the reaction of the nitrogen atom in the phenyl-amino group with the formylation reagent. The synthesis of compounds by the Vilsmeier-Haack reaction is not known in the literature. The product **(6)** has been reported in the literature (Scheme 3) [8].

In the literature, the formylation reaction of the compound **(5)** was carried out with the SDS(sodium dodecyl sulfate)/DMF/$POCl_3$ system (Scheme 2). When we did the same reaction without using SDS, it was observed that the compound numbered **(6)** was formed as the main product and the product numbered **(9)** was formed as a by-product. Formylation reaction conditions of compound **(8)** are summarized in Table 1. $POCl_3$/DMF and $SOCl_2$/DMF reagents were used in formylation experiments.

It was observed that the use of a different solvent other than DMF in the formylation reactions of the compound numbered **(9)** indicated an increased reaction yield (Table 3). It was found that the best reaction conditions in the experiments at different temperatures and solvent conditions were the condition in the 5th experiment. No product formation was observed from the reactions at room temperature and reflux conditions with the $SOCl_2$/DMF/DCM system.

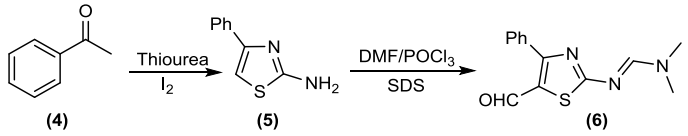
2.2. Crystallographic studies

Suitable single crystals of (E)-*N'*-(5-formyl-4-phenylthiazol-2-yl)-*N,N*-dimethylform imidamide **(6)** and *N*-phenyl-*N*-(4-phenylthiazol-2-yl) formamide **(14)** were chosen for an X-ray crystallographic study. White crystals were obtained from compound **(14),** and burgundy crystals from compound **(6).** These block-shaped crystals were recorded on a Rigaku-Oxford Xcalibur diffractometer with an Eos Charge Coupled

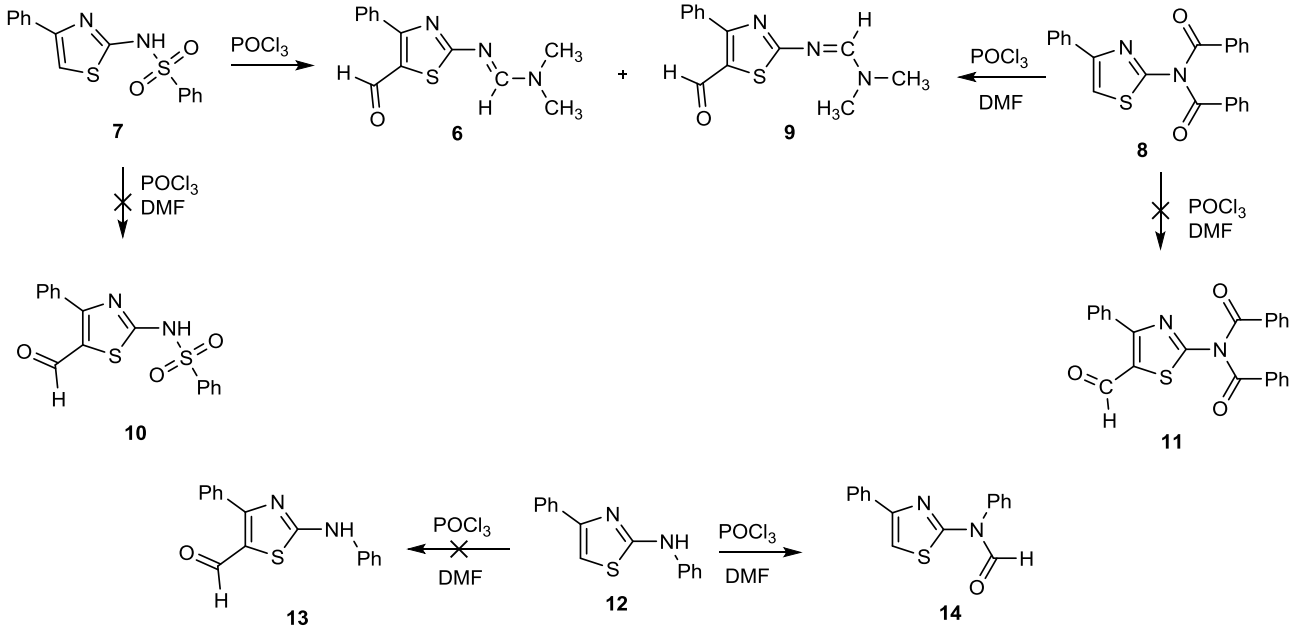
Table 1
Formylation reaction conditions of compound **(8)**.

	DMF	Reagent	Solvent	Temperature	Time
1	2 eq.	1 eq. $POCl_3$	–	reflux	24 h
2	1 eq.	1 eq. $POCl_3$	–	rt	24 h
3	2 eq.	1 eq. $POCl_3$	1,2 dichloroethane	rt	24 h
4	2 eq.	1 eq. $POCl_3$	DCM	rt	18 h
5	2 eq.	1 eq. $POCl_3$	DCM	0°C→ rt	18 h
6	3 eq.	1.4 eq.. $SOCl_2$	DCM	0°C→ rt	24 h
7	3 eq.	1.4 eq.. $SOCl_2$	DCM	rt	24 h
8	3 eq.	1.4 eq.. $SOCl_2$	DCM	reflux	24 h

Eq.: equvalent.



Scheme 2. Formilation reaction in micellar media.



Scheme 3. Products obtained by Vilsmeier-Haack reactions.

Table 2
Crystallographic data of compounds **(6)** and **(14).**

Bileşik Numarası	(6)	(14)
Empirical formula	$C_{13}H_{13}N_3OS$	$C_{16}H_{12}N_2OS$
Formula weight (g/mol)	259.32	280.34
Crystal system	orthorhombic	monoclinic
Space group	Pccn	$P2_1/c$
Unit Cell Dimensions (Å,°)	$a = 14.2955(19)$	$a = 12.6050(16)$
	$b = 17.528(3)$	$b = 5.8979(7)$
	$c = 10.2255(13)$	$c = 18.656(2)$
Unit Cell Volume **(Å^3)**	2562.3(6)	1354.8(3)
Z / Density (g/cm^3)	8/ 1.344	1.374
Absorption coefficient (mm^{-1})	0.244	0.235
F(000)	1088.0	584.0
Crystal size (mm)	0.209 × 0.163 × 0.123	0.514 × 0.18 × 0.15
Index Ranges	$-18 \le h \le 18$,	$-16 \le h \le 16$,
	$-22 \le k \le 22$,	$-6 \le k \le 7$,
	$-13 \le l \le 11$	$-24 \le l \le 15$
Reflections collected / unique	2939/0/165	3107/0/181
Goodness-of-fit on F2	1.018	1.036
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0423$,	$R_1 = 0.0419$,
	$wR_2 = 0.0990$	$wR_2 = 0.0976$
R indicesall data	$R_1 = 0.0757$,	$R_1 = 0.0700$,
	$wR_2 = 0.1154$	$wR_2 = 0.1113$
Large diff. peak and hole	0.14/−0.20	0.15/−0.21

Table 3
Bond lengths of **(6)** and **(14)** compounds.

Compound 14			Compound 6		
Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
C1	C2	1.369(3)	C1	C2	1.381(3)
C1	C6	1.382(3)	C1	C6	1.388(3)
C2	C3	1.364(4)	C2	C3	1.365(4)
C3	C4	1.376(4)	C3	C4	1.370(4)
C4	C5	1.380(3)	C4	C5	1.388(4)
C5	C6	1.386(3)	C5	C6	1.386(3)
C6	C7	1.468(3)	C6	C7	1.474(3)
C7	C8	1.349(3)	C7	C8	1.377(2)
C7	N1	1.392(2)	C7	N1	1.370(2)
C8	S1	1.706(2)	C8	C9	1.434(3)
C9	N1	1.295(2)	C8	S1	1.725(2)
C9	N2	1.394(2)	C9	O1	1.217(2)
C9	S1	1.7345(17)	C10	N1	1.313(2)
C10	N2	1.365(2)	C10	N2	1.366(2)
C10	O1	1.210(2)	C10	S1	1.7309(18)
C11	C12	1.373(2)	C11	N2	1.299(2)
C11	C16	1.373(2)	C11	N3	1.313(2)
C11	N2	1.446(2)	C12	N3	1.452(3)
C12	C13	1.379(2)	C13	N3	1.443(3)
C13	C14	1.366(3)			
C14	C15	1.368(3)			
C15	C16	1.382(3)			

Device (CCD) detector using graphite-monochromated Mo Ka radiation (k: 0.71073 A) with CrysAlisPro software [9]. Scaling and analytical absorption corrections and data reduction were achieved using by CrysAlisPro. The structure solution and full-matrix least-squares refinement based on F2 for the compounds were performed by the direct methods with SHELXT [10] and SHELXL [11], respectively, corporated into the OLEX2 program package [12]. Crystallographic details are given in Table 2 and Table 3.

3. Experimental section

3.1. General

All chemicals were purchased from commercial suppliers and were used without further purification. FTIR spectra were recorded on Perkin Elmer FTIR spectrometer using the KBr disk in the range of 4000–400 cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Inova 500 MHz spectrometer using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as an internal standard. Splitting patterns are designated as follows; s, singlet; d, doublet; m, multiplet. Chemical shift (d) values are given in ppm. X-ray diffraction studies were performed in Bruker APEX II Quazar diffractometer.

3.2. Chemistry

Synthesis of compound (E)-*N'*-(5-formyl-4-phenylthiazol-2-yl)-*N,N*-dimethylformimidamide **(6)** and (Z)-*N'*-(5-formyl-4-phenylthiazol-2-yl)-*N,N*-dimethylformimidamide **(9):**

The compounds **(6)** and **(9)** were synthesized, while $POCl_3$ (1 equivalent, 0.52 mL), DMF (2 equivalents, 1.50 mL). Vilsmeier–Haack reagent was prepared by mixing in 10 mL of dry DCM at 0 °C for half an hour. Then, compound **(7)** (1 equivalent, 0.52 g) was dissolved in 1.5 mL of DMF and 5 mL of dry DCM and added dropwise to Vilsmeier's reagent. It was observed that the color of the reaction mixture changed from yellow to dark green after the addition was complete. The reaction was continued for some time under room conditions. In the reaction follow-up with TLC, two product spots with blue fluorescence and yellow color were observed. The reaction mixture was purified by column chromatography using a 20% EtOAc/Hexane system. Compound **(6)** was observed in yellow color in TLC and was obtained in 25% yield, compound **(9)** gave a blue fluorescence spot in TLC and was obtained in 40% yield. The molecule **(6)** was crystallized with MeOH to obtain a single crystal and its structure was elucidated by X-ray spectroscopy. Rf for compound **(6)** was calculated as 0.40 (30% EtOAc/Hexane)) and for compound (9) Rf: 0.21 (30% EtOAc/Hexane). The FT-IR, ^{1}H NMR, and ^{13}C NMR spectrum for the compounds is given in SI.

Formylation conditions of compound **(8)** were used in the formylation reaction of compound **(7)**. At the end of the reaction, products **(6)** and **(9)** were obtained. In this reaction, substance **(6)** was obtained in 26% yield, and substance **(9)** in 42% yield.

Formylation conditions of compound **(8)** were used in the formylation reaction of compound **(12)**. The crude product was purified by column chromatography using a 20% EtOAc/Hexane solvent system. Compound **(14)** (*N*-phenyl-*N*-(4-phenylthiazol-2-yl)formamide) was obtained in 48% yield. Rf for molecule **(14)** was calculated as 0.38 (20% EtOAc/Hexane). The FT-IR, ^{1}H NMR, and ^{13}C NMR spectrum for the compound **(14)** is given in SI.

Spectral data for compound **(6)**: IR (cm^{-1}): 775 (C-S stretch.), 1657 (C = O stretch.), 2845(-CO—H stretch.), 2940 (Alip. C-S stretch.), 3166 (Ar CH stretch.). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.81 (s, 1H), 8.43 (s, 1H), 7.70 (s, 2H), 7.46 (s, 3H), 3.18 (s, 3H), 3.15 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.21, 155.95, 151.68, 135.12, 128.55, 127.57, 126.07, 106.38, 77.70, 77.44, 77.18, 40.67, 34.91.

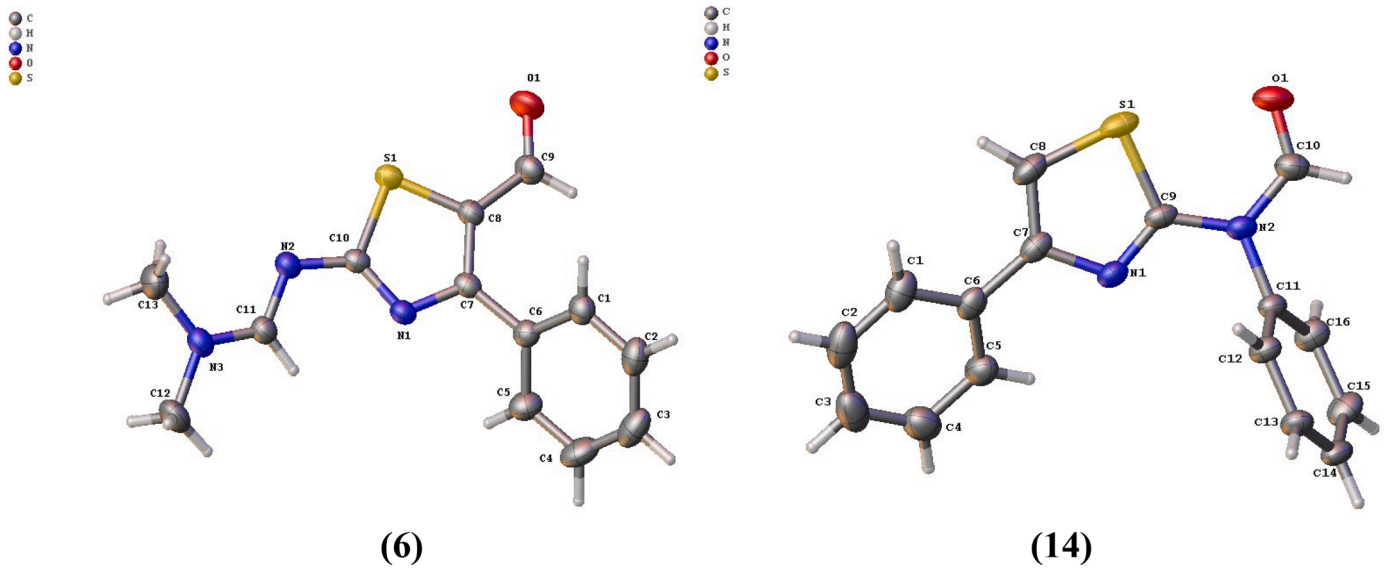
Spectral data for compound **(9)**: IR (cm^{-1}): 768 (C-S stretch.), 1607 (C = O stretch.), 2817 (-CO—H stretch.), 2937 (Alip. C—H stretch.), 3055 (Ar -CH stretch.) ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.81 (s, 1H), 8.43 (s, 1H), 7.69 (s, 2H), 7.47 (s, 3H), 3.17 (s, 3H), 3.15 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 183.60, 179.48, 163.08, 156.93, 133.78, 129.78, 129.72, 128.61, 127.82, 77.34, 77.09, 76.83, 41.29, 35.40.

Spectral data for compound **(14)**: IR (cm^{-1}):798 (C-S stretch.), 1662 (C = O stretch.), 2849 (-CO—H stretch.), 2922 (Alip. C—H stretch.), 3023 (Ar-CH stretch.). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.70 (s, 1H), 7.71–7.48 (m, 6H), 7.32 (t, $J = 7.6$ Hz, 4H), 7.28 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.16, 157.74, 149.64, 138.07, 134.24, 129.55, 129.03, 128.57, 128.03, 127.95, 126.05, 108.40.

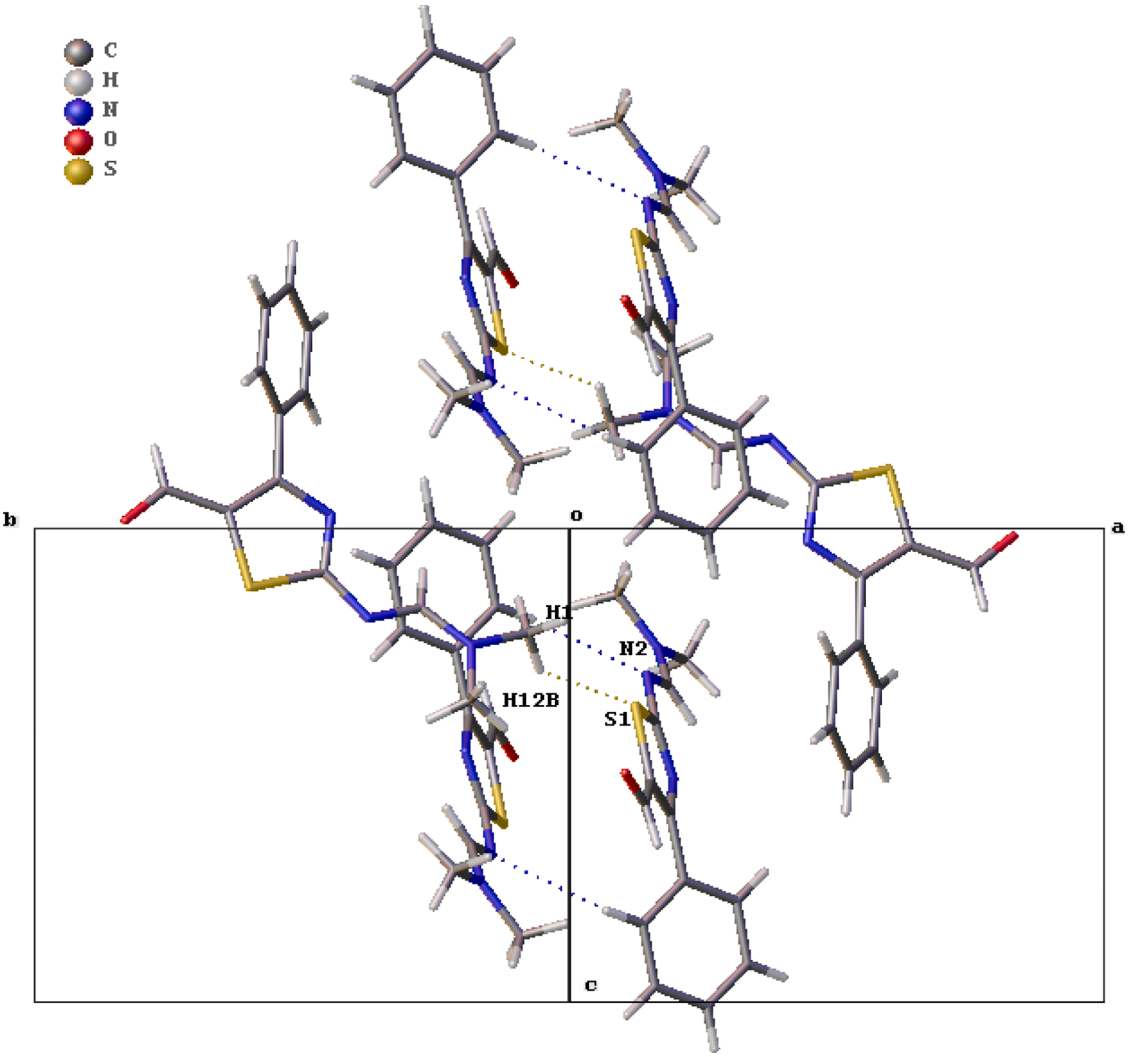
3.3. X-ray crystallography

The molecular structure of compounds **(6** and **14)** has been verified by X-ray crystallography and molecular diagrams of the compounds are demonstrated in Scheme 4. Selected geometrical data of crystals are summarized in Tables 2 and 3.

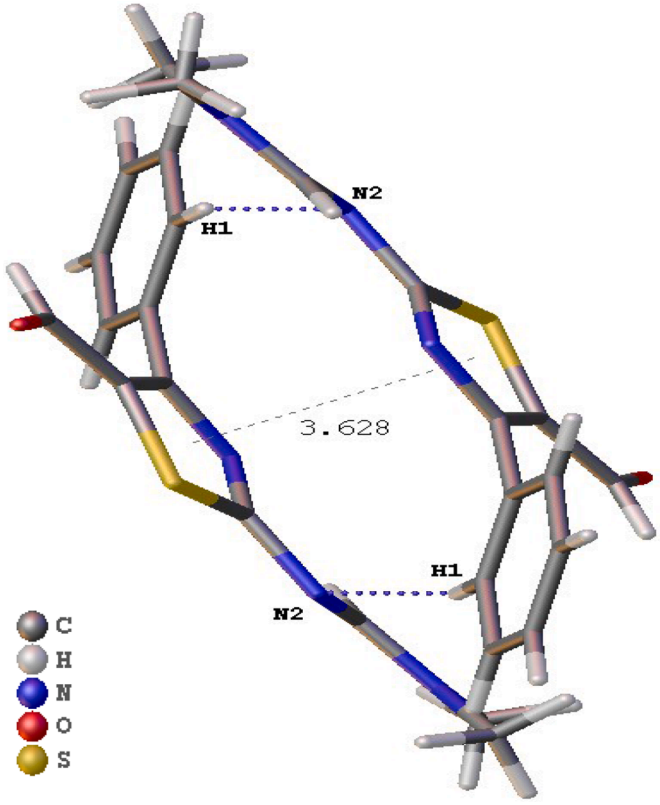
The single crystal structures of the molecules belong to the



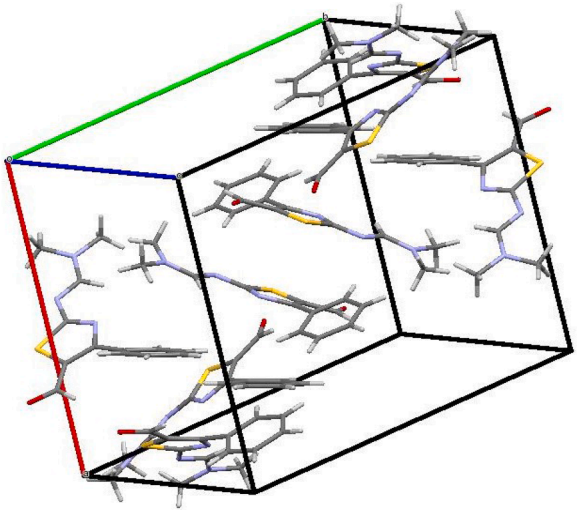
Scheme 4. ORTEP diagrams of **(6)** and **(14)** compounds.



Scheme 5. Intermolecular interactions of compound **(6)**.



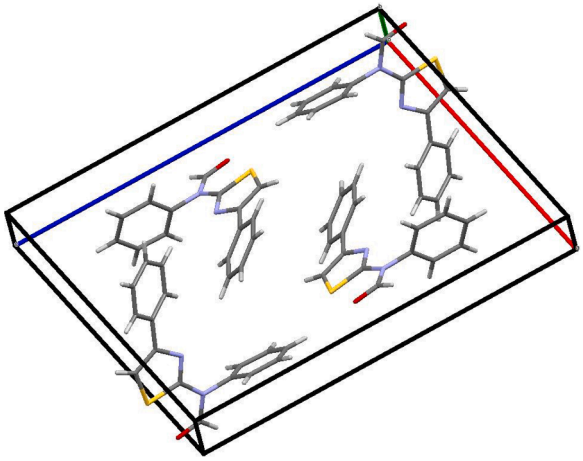
Scheme 6. $\pi\ldots\pi$ interactions in compound **(6)**.



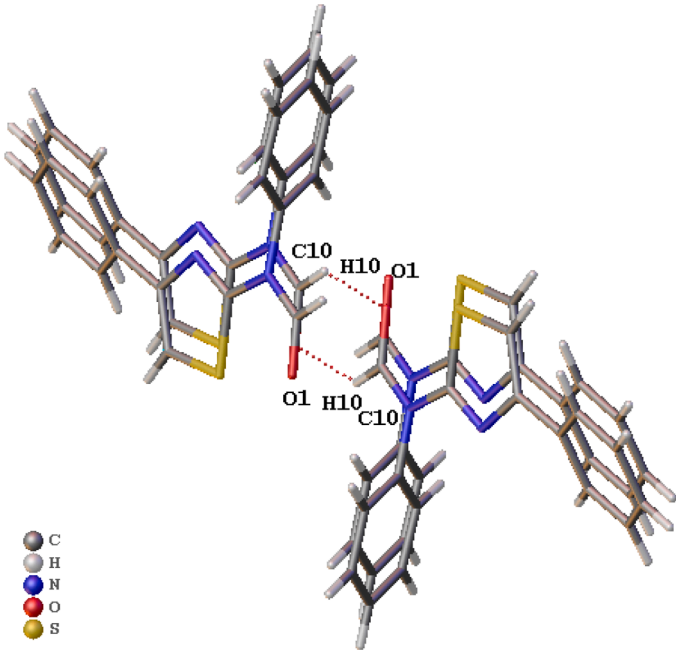
Scheme 7. The crystalline unit cell structure **(6)**.

orthorhombic space group Pccn, with dimensions $a = 14.2955(19)$ Å, $b = 17.528(3)$ Å, $c = 10.2255(13)$ Å, Z: 8 for **(14)** and monoclinic space group $P2_1/c$ $a = 12.6050(16)$ Å, $b = 5.8979(7)$ Å, $c = 18.656(2)$, $Z = 4$ for **(6)** (Scheme 4). Good-quality single-crystal of dimensions 0.209 × 0.163 × 0.123 for compound **(6)** and 0.514 × 0.18 × 0.15 for compound **(14)** was selected for the X-ray diffraction experiment at $T = 296$ K. Diffraction data was collected on an Oxford Diffraction X-Calibur equipped with an Eos-CCD detector, operated at 50 kV and 40 mA with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation for the compound.

In compound **(6)** the dihedral angle between the thiazole ring and the phenyl ring is 45.2 (3)°, the dihedral angle between the thiazole ring



Scheme 8. The crystalline unit cell structure **(14)**.



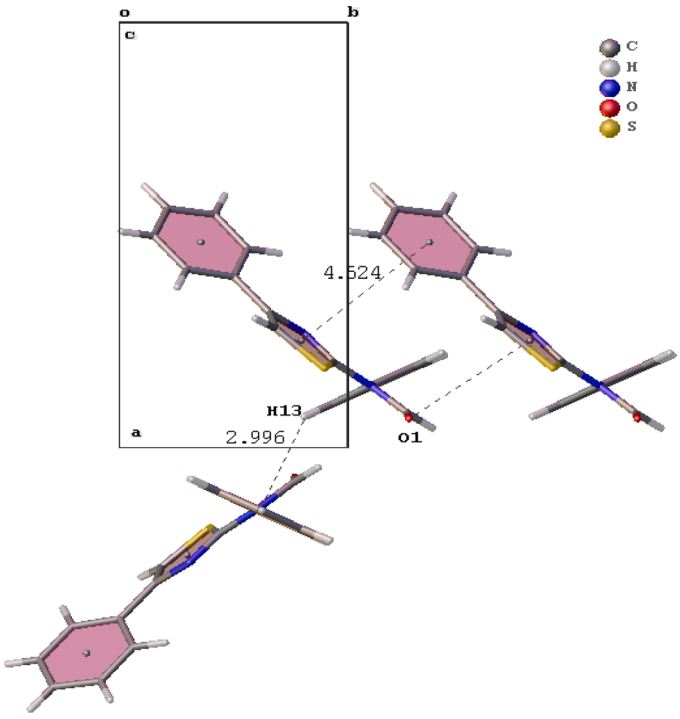
Scheme 9. Carbonyl group interaction in two molecules for compound **(14)**.

and the aldehyde group is 5.2 (3)°, the dihedral angle between the thiazole ring and the aliphatic chain with the imine group is 6.8 (2)° has been observed.The aliphatic chain with the thiazole ring, the aldehyde group, and the imine group are almost planar (Scheme 7).

Intermolecular interactions of compound **(6)** are shown in Scheme 5. There is intermolecular short interactions between the S1-H12B and N2-H1 atoms. These interactions are responsible for the formation of the packing structure of the molecule (Scheme 5).

In compound **(6)**, there is strong intermolecular $\pi\ldots\pi$ stacking interactions between thiazole rings and the interfacial distance between the two rings is 3.628 Å. In addition to $\pi\ldots\pi$ interactions, there is also intermolecular short interactions between N2-H1 atoms (Scheme 6).

In compound **(14)**, the dihedral angle between the thiazole ring and the phenyl ring was measured as 30.9 (3)°. The dihedral angle of the thiazole ring with the aldehyde group attached to the N2 nitrogen atom is 6.8 (2)°, and the dihedral angle formed by the phenyl group attached to the N2 atom with the C9-N2 bond is 65.6 (2)°. The dihedral angle between the thiazole ring and the phenyl ring directly attached to this ring is 29.2 (3)° (Scheme 8).



Scheme 10. $\pi\ldots\ \pi$ interactions in compound **(14)**.

In the dimeric structure of compound **(14)**, O1-C10 atoms in aldehyde groups interact with each other in C = O–H type intermolecular interactions (Scheme 9).

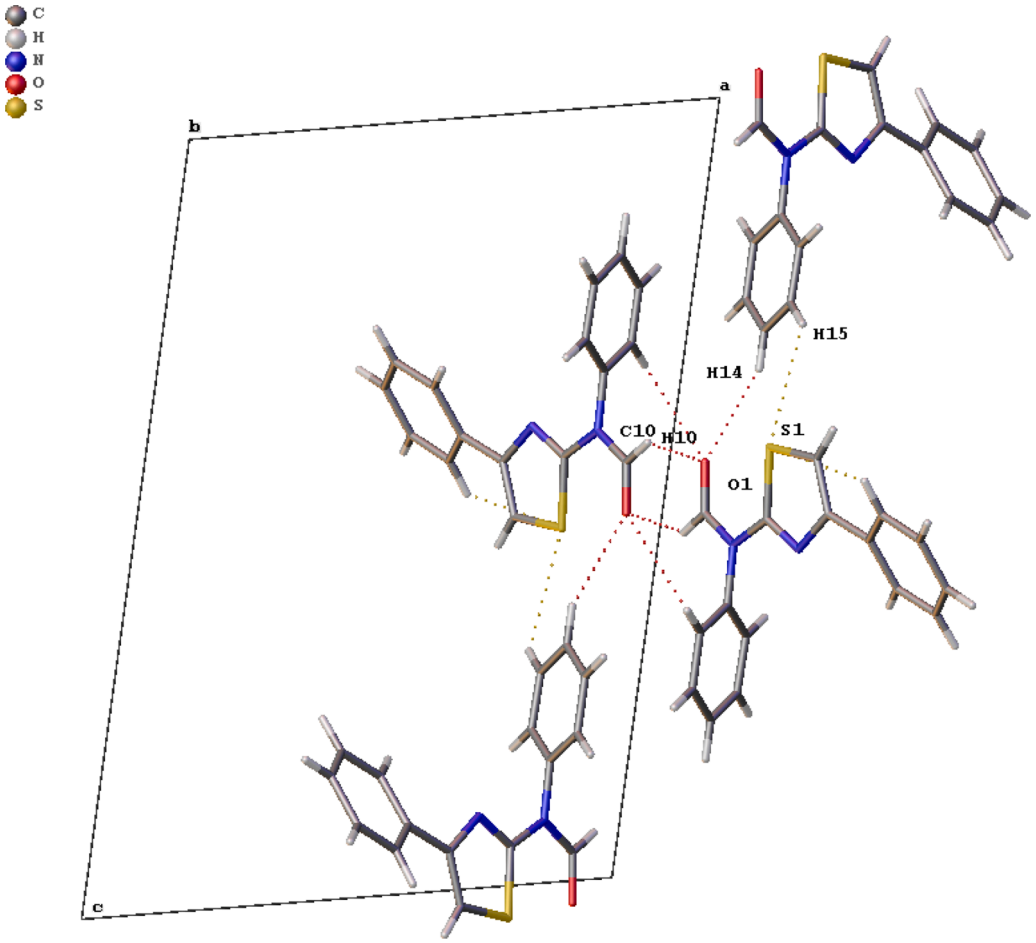
When the dimeric structure of the compound **(14)** is examined, there is a $\pi\ldots\ \pi$ interaction between the thiazole ring(Cg(1)) and the phenyl ring (Cg(2): C1/C6) attached to the thiazole ring, and the interfacial distance between the rings is 4.524 Å. In the compound numbered **(14)**, there are $C{=}O\ldots\pi$ interactions between the unpaired electrons in the p orbitals of the carbonyl oxygen in the aldehyde group and the thiazole ring. In the compound **(14)**, there is a interfacial distance of 4.524 Å between the phenyl ring (Cg(3): C11/C16) attached to the nitrogen and the H13 atom, and there is C—H….π intermolecular interaction (Scheme 10).

Compound **(14)** has intramolecular interactions between H1-C8, and strong intermolecular interactions between O1-C10 (nonclassical C—H.. O hydrogen bonds), S1-H15, O1-H14, C12-O1. Intermolecular and intramolecular interactions play an important role in the crystal stabilization (Scheme 11).

Single crystals of the products **(6)** and **(14)** were obtained and their structures were elucidated by X-ray spectroscopy. When the X-ray structures of the obtained molecules are examined, it is seen that the aldehyde group prefers O,S-syn conformation.

4. Conclusion

In this study, 4-phenyl-*N,N*'-benzoyl and 4-phenyl-*N*-substituted (*N*-sulphonyl and *N*-phenyl) 2-aminothiazole molecules, sulfonamide, and amide groups are hydrolyzed from the molecule in the reaction medium and the **(5)** numbered molecule formed both the free amino group and



Scheme 11. Intramolecular and intermolecular interactions of compound **(14)**.

the thiazole ring of the thiazole compound reacted with formylation reagents to give molecules **(6)** and **(9)**.

In the *N*-phenyl substituted thiazole compound **(12),** the formylation was over the more active amino group, and the thiazole ring did not give a formylation reaction. When the X-ray structures of the obtained crystals were examined, it was observed that the oxygen atom of the aldehyde group and the sulfur atom of the thiazole ring were in the same direction (O,S syn conformation). This synthesis pathway can be considered a useful method in the formulation step in multi-step synthesis from starting compounds containing amide and sulfonamide structures.

CRediT authorship contribution statement

Abdullah Biçer: Conceptualization, Writing – original draft, Investigation, Funding acquisition, Methodology, Project administration. **Ramazan Altundaş:** Methodology, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Abdullah Bicer reports financial support was provided by Scientific and Technological Research Council of Turkey. Abdullah Bicer reports a relationship with Scientific and Technological Research Council of Turkey that includes: funding grants.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2023.135840.

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