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MOLECULAR STRUCTURE INVESTIGATION OF
Z-3N(2-ETHOXYPHENYL)-2-N'(2-ETHOXYPHENYL)-IMINO-THIAZOLIDIN-4-ONE
BY *AB INITIO*, DFT AND X-RAY DIFFRACTION METHODS

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We report here the synthesis of the Z-3N(2-ethoxyphenyl)-2-N'(2-ethoxyphenyl)-imino-thiazolidin-4-one compound. The crystal structure is determined by X-ray diffraction. The compound crystallizes in the monoclinic system with the space group $P2_1/n$ and cell parameters: $a = 9.4094(10) \text{ \AA}$, $b = 9.3066(10) \text{ \AA}$, $c = 20.960(2) \text{ \AA}$, $\beta = 99.0375(10)^\circ$, $V = 1812.7(3) \text{ \AA}^3$ and $Z = 4$. The structure is refined to final $R = 0.05$ for 2083 observed reflections. The molecule in the crystal exhibits the intermolecular hydrogen bonds of C—H...O, C—H...N, and C—H...S types. *Ab initio* calculations are also performed at Hartree—Fock (HF) and density functional theory (DFT) levels. The full HF and DFT geometry optimization is carried out using the 6-31G(*d,p*) basis set. The observed molecular structure is compared with that calculated by both HF and DFT methods. The optimized geometry of the titled compound is found to be consistent with the structure determined by X-ray diffraction.

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Keywords: synthesis, structure, X-ray diffraction, thiazolidin-4-one, theoretical calculations, organic compounds.

INTRODUCTION

Thiazoles are an important class of heterocyclic compounds. The thiazole moiety belongs to an important class of N- and S-containing heterocycles. This heterocyclic system is responsible for a broad spectrum of biological activities. There are numerous studies of simple thiazoles, reporting their biological activity [1—6]. Due to their properties, thiazole derivatives are interesting candidates for obtaining new materials. Thiazole compounds have also been studied for their nonlinear optical properties [7, 8].

Prompted by these investigations and in continuation of our search on the development of organic heterocyclic compounds [9, 10], in this paper we report the synthesis and crystal structure of compound **I**, Z-3N(2-ethoxyphenyl)-2-N'(2-ethoxyphenyl)-imino-thiazolidin-4-one $C_{19}H_{20}N_2O_3S$ (Fig. 2) and compare the observed molecular geometries with those optimized by density functional theory (DFT) and Hartree—Fock methods.

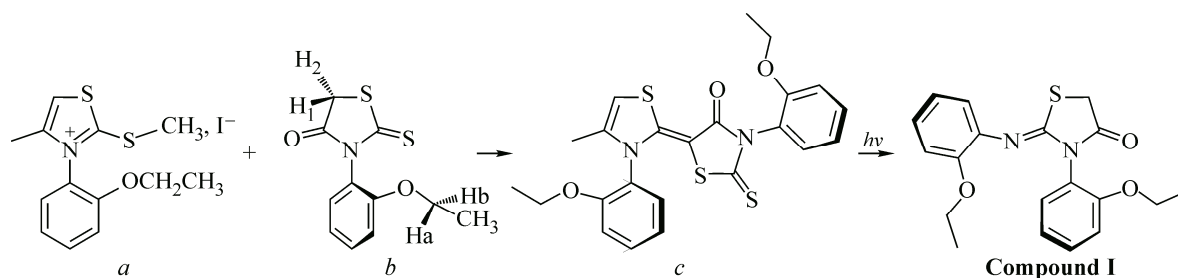


Fig. 1. Preparation and chemical structure of Z-3N(2-ethoxyphenyl)-2-N'(2-ethoxyphenyl)-imino-thiazolidin-4-one (compound I)

EXPERIMENTAL AND COMPUTATIONAL METHODS

Synthesis. Compound I was prepared by the reaction of S-methyl iodide, 4-Me-3-N (*o*-ethyl phenyl) Δ^4 thiazolium (0.01 mol), 2-thioxo-3-N'(2-ethoxyphenyl thiazolidine)-4-one (0.01 mol), 20 ml of acetone in a 150 ml boiling flask. Then 2 ml of triethylamine were added to this mixture. The system was refluxed for 24 hours at ambient temperature, forming a yellow solid. The crystals obtained were filtered and recrystallized in acetone. Fig. 1 shows the preparation and chemical structure of compound I and its photodegradation by UV-visible light leading to the studied molecule (compound I).

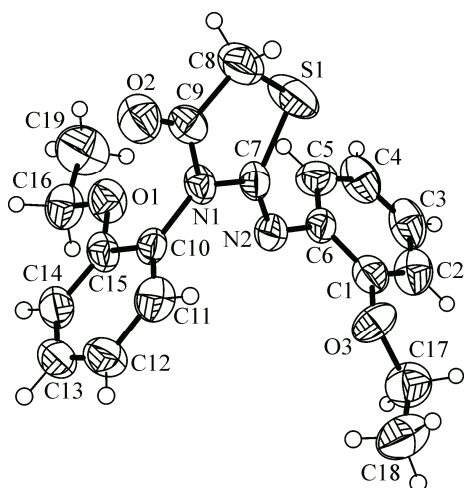
Spectral analysis. All reagents and solvents for the synthesis and spectroscopic studies were commercially available and used as received without further purification. The IR spectra were measured on a JASCO 4200 FT-IR spectrometer as a KBr pellet. The ^1H and ^{13}C NMR spectra were measured in CDCl_3 on a BRUKER Ac DPX-200 (300 MHz) spectrometer at 25 °C.

Spectral data. Yellow solid, yield 78 %, m.p. 210 °C, IR (KBr, cm^{-1}): 3407 broad band, 3035 (C—N), 1710 (C=O), 1256 (C—S).

^1H NMR, (CDCl_3 , 300 MHz) δ (ppm) J(HZ): 1.276 (t, 3H, —O—CH₂—CH₃ thione), 1.930 (t, 3H, —O—CH₂—CH₃, thiazolidène); 1.930 (s, 3H, Me thia, $J = 1.06$); 4.031 (q, 2H, —O—CH₂—CH₃ thione); 4.135 (q, 2H, —O—CH₂—CH₃ thiazolidène); 6.34 (s, 1H, $J = 1.06$); 7.621—7.023 (m, 8H aryle).

^{13}C NMR, (CDCl_3 , 300 MHz) δ (ppm): 8.65 (O—CH₂—CH₃); 14.76 (Me₄); 56.14 (C thia-Me₄); 64.43 (—O—CH₂—CH₃); 112.80; 113.63; 120.83; 121.41; 123.57; 125.40; 130.02; 130.63; 137.81; 129.99 (C thia-Me₄); 133.29 (C thia-H₅); 103.48 (C=C); 154.63 (C=C); 155.86 (C—S); 189.52 (C=O).

X-ray structure determination. A yellow prismatic crystal with approximate dimensions of 0.20×0.15×0.10 mm was selected for data collection. The X-ray diffraction data were collected on a Kappa CCD Bruker-Nonius diffractometer. The SHELX program [11] was used for the structure solution and refinement. The structure was solved by direct methods. A Fourier synthesis revealed the complete structure, which was refined by the full-matrix least squares technique. All non-H atoms



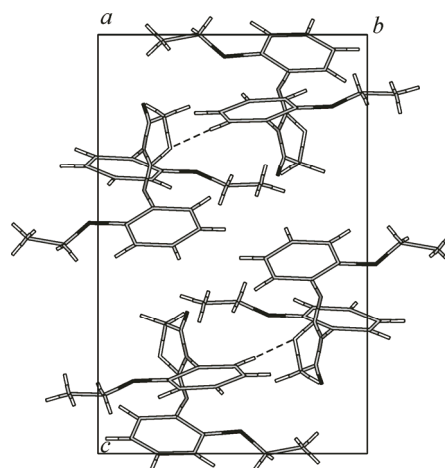
were refined anisotropically. The positions of H atoms bonded to C atoms were calculated. An ORTEP [12] view of the molecular structure with the atomic numbering is shown in Fig. 2. Atomic scattering factors for heavy atoms were taken from International Tables for X-ray Crystallography [13] while the factors for H were those of Stewart, Davidson, and Simpson [14]. The details of the crystal data and refinement: $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$, $M = 356.44$, $T = 294(2)$ K, monoclinic, space group $P2_1/n$, $a = 9.4094(10)$, $b = 9.3066(10)$, $c = 20.960(2)$ Å, $\beta = 99.0375(10)^\circ$, $V = 1812.7(3)$ Å³, $\lambda =$

Fig. 2. General view of the molecule (compound I) with the atomic numbering scheme (thermal ellipsoids drawn at a 50 % probability). H atoms are shown as small spheres of arbitrary radii

Fig. 3. A perspective view of the crystal packing in the unit cell

$= 0.71073 \text{ \AA}$, $Z = 4$, $d_c = 1.303 \text{ mg/m}^3$, $F(000) = 752$, θ range $5.02\text{--}27.51^\circ$, index ranges $-12 \leq h \leq 12$, $-10 \leq k \leq 12$, $-27 \leq l \leq 27$, 4141 reflections collected, 2083 observed ($I \geq 2\sigma(I)$), 229 parameters, final $R_1 = 0.0504$, $wR_2 = 0.1601$, $\text{GOOF} = 0.855$ (observed), $R_1 = 0.3535$, $wR_2 = 0.1607$ (all data), CCDC 989101.

Computational method. Theoretical calculation methods are presently considered to be one of the most successful models in the world of computational chemistry since it yields accurate results for several physicochemical properties. For calculations involving hydrogen bonding interaction systems it is very important to select an appropriate method and carefully consider and evaluate the accuracy and speed of the calculation. DFT methods are fast and can be used to compute mid-sized and even large molecular systems. In this work, the full geometry optimization has been performed using the GAUSSIAN03 package [15] and the Gauss-View molecular visualization program [16] with the Becke 3-parameter hybrid exchange functions and the Lee—Young—Parr correlation functional (B3LYP) [17, 18] and HF theory [19], using the 6-31G(*d,p*) basis set by the Berny method [20, 21].



RESULTS AND DISCUSSION

Crystal structure description. The molecular structure of compound **I** with atomic labeling (thermal ellipsoids are drawn at a 50 % probability) is shown in Fig. 2. Fig. 3 shows a perspective view of the crystal packing in the unit cell. Selected bond lengths, bond and torsion angles for all non-hydrogen atoms determined by X-ray diffraction are listed in Table 1, together with the calculated parameters, respectively. The average values of bond distances and angles in the two benzene rings for both experimental and calculated data are in good agreement with the literature values. The two C—S distances (S1—C7 and S1—C8 of $1.756(6) \text{ \AA}$ and $1.779(6) \text{ \AA}$, respectively) in the thiazole ring have the values intermediate between those reported for single (1.81 \AA) and double (1.61 \AA) bonds [14]. The C9—O2 bonds show a typical double bond character with a bond length of $1.204(7) \text{ \AA}$. All of the C—N bonds (C6—N2 = $1.414(7) \text{ \AA}$, C7—N1 = $1.382(6) \text{ \AA}$, C9—N1 = $1.369(7) \text{ \AA}$, C10—N1 = $1.454(6) \text{ \AA}$) also indicate a partial double bond character. The double bond C7—N2 = $1.255(6) \text{ \AA}$ is slightly shorter than the other C—N bonds. The fragment formed by O2, C9, N1, C7, and N2 atoms is a conjugated system with the delocalization of π electron densities. This conjugated system is responsible for the charge transfer within the molecule.

The mean value of bond angles in the thiazole ring is $107.81(2)^\circ$. In the rest of the molecule, all bond angles (C—C—C, C—N—C, and C—C—N, ...) are close to 120° , indicating that the π electrons are delocalized in the titled compound. The torsion angles C7—N1—C9—C8 ($0.8(7)^\circ$), C7—S1—C8—C9 ($-3.5(5)^\circ$), S1—C8—C9—O2 ($-177.8(5)^\circ$), and S1—C8—C9—N1 ($2.2(6)^\circ$) indicate that the five-membered heterocycle has a planar conformation.

Geometry optimization. The ground state geometries were optimized at the Hartree Fock and DFT levels of theory, using the 6-31G(*d,p*) basis set. The optimized structure of the titled compound is illustrated in Fig. 4 and the corresponding main geometrical parameters (bond lengths, bond and torsion angles) are listed in Tables 1. As we can see there is good agreement between the calculated and the experimental values. The

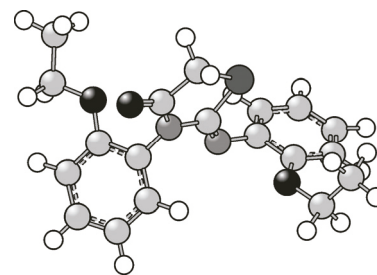


Fig. 4. Theoretical crystal structure of the titled compound at the B3LYP/6-31G(*d,p*) level

Table 1

Bond distances, bond angles and torsion angles for non-hydrogen atoms from X-ray diffraction measurements and theoretical calculations (e.s.d. are given in parenthesis)

Bond distances, Å Bond angles, deg.	X-ray	6-31G(<i>d,p</i>)		Bond torsion angles, deg.	X-ray	6-31G(<i>d,p</i>)	
		HF	B3LYP			HF	B3LYP
S1—C7	1.756(6)	1.781	1.801	C17—O3—C1—C2	-22.3(8)	0.23	2.74
S1—C8	1.779(6)	1.807	1.827	C17—O3—C1—C6	159.3(5)	179.9	-178.1
N1—C9	1.369(7)	1.372	1.390	O3—C1—C2—C3	-179.0(5)	179.3	178.8
N1—C7	1.382(6)	1.391	1.402	C4—C5—C6—N2	-174.2(5)	-176.4	-175.6
N1—C10	1.454(6)	1.428	1.433	O3—C1—C6—C5	179.6(5)	-178.8	-178.3
O1—C15	1.353(6)	1.343	1.357	O3—C1—C6—N2	-7.0(7)	-3.5	-3.7
O1—C16	1.428(6)	1.408	1.429	C2—C1—C6—N2	174.5(5)	176.2	175.4
O2—C9	1.204(7)	1.188	1.212	C5—C6—N2—C7	-55.1(8)	-98.3	-100.8
O3—C1	1.362(7)	1.350	1.368	C1—C6—N2—C7	131.8(6)	86.3	84.6
O3—C17	1.411(7)	1.407	1.428	C6—N2—C7—N1	177.1(5)	-179.2	-177.4
C6—N2	1.414(7)	1.409	1.409	C6—N2—C7—S1	-5.1(8)	0.7	2.8
N2—C7	1.255(6)	1.242	1.264	C9—N1—C7—N2	174.7(5)	-177.6	179.9
C16—C19	1.484(8)	1.514	1.517	C10—N1—C7—N2	-10.7(8)	-4.7	-0.6
C17—C18	1.491(8)	1.520	1.525	C9—N1—C7—S1	-3.5(6)	2.5	-0.2
C7—S1—C8	92.2(3)	92.3	91.9	C10—N1—C7—S1	171.2(4)	175.3	179.3
C9—N1—C7	117.9(5)	117.7	117.6	C8—S1—C7—N2	-174.0(6)	178.7	178.7
C9—N1—C10	120.6(4)	120.7	120.8	C8—S1—C7—N1	4.0(4)	-1.3	-1.1
C7—N1—C10	121.3(5)	121.1	121.3	C7—S1—C8—C9	-3.5(5)	-0.2	2.0
C15—O1—C16	117.9(5)	120.3	118.9	C7—N1—C9—O2	-179.2(5)	178.1	-178.0
C1—O3—C17	117.2(6)	121.7	119.8	C10—N1—C9—O2	6.1(9)	5.1	2.5
O3—C1—C2	123.6(6)	125.0	125.3	C7—N1—C9—C8	0.8(7)	-2.5	1.7
O3—C1—C6	116.2(6)	115.7	115.2	C10—N1—C9—C8	-173.9(5)	-175.4	-177.7
C5—C6—N2	122.9(6)	120.1	120.7	S1—C8—C9—O2	-177.8(5)	-179.2	177.3
C1—C6—N2	118.0(6)	120.3	119.8	S1—C8—C9—N1	2.2(6)	1.3	-2.4
C7—N2—C6	120.6(5)	121.1	121.2	C9—N1—C10—C11	-77.9(7)	-101.3	-112.9
N2—C7—N1	121.4(5)	122.3	122.4	C7—N1—C10—C11	107.5(6)	86.0	67.6
N1—C7—S1	110.8(4)	110.3	110.6	C9—N1—C10—C15	101.0(6)	78.4	66.9
C9—C8—S1	108.7(4)	107.8	108.3	C7—N1—C10—C15	-73.5(6)	-94.3	-112.5
O2—C9—N1	126.0(5)	125.0	125.0	N1—C10—C11—C12	178.2(5)	179.5	179.1
O2—C9—C8	123.8(6)	123.2	123.6	C16—O1—C15—C14	-3.0(8)	4.3	7.4
N1—C9—C8	110.2(6)	111.7	111.4	C16—O1—C15—C10	177.0(5)	-175.9	-173.2
C11—C10—N1	121.2(5)	120.4	120.3	C13—C14—C15—O1	178.4(5)	179.5	178.4
C15—C10—N1	118.0(5)	118.8	119.0	C11—C10—C15—O1	-178.4(5)	-179.4	-178.1
O1—C15—C14	126.1(6)	124.9	124.8	N1—C10—C15—O1	2.6(7)	0.8	2.1
O1—C15—C10	115.4(5)	116.2	116.3	N1—C10—C15—C14	-177.3(5)	-179.3	-178.4
O1—C16—C19	105.3(5)	107.4	107.3	C15—O1—C16—C19	-178.7(5)	177.2	175.2
O3—C17—C18	108.4(6)	112.5	112.7	C1—O3—C17—C18	-176.1(5)	82.3	80.1

largest deviation between the X-ray data and theoretical calculations at the HF/6-31G(*d,p*) level is around 0.08 Å for distances and 2.7° for bond angles. The B3LYP/6-31G(*d,p*) results deviate in the range from 0.002 Å to 0.8 Å for bond lengths, and from 0.03° to 2.66° for bond angles. The difference between the experimental and calculated bond lengths calculated at the HF level with 6-31G(*d,p*) basis set does not exceed 0.058 Å, whereas in the case of B3LYP with the same basis set, the largest difference between the observed and calculated values is about 0.05 Å. The bond angles for HF/6-31G(*d,p*) calculations are very close to the experimental values (Table 1), and the maximum difference is about 2.5°. For DFT with the 6-31G(*d,p*) basis set, the bond angle difference does not exceed 3°.

Table 2

Geometry of the C—H...O, C—H...N and C—H...S H-bonds in **I** obtained by X-ray diffraction

D—H...A	D—H	H...A	D...A	D—H...A	D—H...A	D—H	H...A	D...A	D—H...A
C5—H5...S1	0.93	2.87	3.173(7)	100.5	C11—H11...S1 ⁱⁱⁱ	0.93	2.79	3.852(5)	159.1
C3—H3...O2 ⁱ	0.93	2.92	3.788(8)	155.0	C12—H12...O2 ^{iv}	0.93	2.58	3.428(7)	151.9
C8—H8B...O3 ⁱⁱ	0.97	2.79	3.625(7)	144.4	C16—H16A...O2 ^v	0.97	2.62	3.454(7)	144.1
					C17—H17B...N2 ^{vi}	0.97	2.90	3.635(7)	133.3

Symmetry codes: ⁱ $x+1/2, -y+3/2, z-1/2$; ⁱⁱ $-x+1/2, y+1/2, -z+1/2$; ⁱⁱⁱ $-x+1/2, y-1/2, -z+1/2$; ^{iv} $-x-1/2, y-1/2, -z+1/2$; ^v $-x-1/2, y+1/2, -z+1/2$; ^{vi} $-x, -y+1, -z$.

In summary, the optimized bond lengths and bond angles obtained using the DFT method are in good agreement with the corresponding X-ray structural parameters. It is worth noting that some of the optimized torsion angles have slightly different values from the corresponding experimental ones, due to the fact that the theoretical calculations consider only isolated molecules in the gas phase while the experimental results refer to molecules in the crystal environment.

Intermolecular H-bonds. The crystal structure exhibits intermolecular interactions of the C—H...O, C—H...N, and C—H...S types, in which C atoms (C3, C5, C8, C11, C12, C16, and C17) act as donors and O (O2 and O3), N2, and S1 atoms act as acceptors. In the crystalline state, these intermolecular interactions stabilize the crystal structure. The geometry of the hydrogen bonded interactions is listed in Table 2. Fig. 5 shows some H bonds in the crystal.

CONCLUSIONS

In this study, we have synthesized the Z-3N(2-ethoxyphenyl)-2-N'(2-ethoxyphenyl)-iminothiazolidin-4-one compound (compound **I**), and its crystal structure was determined by single crystal X-ray diffraction and a theoretical calculation. This compound belongs to the centrosymmetric space group $P2_1/n$. The X-ray diffraction results were assessed by DFT and HF *ab initio* calculations with the 6-31G(*d,p*) basis set. The two computational methods gave very similar results, which are very close to those of X-ray measurements. The crystal structure is stabilized by C—H...O, C—H...N, and C—H...S type hydrogen bonds. The optimized geometrical parameters (B3LYP) are in agreement with those for the similar derivatives reported. Any discrepancy noted between the observed and calculated values can be due to the fact that the calculations were actually made for a single molecule in the gas phase contrary to the experimental values recorded in the solid state where the intermolecular Coulomb interactions are present. All the calculated and experimental data on the studied molecule are useful for the application in fundamental researches in chemistry and biology in the future.

We can also conclude that the chirality of this type of compound is evidenced by the high value of the dihedral angle (79.7°) formed by the heterocyclic ring and the aryl linked with the nitrogen atom. The chirality of compound **I** is induced by one of their 3-N-(2-alkyloxyaryl)-2-thioxothiazolidin-4-one precursors, whose chirality in turn is due to the presence of a C2 axis of chirality.

In a forthcoming paper, we are going to present a spectroscopic study and other theoretical calculations on the same compound in order to evaluate the main physicochemical properties.

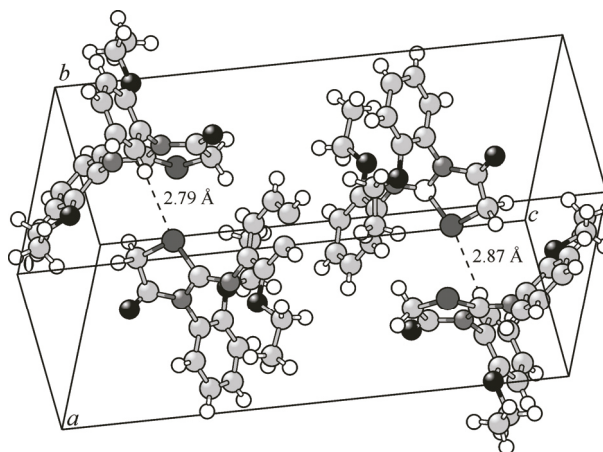


Fig. 5. View of two H-bonds in the crystal

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC 989101. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Facsimile (44) 01223 336 033, E-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.com.ac.uk/deposit>.

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