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Synthesis and Molecular Structure Investigation by DFT and X-Ray Diffraction of ARNO

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Abstract We report here the synthesis of (Z)-5-(4-nitro-benzyliden)-3-N(2-ethoxyphenyl)-2-thioxo-thiazolidin-4-one (ARNO) compound. The crystal structure has been determined by X-ray diffraction. The compound crystallizes in the triclinic system with space group $P\bar{1}$ and cell parameters: $a = 9.1289(19), b = 9.3717(7), c = 12.136(3)$ Å, $\alpha = 102.133$ $(11)°$, $\beta = 90.99(2)°$, $\gamma = 117.165(9)°$, $V = 895.4(3)$ Å^3 and $Z = 2$. The structure has been refined to a final R = 0.05 for 2591 observed reflections. The refined structure was found to be significantly non planar. The molecule exhibits intermolecular hydrogen bond of type C–H···O and C–H···S. ab initio calculations were also were performed at Hartree–Fock and density functional theory levels. The full HF and DFT geometry optimization was carried out using LANL2DZ, 6-31G* and B3LYP/6-31+G** basis sets. The optimized geometry of the title compound was found to be consistent structure determined by X-ray diffraction. The minimum energy of geometrical structure is obtained by using level HF/LANL2DZ basis sets.

Introduction

Research on new materials exhibiting nonlinear optical (NLO) behavior continues to be of primary interest for basic research as well as for industrial applications. The research on new materials with NLO properties for telecommunications and optoelectronics is directly related to the determination of their three-dimensional structure. Polymers represent a large family of interesting materials for nonlinear optics applications. In particular, compounds derived from thiazoles have recently received particular attention due to their NLO properties [1–3].

Density functional theory (DFT) is presently considered one of the most successful models in the world of computational chemistry since it yields accurate results for several physico-chemical properties, especially when hybrid DFT is used. The hybrid DFT functional offers reliable information for the excited state properties of small molecules [4], donor and acceptor systems [5], as well as metal complexes [6].

In this paper we present a structural study of the (Z)-5-(4-nitrobenzyliden)-3-N(2-ethoxyphenyl)-2-thioxo-thiazo-lidin-4-one compound, hereafter known as ARNO (to avoid rewriting the IUPAC name every time), by single-crystal X-ray diffraction to determine the most stable conformation in the crystalline state. To gain a better picture of the conformational profile of the given compound, we have also performed theoretical calculations using classical ab initio methods based on self-consistent field-molecular-orbital Hartree–Fock (HF) theory and Density Functional Theory (DFT) with the LANL2DZ, 6-31G* and 6-31+G** basis sets.

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The results from X-ray diffraction have been compared to those obtained from ab initio DFT and HF calculations, finding a good agreement with the structure determined from the single-crystal measurements.

Experiment and Computational Methods

Synthesis

The title compound was prepared by reaction of *N*-aryl-rhodanine (0.01 M), aldehyde (0.01 M), 5 mL of acetic acid and sodium acetate (0.02 M) in a 150 mL boiling flask. Then 2 mL of triethylamine are added to this mixture. The system is refluxed for 4 h, forming a yellow solid. The crystals obtained are filtered and recrystallized in ethanol. Synthesis of the compound was performed as follows (Fig. 1).

Spectral Analysis

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

Spectral Data of ARNO

(*Z*)-5-(4-nitrobenzyliden)-3-*N*(2-ethoxyphenyl)-2-thioxo-thiazolidin-4-one (2g, yield 75%, yellow solid, 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, 42 (t, 3H, –O–CH_2–CH_3, $J^3 = 6.97$), 4.06 (oct, 1H, $J^2 = 2.2$, $J^3 = 6.95$) (–O–CH_2–CH_3), 4.11 (oct, 1H, $J^2 = 2.2$; $J^3 = 6.95$), (–O–CH_2–CH_3), 7.53–7.08 (m, 4H), 7.71 (d, 2H, J = 8.75) 7.79 (s, 1H, –CH=C–), 8.53 (d, 2H, J = 8.80).

^{13}C NMR, ($CDCl_3$, 300 MHz) δ (ppm): 14.17 (O–CH_2–CH_3), 64.43 (–O–CH_2–CH_3), 113.48, 121.00, 123.26, 124.46, 128.35, 129.12, 129.77, 130.95, 131.63, 139.44, 147.96, 154.21, 167.19 (C=S), 191.65 (C=O).

X-Ray Structure Determination

A yellow prismatic crystal with approximate dimensions of $0.20 \times 0.15 \times 0.10$ mm was selected for data collection. The X-ray diffraction data were collected on a Kappa CCD Nonius diffractometer. Reflection data were measured at 298 K using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Intensities for 4080 reflections were measured with indices $-11 < h < 11$, $-12 < k < 11$, $-15 < l < 15$. The structure was determined by considering 2591 reflections with $I \geq 4\sigma(I)$. The structure was solved by direct methods using the SHELXS-97 [7]. A Fourier synthesis revealed the complete structure, which was refined by full-matrix least squares. All non-H atoms refined anisotropically. The positions of the H atoms bonded to C atoms were calculated. The H atoms were located from a difference Fourier map and included in the refinement with the isotropic temperature factor of the carrier atom. The final least-squares cycle using SHELXL-97 [8] gave R = 0.05 for the observed reflections with S = 0.95, $(\Delta\rho)_{min} = -0.425$ e/Å^3, $(\Delta\rho)_{max} = 0.219$ e/Å^3. An ORTEP [9] 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 [10] while the factors for H were
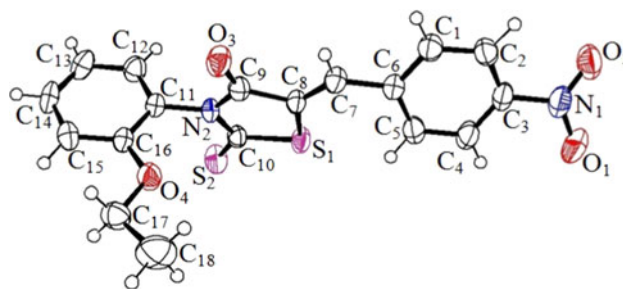
Fig. 2 General view of molecule with atomic numbering scheme (thermal ellipsoids drawn at 50% probability). H atoms are shown as small spheres of arbitrary radii
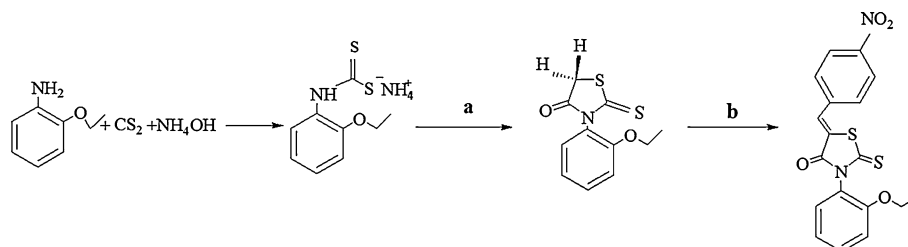
Fig. 1 Preparation and chemical structure of (*Z*)-5-(4-nitrobenzyliden)-3-*N*(2-ethoxyphenyl)-2-thioxo-thiazolidin-4-one (ARNO). Reagents and conditions: (*a*) $ClCH_2CO_2H$, 70 °C; (*b*) $NO_2C_6H_4CHO$, CH_3COOH, CH_3COONa, 90 °C

Table 1 Crystal data and structure refinement details

Compound	ARNO
Empirical formula	$C_{18}H_{14}O_4N_2S_2$
CCDC reference no.	805892
Formula weight	386.45
Crystal size (mm)	$0.20 \times 0.15 \times 0.10$
Temperature (K)	298(2)
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	
a (Å)	9.1289(19)
b (Å)	9.3717(7)
c (Å)	12.136(3)
α (°)	102.133(11)
β (°)	90.99(2)
γ (°)	117.165(9)
Wavelength (Å)	0.71073
Volume (Å³)	895.4(3)
Z, calculated density (mg/m³)	2/1.433
F(000)	400
θ range for data collection	5.01–27.50
Limiting indices	$-11 \le h \le 11$, $-12 \le k \le 11$, $-15 \le l \le 15$
Reflections collected/unique	4080/2591
Refinement method	Full-matrix least-squares on F^2 data
Parameters	227
Goodness of fit on F^2	0.935
Final R indices [$F_0 > 4\sigma(F_0)$]	
R_1	0.0523
wR_2	0.1316
R indices (all data)	
R_1	0.0994
wR_2	0.1607

those of Stewart et al. [11]. The details of crystal data and refinement are given in Table 1.

Computational Method

For calculations involving hydrogen-bonding interaction systems it is very important to select an appropriate method, and carefully considering and evaluating its accuracy and speed of calculation. DFT methods are fast and can be used to compute mid-sized and even large molecular systems. In this work, full geometry optimization has been performed using the GAUSSIAN03 package [12] and the Gauss-View molecular visualization program [13], at the Becke3-parameter hybrid exchange functions and Lee-Young–Parr correlation functional (B3LYP) level [14, 15] and HF theory [16], using the LANL2DZ, 6-31G* and 6-31+G** basis sets by the Berny method [17, 18].
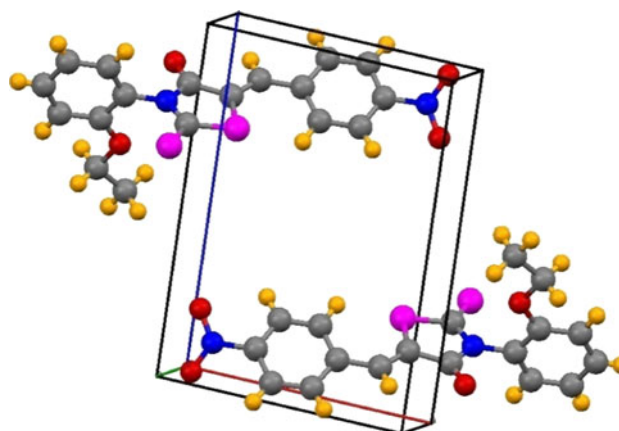
Fig. 3 A perspective view of the crystal packing in the unit cell

Results and Discussion

Description of the Crystal Structure

A general view of the molecule with atomic labeling (thermal ellipsoids are drawn at 50% probability) is shown in Fig. 2. Figure 3 shows a perspective view of the crystal packing in the unit cell. Selected bond lengths, bond angles and torsion angles for all non-hydrogen atoms by X-ray diffraction are listed in Tables 2, 3, and 4, together with the calculated parameters, respectively. The average values of bond distances and angles in the two benzene rings for both experimental and calculated are in good agreement with literature values. The three C–S distances, S1–C8, S1–C10 and S2 = C10 [1.753(3), 1.753(3) and 1.626(3) Å], respectively in the thiazole ring have values intermediate between those reported for C(Sp3)–S single [1.81 Å] and double [1.61 Å] bonds [10]. The mean value of bond angles in thiazole ring is 107.96(2)°. The crystal structure exhibits intermolecular interaction of the type C–H⋯O and C–H⋯S in which C atoms (C2, C4, C5, C7, C13 and C14) act as donors and O (O1, O2 and O3) and S1 atoms acts as acceptors. In the crystalline state, these intermolecular interactions stabilize the crystal structure. The geometry of the hydrogen-bonded interactions is listed in Table 5. Figure 4 shows some hydrogen bonds in the crystal. All bond angles C–C–C, C–N–C and C–C–N are close to 120°, indicating that the π electrons in the ARNO molecule are delocalized.

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 805892.[1]

Table 2 Bond distances for non-hydrogen atoms by X-ray and theoretical calculations (e.s.d.'s are given in parenthesis)

Bond distances (Å)	X-ray	HF			B3LYP		
		LANL2DZ	6-31G*	6-31+G**	LANL2DZ	6-31G*	6-31+G**
S1–C10	1.753(3)	1.809	1.760	1.760	1.846	1.785	1.782
S1–C8	1.753(3)	1.807	1.761	1.760	1.820	1.761	1.761
S2–C10	1.626(3)	1.667	1.629	1.629	1.678	1.640	1.640
O1–N1	1.223(3)	1.238	1.193	1.194	1.280	1.231	1.232
O2–N1	1.227(4)	1.239	1.193	1.194	1.280	1.231	1.232
O3–C9	1.211(3)	1.216	1.186	1.187	1.244	1.213	1.215
O4–C16	1.364(3)	1.368	1.340	1.339	1.388	1.356	1.357
O4–C17	1.447(4)	1.447	1.410	1.412	1.471	1.432	1.435
N1–C3	1.473(4)	1.461	1.458	1.461	1.474	1.470	1.471
N2–C10	1.384(3)	1.371	1.362	1.364	1.388	1.378	1.380
N2–C9	1.398(4)	1.403	1.394	1.393	1.424	1.412	1.410
N2–C11	1.439(3)	1.438	1.432	1.433	1.447	1.437	1.437
C1–C2	1.383(4)	1.388	1.380	1.382	1.398	1.387	1.389
C1–C6	1.392(4)	1.404	1.395	1.396	1.423	1.413	1.414
C2–C3	1.382(4)	1.390	1.383	1.383	1.406	1.394	1.395
C3–C4	1.379(4)	1.390	1.382	1.382	1.406	1.394	1.395
C4–C5	1.394(4)	1.389	1.382	1.383	1.399	1.389	1.390
C5–C6	1.390(4)	1.404	1.394	1.395	1.422	1.412	1.413
C6–C7	1.472(4)	1.472	1.474	1.474	1.462	1.455	1.456
C7–C8	1.331(4)	1.334	1.327	1.328	1.361	1.353	1.354
C8–C9	1.494(4)	1.487	1.491	1.493	1.492	1.492	1.493
C11–C12	1.373(4)	1.383	1.376	1.377	1.398	1.389	1.389
C11–C16	1.404(4)	1.397	1.394	1.395	1.414	1.408	1.408
C12–C13	1.390(4)	1.395	1.386	1.388	1.407	1.395	1.397
C13–C14	1.378(5)	1.392	1.381	1.383	1.406	1.393	1.395
C14–C15	1.380(5)	1.396	1.388	1.389	1.407	1.397	1.398
C15–C16	1.399(4)	1.393	1.386	1.388	1.409	1.399	1.401
C17–C18	1.493(6)	1.519	1.514	1.514	1.524	1.518	1.518

Geometry Optimization

The ground state geometries were optimized by the Hartree Fock and DFT levels of theory, using LANL2DZ, 6-31G(d) and 6-31+G(d,p) basis sets. The optimized structure of ARNO is illustrated in Fig. 5 and the corresponding main geometrical parameters (bonds lengths, bond angles and torsion angles) are listed in Tables 2, 3, and 4, as we can see there is a good agreement between the calculated and the experimental values. We also checked the effect of basis sets on the calculations. The largest deviation between X-ray data and theoretical calculations at the HF/LANL2DZ level is the S1–C10 distance, around 0.06 Å, and the C16–O4–C17 angle, which is larger than 3°. The B3LYP/LANL2DZ results deviate in the range from 0.001 to 0.9 Å for bond lengths, and from 0.02° to 2.56° (C8–C7–C6) for bond angles. The difference between the experimental and calculated bond lengths calculated at the HF level with 6-31G(d) basis set does not exceed 0.037 Å (O4–C17), whereas in the case of B3LYP with same basis set, the largest difference between the observed and the calculated values is about 0.03 Å. The bond angles for HF/631G(d) calculations are very close to the experimental values (Table 3), and the maximum difference is about 2.42°. For DFT with 6-31G(d) basis the bond angle difference does not exceed 2.67°. The HF/6-31+G(d,p) and B3LYP/6-31+G(d,p) results deviate in the range from 0.001 to 0.035 Å (O4–C17) and 0.001 to 0.029 Å for the bond lengths, and from 0.04° to 2.57° (C16–O4–C17) and 0.04° to 2.48° (C8–C7–C6) for the bond angles, respectively. X-ray structure of the title compound is compared with its optimized counterparts (see Fig. 6).

In summary, the optimized bond lengths and bond angles obtained using the DFT method are in good

Table 3 Bond angles for non-hydrogen atoms by X-ray and theoretical calculations (e.s.d.'s are given in parenthesis)

Bond angles (°)	X-ray	HF			B3LYP		
		LANL2DZ	6-31G*	6-31+G**	LANL2DZ	6-31G*	6-31+G**
C10–S1–C8	93.12(13)	91.65	92.44	92.47	91.43	92.85	92.90
C16–O4–C17	118.0(2)	121.95	120.42	120.57	119.20	118.92	119.14
O1–N1–O2	124.2(3)	123.71	124.85	124.88	123.78	124.79	124.57
O1–N1–C3	118.3(3)	118.18	117.60	117.58	118.15	117.63	117.74
O2–N1–C3	117.5(3)	118.11	117.56	117.54	118.08	117.58	117.68
C10–N2–C9	117.1(2)	118.15	117.36	117.28	118.41	117.51	117.43
C10–N2–C11	122.1(2)	122.02	122.58	122.55	121.93	122.42	122.26
C9–N2–C11	120.8(2)	119.43	119.77	119.87	119.46	119.85	120.14
C2–C1–C6	121.4(3)	121.34	121.04	121.06	121.57	121.56	121.58
C3–C2–C1	118.6(3)	118.35	118.52	118.48	118.43	118.55	118.56
C2–C3–C4	122.1(3)	122.03	121.99	122.04	121.86	121.79	121.77
C2–C3–N1	119.6(3)	118.97	119.00	118.97	119.07	119.11	119.13
C4–C3–N1	118.3(3)	119.00	119.01	118.99	119.08	119.09	119.10
C3–C4–C5	118.0(3)	118.95	118.86	118.85	119.03	119.06	119.06
C6–C5–C4	121.6(3)	120.69	120.66	120.66	120.91	121.00	121.03
C5–C6–C1	118.2(3)	118.64	118.91	118.90	118.21	118.03	118.01
C5–C6–C7	123.1(3)	124.63	123.28	123.41	124.70	124.62	124.64
C1–C6–C7	118.7(3)	116.72	117.79	117.68	117.09	117.35	117.35
C8–C7–C6	128.8(3)	131.44	129.42	129.48	131.36	131.47	131.28
C7–C8–C9	121.8(3)	120.03	119.80	119.79	120.02	119.18	119.45
C7–C8–S1	128.5(2)	130.89	130.88	130.94	130.04	131.03	130.83
C9–C8–S1	109.47(19)	109.08	109.28	109.23	109.94	109.79	109.71
O3–C9–N2	122.8(3)	123.54	124.05	124.04	123.32	123.70	123.73
O3–C9–C8	127.2(3)	125.27	125.75	125.69	125.70	126.17	126.05
N2–C9–C8	110.0(2)	111.19	110.19	110.26	110.97	110.13	110.21
N2–C10–S2	128.0(2)	127.90	127.74	127.61	128.43	128.11	127.85
N2–C10–S1	110.13(19)	109.89	110.69	110.72	109.22	109.68	109.72
S2–C10–S1	121.91(17)	122.21	121.57	121.66	122.35	122.21	122.43
C12–C11–C16	121.4(3)	121.12	121.16	121.18	121.00	121.13	121.12
C12–C11–N2	120.9(2)	120.92	120.35	120.31	120.62	120.42	120.25
C16–C11–N2	117.7(2)	117.96	118.48	118.50	118.37	118.43	118.62
C11–C12–C13	119.5(3)	119.86	120.14	120.16	119.92	120.0	120.05
C14–C13–C12	119.7(3)	119.22	118.94	118.92	119.34	119.22	119.17
C13–C14–C15	121.4(3)	121.02	121.27	121.25	120.97	121.13	121.11
C14–C15–C16	119.6(3)	119.54	119.78	119.77	119.68	119.87	119.87
O4–C16–C15	125.7(3)	124.90	125.16	125.11	125.04	125.36	125.25
O4–C16–C11	115.9(2)	115.86	116.13	116.18	115.88	115.98	116.08
C15–C16–C11	118.4(3)	119.24	118.70	118.71	119.08	118.65	118.66
O4–C17–C18	106.9(3)	107.03	107.43	107.58	106.92	107.42	107.59

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 gaseous phase while the experimental results refer to molecules in the crystal environment.

Conclusions

In this study, we have synthesized the (Z)-5-(4-nitrobenzyliden)-3-N(2-ethoxyphenyl)-2-thioxo-thiazolidin-4-one (ARNO) compound and its crystal structure was determined by X-ray diffraction. This compound belongs to the centrosymmetric space group $P\bar{1}$. From the crystal

Table 4 Torsion angles involving non H-atoms by X-ray and theoretical calculations (e.s.d.'s are given in parenthesis)

Torsion angles (°)	X-ray	HF			B3LYP		
		LANL2DZ	6-31G*	6-31+G**	LANL2DZ	6-31G*	6-31+G**
C6–C1–C2–C3	−1.3(5)	−0.2	−0.92	−0.88	0.02	−0.20	−0.12
C1–C2–C3–C4	0.4(5)	−0.05	−0.26	−0.26	0.02	−0.04	0.01
C1–C2–C3–N1	−179.3(3)	−179.9	−179.7	−179.7	−179.9	−179.9	−179.9
O1–N1–C3–C2	−18.1(4)	−0.09	−0.38	−0.53	0.02	0.05	0.08
O2–N1–C3–C2	161.5(3)	179.9	179.6	179.5	−179.99	−179.97	−179.9
O1–N1–C3–C4	162.2(3)	−179.96	−179.8	180.0	−179.98	−179.8	−179.9
O2–N1–C3–C4	−18.2(4)	0.02	0.18	0.00	0.01	0.17	0.12
C2–C3–C4–C5	0.4(5)	0.16	0.68	0.68	−0.03	0.16	0.07
N1–C3–C4–C5	−179.9(3)	−179.97	−179.9	−179.9	179.96	−179.98	−179.99
C3–C4–C5–C6	−0.3(5)	−0.01	0.07	0.03	0.01	−0.04	−0.05
C4–C5–C6–C1	−0.5(5)	−0.23	−1.21	−1.12	0.03	−0.19	−0.05
C4–C5–C6–C7	−179.8(3)	−179.95	179.9	−179.98	−179.93	−179.99	−179.89
C2–C1–C6–C5	1.3(5)	0.35	1.65	1.55	−0.04	0.31	0.14
C2–C1–C6–C7	−179.3(3)	−179.9	−179.4	−179.5	179.92	−179.88	179.99
C5–C6–C7–C8	21.0(5)	−4.77	−29.13	−28.14	0.17	−3.62	−1.95
C1–C6–C7–C8	159.7(3)	175.5	151.98	152.98	−179.79	176.58	178.21
C6–C7–C8–C9	−177.4(3)	−179.8	−178.7	−178.6	179.90	−179.96	−179.8
C6–C7–C8–S1	−3.6(5)	−0.32	−1.38	−1.24	−0.01	−0.51	−0.40
C10–S1–C8–C7	−170.7(3)	−179.8	−177.3	−177.5	179.76	−179.48	−179.5
C10–S1–C8–C9	3.8(2)	−0.29	0.23	0.07	−0.16	0.01	−0.02
C10–N2–C9–O3	178.2(3)	−178.95	−178.5	−178.7	−179.0	−178.34	−178.9
C11–N2–C9–O3	−3.7(4)	−5.95	−4.44	−4.74	−4.08	−3.57	−3.48
C10–N2–C9–C8	−0.4(3)	1.87	2.36	2.15	1.61	2.14	1.61
C11–N2–C9–C8	177.8(2)	174.9	176.4	176.1	176.5	176.90	177.0
C7–C8–C9–O3	−6.2(5)	−0.29	−2.72	−2.43	0.02	−1.07	−0.80
S1–C8–C9–O3	178.9(3)	−179.6	179.4	179.6	179.9	179.37	179.67
C7–C8–C9–N2	172.3(3)	178.9	176.4	176.7	179.4	178.43	178.70
S1–C8–C9–N2	−2.6(3)	−0.46	−1.41	−1.18	−0.70	−1.12	0.83
C9–N2–C10–S2	−176.4(2)	178.3	178.3	178.4	178.4	178.21	178.8
C11–N2–C10–S2	5.5(4)	5.46	4.42	4.64	3.58	3.59	3.48
C9–N2–C10–S1	3.2(3)	−2.07	−2.19	−2.10	−1.70	−2.12	−1.62
C11–N2–C10–S1	−174.91(19)	−174.9	−176.0	−175.8	−176.5	−176.74	−176.9
C8–S1–C10–N2	−4.0(2)	1.27	1.04	1.08	0.99	1.13	0.88
C8–S1–C10–S2	175.66(19)	−179.0	−179.4	−179.4	−179.1	−179.17	−179.47
C10–N2–C11–C12	−82.7(3)	−89.9	−91.40	−91.56	−87.3	−91.15	−91.84
C9–N2–C11–C12	99.2(3)	97.4	94.88	94.86	97.98	94.36	93.00
C10–N2–C11–C16	98.4(3)	90.8	89.57	89.47	93.61	90.01	89.32
C9–N2–C11–C16	−79.7(3)	−81.9	−84.1	−84.11	−81.1	−84.49	−85.84
C16–C11–C12–C13	−0.5(5)	−0.33	−0.33	−0.39	−0.29	−0.31	−0.41
N2–C11–C12–C13	−179.4(13)	−179.7	−179.3	−179.33	−179.4	−179.12	−179.2
C11–C12–C13–C14	−1.3(5)	0.13	0.13	0.16	0.18	0.15	0.15
C12–C13–C14–C15	1.2(5)	0.10	0.07	0.07	0.03	0.05	0.09
C13–C14–C15–C16	0.6(5)	−0.13	−0.09	−0.09	−0.13	−0.09	−0.08
C17–O4–C16–C15	−3.1(4)	1.95	2.55	1.68	−0.50	0.93	0.02
C17–O4–C16–C11	177.4(3)	−178.3	−177.6	−178.4	179.5	−179.11	−179.96
C14–C15–C16–O4	178.1(3)	179.7	179.7	179.79	−179.96	179.89	179.85
C14–C15–C16–C11	−2.4(4)	−0.06	−0.10	−0.12	0.02	−0.06	−0.17

Table 4 continued

Torsion angles (°)	X-ray	HF			B3LYP		
		LANL2DZ	6-31G*	6-31+G**	LANL2DZ	6-31G*	6-31+G**
C12–C11–C16–O4	−178.1(3)	−179.5	−179.5	−179.6	−179.8	−179.70	−179.60
N2–C11–C16–O4	0.8(4)	−0.15	−0.53	−0.60	−0.71	−0.86	−0.77
C12–C11–C16–C15	2.4(4)	0.29	0.3	0.36	0.19	0.26	0.42
N2–C11–C16–C15	178.7(2)	179.7	179.3	179.3	179.3	179.10	179.25
C16–O4–C17–C18	−176.1(3)	179.01	178.5	179.0	−179.8	179.18	179.92

Table 5 Geometry of the C–H⋯O and C–H⋯S hydrogen bonds in ARNO crystal by X-ray diffraction

D–H⋯A	D–H (Å)	H⋯A (Å)	D⋯A (Å)	D–H⋯A (°)
C2–H2⋯O1	0.93(3)	2.49(3)	2.761(5)	96.5(3)
C4–H4⋯O2	0.93(4)	2.45(2)	2.724(4)	96.9(3)
C5–H5⋯S1	0.93(3)	2.55(1)	3.198(3)	127.0(2)
C7–H7⋯O3	0.93(4)	2.61(2)	2.936(4)	101.1(2)
C4–H4⋯O3[i]	0.93(4)	2.93(3)	3.278(6)	103.4(3)
C7–H7⋯O3[ii]	0.93(4)	2.59(3)	3.267(4)	129.5(2)
C13–H13⋯O2[iii]	0.93(3)	2.80(3)	3.385(5)	121.9(3)
C14–H14⋯O2[iii]	0.93(4)	2.76(3)	3.373(5)	124.0(2)

Symmetry code: (i) x − 1, +y, +z; (ii) −x + 2, −y, −z; (iii) x + 2, +y + 1, +z

Fig. 6 Atom-by-atom superimposition of the structures calculated (*dashed line*) [A = HF, B = B3LYP] over the X-ray structure (*solid line*) for the title compound

structure, this compound seems to be potentially useful for non-linear optical applications. The results from X-ray diffraction were assessed by DFT and HF ab initio calculations using three different basis set LANL2DZ, 6-31G* and B3LYP/6-31+G**. The two ab initio computational methods gave very similar results, which are very close to those of X-ray data.

In a forthcoming paper, we will present a spectroscopic study and other theoretical calculations on the same compound in order to evaluate the main physico-chemical properties, such as the atomic charge distribution and the dipole moment, necessary to assess the efficiency and applicability of the title compound in the nonlinear optics field.

Fig. 4 View of the two H-bonds C7–H7⋯O3 in the ARNO crystal
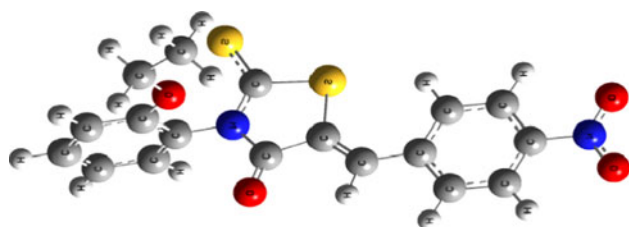
Fig. 5 Theoretical crystal structure of ARNO with B3LYP/6-31G(d) level

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