SPECTRAL AND SINGLE CRYSTAL X-RAY DIFFRACTION STUDIES OF 3-ACYL 2-(2'HYDROXY-5-NITRO PHENYL) BENZOTHIAZOLINE

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ABSTRACT:
The 3-acyl 2-(2' hydroxy-5-nitro phenyl)benzothiazoline (AHNPBT) is prepared by the condensation of 5-nitro salicylaldehyde with 2-aminothiophenol and the subsequent acylation of the same. The compound has been characterised by IR, ^{1}H, ^{13}C NMR, mass and single crystal XRD studies. The crystal structure of AHNPBT reveals the presence of intramolecular and intermolecular hydrogen bonding interactions. AHNPBT crystallises in the orthorhombic space group *Pna2(1)*. The XRD studies reveal that AHNPBT exists as '*R*' isomer.
Keyword: Benzothiazoline; X–ray diffraction; Mass spectrometry; Single crystal; Hydrogen bonding.

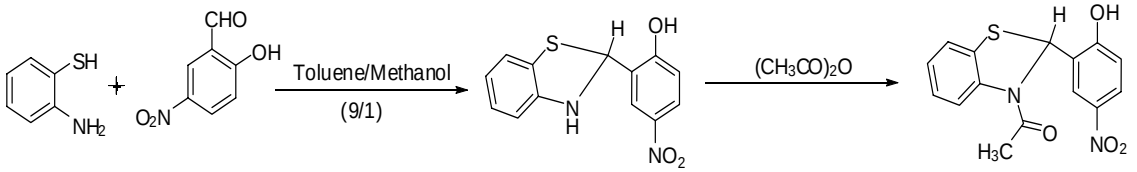
1. Introduction

Many studies on benzothiazolines were made as they contain two different hetero atoms linked by carbon in the ring. Benzothiazolines and other compounds containing $–NC_6H_4S-$ are reported to have biological activities[1]. A large number of benzothiazolines have been prepared by the reactions of aldehyde and ketones with 2-aminothiophenol[2-4]. Benzothiazolines derivatives constitute an important class of bidentate as well as multidentate ligands[5-7]. The use of these Lewis base functionalized ligands can be effective in increasing the coordination number of the central metal atom at the expense of the benzothiazoline ring to the corresponding schiff base derivatives, leading to the greater stability of the resulting compounds.

The aluminium (III) [8] and antimony (III) [9] derivatives of the benzothiazoline have been reported to have antifertility activity. 3-Acyl derivatives were disclosed by Bruer[10], Chioccara[11] and Horr[12] et al. The structural properties of 3-acyl 2-(2' hydroxy-5-nitro phenyl)benzothiazoline by IR, ^{1}H and ^{13}C NMR, mass spectral and single crystal XRD studies are described and discussed in the present paper.

2. Experimental

Starting materials are commercial reagents, 2-aminothiophenol from Alfa Aesar Lancaster and 5-nitro salicylaldehyde from Sigma Aldrich. The benzothiazoline ring was formed by condensation of 2-aminothiophenol with 5-nitro salicylaldehyde in equimolar ratio in a polar solvent. Acylation of the 3-amino group was achieved by using acetic anhydride[13]. The product 3-Acyl-2-(2'-hydroxy-5-nitro phenyl) benzothiazoline (AHNPBT) is recrystallized in warm methanol to yield yellow crystals m.p.= 215^{0}C. (Fig .1)



(AHNPBT)

Fig. 1. 3-Acyl-2-(2'-hydroxy-5-nitro phenyl) benzothiazoline(AHNPBT)

The MS data for AHNPBT was collected on Agilent Single Quad Mass Spectrometer. The IR Spectra (KBr) was recorded on a Bruker Optics Tensor-27 FTIR. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Biospin-400 MHz

Ultrashield Liquid NMR, with TMS as an internal standard.

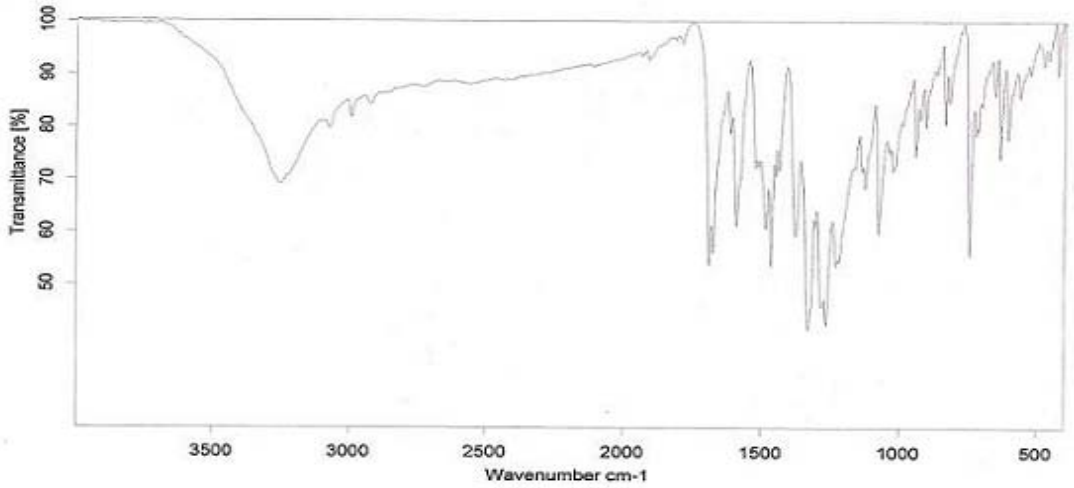
X-ray diffraction data for AHNPBT was collected on Bruker Smart APEX CCD diffractometer, area detector system equipped with a graphite monochromated Mo-Kα (λ= 0.71073 Å) radiation at 298 K. The single crystal was mounted in a Lindemann capillary and 2400 frames were recorded with scanning angle ω of 0.3°, each frame was exposed for 5 seconds with 0.5 mm collimated X-ray. The crystal and the detector were separated by distance of 60mm for high resolution. The solution and refinement procedures to the collected data were made by SAINTPLUS[14] software package. An empirical absorption correction was applied to the collected reflections with SADABS[15] The structure was solved with the SHELXS-97package and the refinement done against F^2 using SHELXL-97.[16] The crystal-packing was generated by Diamond 3.1. All non-hydrogen atoms were refined anisotropically and hydrogens were introduced on calculated positions and included in the refinement riding on their respective parent atoms.

3. Results and Discussion

3.1 Spectral Studies

3.1.1 IR Spectrum: The IR spectrum of AHNPBT (Fig.2) shows the presence of a broad band centred at 3253 cm^{-1} attributable to ν_{O-H} stretching vibrations. A sharp intense band at 1676-1690 cm^{-1} corresponds to the C=O stretching vibration. The other absorptions at 1466 cm^{-1}, 1377 cm^{-1}, 1267-1331 cm^{-1} corresponds to $\nu_{N=O}$ of nitro group, ν_{C-O} and $\nu_{C-N.}$

Fig.2 IR Spectrum of AHNPBT



3.1.2 Mass Spectrum: The mass spectrum displayed peak at m/z 317 corresponding to the $[M+1^+$ peak, along with other $[M+2^+$ and $[M+3^+$ peaks at m/z 318 and 319 respectively.

3.1.3 ^{1}H NMR: The ^{1}H NMR spectrum of AHNPBT in DMSO-d_6 shows a multiplet corresponding to aromatic protons at δ7 to 8.1ppm(m,7H). The peak corresponding to methine proton, is observed with the multiplet of aromatic protons. The CH_3 protons of acyl group are observed as singlet at δ2.17 ppm (s,3H, $COCH_3$). The peak at δ9.7 ppm is attributable to hydroxyl proton(s, 1H, OH).

3.1.4 ^{13}C NMR: ^{13}C NMR spectrum of AHNPBT exhibits a signal at δ169.53 ppm which has been assigned to C=O of benzothiazoline ring. Signal at δ160.25 ppm is assigned to aromatic carbon with OH substituent. The signals in the region δ116.53-140.34 corresponds to other various aromatic carbons. The signals at δ61.9 and δ23.6 ppm correspond to carbon atom of thiazole ring and methyl carbon respectively.

3.2 Structure Determination: The 3-Acyl-2-(2' hydroxy-5-nitro phenyl) benzothiazoline is a molecule with fifteen carbons, two nitrogens, four oxygens, one sulphur and twelve hydrogens, with a probability to have hydrogen bonds. The ORTEP[17] view of AHNPBT (C_{15} H_{12} N_2 O_4 S) with the labelling of non hydrogen atoms is shown in Fig.3. The crystal data and structure refinement parameters are listed in Table 1.

The cell parameters have been determined and refined from 8369 reflections. It crystallises in the orthorhombic symmetry, space group *Pna2(1)*,with parameters: a = 9.3875(7) Å, b = 23.9672(19) Å, c = 6.4646(5) Å, α = 90^o , β = 90^o , γ = 90^o. The crystal structure reveals the presence of four molecules per unit cell (Fig.4). Analyses of bond lengths and bond angles (Table 2) reveal that the two benzene rings are non

planar with small dihedral angle due to the slight tilting. The hydrogen atoms were placed geometrically[18,19](C-H=0.93 Å, N-H=0.84 Å, O-H=0.82-0.87 Å). The hydrogen bonding parameters at 298 K are given in Table 3. Topological analysis of hydrogen bonding showed the presence of both inter and intra molecular hydrogen bonds [20, 21] (Table.3). For the sake of clarity only intermolecular hydrogen bonding is depicted in Fig.5. Careful analysis of the structure reveals that one molecule of AHNPBT is associated with two adjacent molecules of it through intermolecular hydrogen bonding by strong O3–H3A···O1#1 interactions with H···O bond distance of 2.05 Å and O3–H3A···O2#1, O3–H3A···N1#1, C7–H7···O4#2, C15–H15A···O4#2 interactions with H3A···O2, H3A···N1, H7···O4 and H15A···O4 bond distances of 2.49, 2.60, 2.44 and 2.50 Å respectively. A comparison of bond lengths of intermolecular hydrogen bonds predicts the order of hydrogen bond strengths as; O—H···O > C—H···O > O—H···N. The arrangement of S1, C1 and N2 atoms at C7 chiral centre reveals the existence of AHNPBT as an *R* isomer.

Fig.3. X-Ray crystal structure of AHNPBT with ellipsoids at 50% probability for non-H atoms

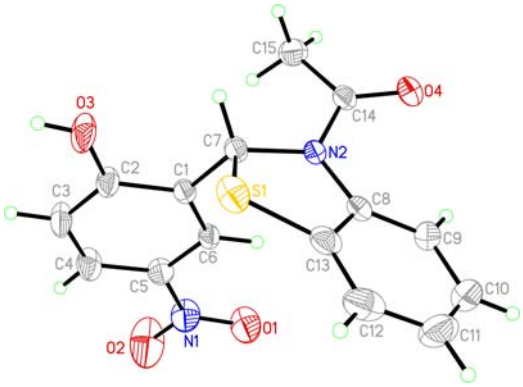


Fig. 4. Unit cell of AHNPBT with atom labelling.

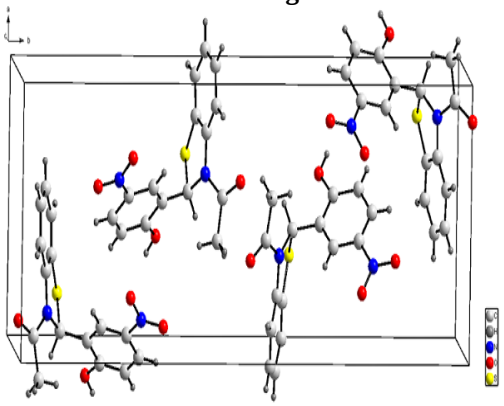


Table 1. Single Crystal X-Ray diffraction data and structure refinement for 3-acyl 2-(2'hydroxy-5-nitro phenyl) benzothiazoline at 298 K

CCDC	782420
Identification code	epr10
Empirical formula	$C_{15}H_{12}N_2O_4S$
Formula weight	316.33
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pna2(1)
Unit cell dimensions	a = 9.3875(7) Å a= 90°. b = 23.9672(19) Å b= 90°. c = 6.4646(5) Å g = 90°.
Volume	1454.48(19) $Å^3$
Z	4
Density (calculated)	1.445 Mg/m^3
Absorption coefficient	0.242 mm^{-1}
F(000)	656
Crystal size	0.42 x 0.28 x 0.22 mm^3
Theta range for data collection	1.70 to 25.99°.
Index ranges	-11<=h<=11, -29<=k<=29, -7<=l<=7
Reflections collected	12662
Independent reflections	2838 [R(int) = 0.0267
Completeness to theta = 25.99°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9486 and 0.9051
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2838 / 1 / 201
Goodness-of-fit on F^2	1.105
Final R indices [I>2sigma(I)]	R1 = 0.0388, wR2 = 0.0991
R indices (all data)	R1 = 0.0409, wR2 = 0.1006
Absolute structure parameter	0.01(10)
Largest diff. peak and hole	0.197 and -0.147 $e.Å^{-3}$

Fig. 5. Intermolecular Hydrogen bonding interactions shown in a unit cell with atom labelling with symmetry codes #1: -1/2+x,1/2-y,1+z; #2: -x,-y,1/2+z.

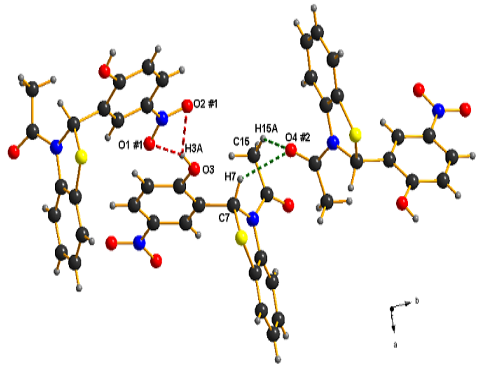


Table 2. Bond lengths [Å and angles [° for 3-acyl 2-(2'hydroxy-5-nitro phenyl) benzothiazoline.

C(1)-C(6)	1.365(3)	C(9)-C(10)	1.380(4)
C(1)-C(2)	1.406(3)	C(9)-H(9)	0.9300
C(1)-C(7)	1.510(3)	C(10)-C(11)	1.367(5)
C(2)-O(3)	1.343(3)	C(10)-H(10)	0.9300
C(2)-C(3)	1.384(3)	C(11)-C(12)	1.394(5)
C(3)-C(4)	1.366(4)	C(11)-H(11)	0.9300
C(3)-H(3)	0.9300	C(12)-C(13)	1.388(4)
C(4)-C(5)	1.380(3)	C(12)-H(12)	0.9300
C(4)-H(4)	0.9300	C(13)-S(1)	1.756(3)
C(5)-C(6)	1.390(3)	C(14)-O(4)	1.213(3)
C(5)-N(1)	1.445(3)	C(14)-N(2)	1.388(3)
C(6)-H(6)	0.9300	C(14)-C(15)	1.494(3)
C(7)-N(2)	1.465(3)	C(15)-H(15A)	0.9600
C(7)-S(1)	1.841(2)	C(15)-H(15B)	0.9600
C(7)-H(7)	0.9800	C(15)-H(15C)	0.9600
C(8)-C(9)	1.379(4)	N(1)-O(2)	1.199(3)
C(8)-C(13)	1.382(4)	N(1)-O(1)	1.221(3)
C(8)-N(2)	1.414(3)	O(3)-H(3A)	0.8200

Bond Angles

C(6)-C(1)-C(2)	119.06(19)	C(10)-C(11)-H(11)	119.5
C(6)-C(1)-C(7)	123.77(17)	C(12)-C(11)-H(11)	119.5
C(2)-C(1)-C(7)	117.11(18)	C(13)-C(12)-C(11)	118.0(3)
O(3)-C(2)-C(3)	123.4(2)	C(13)-C(12)-H(12)	121.0
O(3)-C(2)-C(1)	115.70(19)	C(11)-C(12)-H(12)	121.0
C(3)-C(2)-C(1)	120.9(2)	C(8)-C(13)-C(12)	120.9(3)
C(4)-C(3)-C(2)	120.0(2)	C(8)-C(13)-S(1)	112.58(18)
C(4)-C(3)-H(3)	120.0	C(12)-C(13)-S(1)	126.5(2)
C(2)-C(3)-H(3)	120.0	O(4)-C(14)-N(2)	120.69(19)
C(3)-C(4)-C(5)	118.8(2)	O(4)-C(14)-C(15)	122.0(2)
C(3)-C(4)-H(4)	120.6	N(2)-C(14)-C(15)	117.23(18)
C(5)-C(4)-H(4)	120.6	C(14)-C(15)-H(15A)	109.5
C(4)-C(5)-C(6)	122.2(2)	C(14)-C(15)-H(15B)	109.5
C(4)-C(5)-N(1)	118.6(2)	H(15A)-C(15)-H(15B)	109.5
C(6)-C(5)-N(1)	119.2(2)	C(14)-C(15)-H(15C)	109.5
C(1)-C(6)-C(5)	119.01(19)	H(15A)-C(15)-H(15C)	109.5
C(1)-C(6)-H(6)	120.5	H(15B)-C(15)-H(15C)	109.5
C(5)-C(6)-H(6)	120.5	O(2)-N(1)-O(1)	121.7(2)
N(2)-C(7)-C(1)	114.25(17)	O(2)-N(1)-C(5)	119.9(2)
N(2)-C(7)-S(1)	105.24(14)	O(1)-N(1)-C(5)	118.3(2)
C(1)-C(7)-S(1)	109.43(14)	C(14)-N(2)-C(8)	123.43(17)
N(2)-C(7)-H(7)	109.3	C(14)-N(2)-C(7)	122.08(16)
C(1)-C(7)-H(7)	109.3	C(8)-N(2)-C(7)	113.12(18)
S(1)-C(7)-H(7)	109.3	C(2)-O(3)-H(3A)	109.5
C(9)-C(8)-C(13)	120.2(2)	C(13)-S(1)-C(7)	90.58(11)
C(9)-C(8)-N(2)	126.5(2)		
C(13)-C(8)-N(2)	113.3(2)		
C(8)-C(9)-C(10)	119.3(3)		
C(8)-C(9)-H(9)	120.3		
C(10)-C(9)-H(9)	120.3		
C(11)-C(10)-C(9)	120.7(3)		
C(11)-C(10)-H(10)	119.7		
C(9)-C(10)-H(10)	119.7		
C(10)-C(11)-C(12)	120.9(3)		

Table 3 Hydrogen bonding parameters (Å, deg) of AHNPBT

D–H···A	*d*(D–H)	*d*(H···A)	D(D···A)	∠DHA
Intermolecular				
O3–H3A···O1#1	0.82	2.05	2.809(3)	153
O3–H3A···O2#1	0.82	2.49	3.118(4)	135
O3–H3A···N1#1	0.82	2.60	3.352(3)	153
C7–H7···O4#2	0.98	2.44	3.196(2)	134
C15–H15A···O4 #2	0.96	2.50	3.243(3)	134
Intramolecular				
C6–H6···N2	0.93	2.57	2.891(3)	101
C9–H9···O4	0.93	2.40	2.852(3)	110

Symmetry transformations used to generate equivalent atoms: #1: -1/2+x,1/2-y,1+z; #2: -x,-y,1/2+z.

Conclusion

X- ray diffraction studies reveal that AHNPBT exists as an R isomer. The crystal system is orthorhombic and four molecules are present per unit cell. The single crystal X-ray diffraction analysis of hydrogen bonds indicated presence of both inter- and intra molecular hydrogen bonding.

Supplementary Method

Full crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, UK and copies can be obtained on request, by quoting the publication number and the deposition number.

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