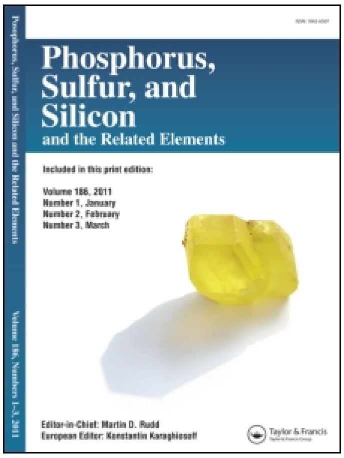

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Synthesis and Characterization of Some New Organic Derivatives of Organobismuth (III) with 2,3-Dihydro-2, 2-Disubstituted Benzothiazole

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Synthesis and Characterization of Some New Organic Derivatives of Organobismuth (III) with 2,3-Dihydro-2, 2-Disubstituted Benzothiazole

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2,3-dihydro-2,2-disubstituted benzothiazole reacts with triphenyl bismuth in a 1:1 molar ratio in dry benzene solution surprisingly to yield substituted derivatives of the type $Ph_2Bi[SC_6H_4N{=}CR(R')]$, *where* $R{=}R'{=}C_2H_5; R{=}CH_3$, *and* $R'{=}CH_3, C_6H_5, C_6H_4CH_3\text{-}4, C_6H_4Cl\text{-}4, R{=}H, R'{=}C_6H_5$. *To ensure completion of the reaction, the mixture was refluxed for ~8–10 hours. The solvent was removed under reduced pressure, which yielded dark brown viscous liquid and solids. The newly synthesized compounds are found to be soluble in common organic solvents (e.g.,* $CHCl_3$, CH_2Cl_2 *etc.) and have been characterized by spectroscopic methods (IR, NMR,* ^1H *, and* ^{13}C*) and physical chemical studies. On the above basis, a bidentate chelating structure has been suggested.*

Keywords 2, 3-Dihydro-2; 2-disubstituted benzothiazole triphenyl bismuth (III) derivatives

INTRODUCTION

In continuation of our earlier investigation on the reaction of triphenylantimony with dialkyl (alkylene) dithiophosphates,[1] a number of metal complexes of 2-aminocyclopentene-1-carbodithioicacid and its nitrogen/sulfur alkyl derivatives have been synthesized during the last few decades[2] as well as interesting patterns of chemical bonding modes have been observed with various metals with these ligands.[3–6]

Recently, auto-oxidation reactions of trithioarsenites[7] and oxidation reactions of trialkyl trithioarsenites[8] have been reported, reflecting interests in arsenic-sulfur compounds. No systematic studies have been carried out on organobismuth (III) with 2,3-dihydro-2,2′-disubstituted

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benzothiazole.[7–16] Triphenyl antimony (V) derivatives of disubstituted benzothiazoline also have been recently reported, which attracted the attention of the chemists.[17]

In view of the interesting results obtained in our laboratories on arsenic(III) and antimony(III) derivatives, which yielded addition products with 2,3-dihydro-2,2-disubstituted benzothiazole. It was considered of interest to study the behavior of the ligand with organobismuth (III) compounds. This article deals with the substitution reactions of organobismuth(III) with 2,3-dihydro- 2,2-disubstituted benzothiazole.

RESULTS AND DISCUSSION

Organobismuth (III) derivatives of 2, 3-dihydro-2,2-disubstituted benzothiazole have been synthesized by the reactions of triphenyl bismuth(III) with 2,3-dihydro-2,2-disubstituted benzothiazole in 1:1 molar ratio in benzene solution.

$$Ph_3Bi + [N(H)C_6H_4SC(R)R'] \rightarrow Ph_2Bi[SC_6H_4N = CR(R')] + C_6H_6 \quad (1)$$

$$(\text{Where } R{=}R'{=}C_2H_5; R{=}CH_3, R'{=}CH_3, C_6H_5, C_6H_4CH_3\text{-}4, C_6H_4Cl\text{-}4; R{=}H, R'{=}C_6H_5)$$

These substitution reactions were completed by refluxing the reaction mixture for 4–5 h in benzene. After completion of the reaction, the excess solvent was removed under reduced pressure. The nature of complexes was found to vary from viscous liquids to solids. These derivatives have been purified by benzene and n- hexane mixture. These compounds have been found to be soluble in common organic solvents.

IR SPECTRA

IR spectra of these derivatives have been recorded in the range 4000–200 cm^{-1}, which show the following characteristics changes (Table I):

1. Disappearance of absorption bands in the range 3340–3366 and ~1600–1650 cm^{-1}, which were observed and assigned in the spectra of ligands for the ν NH stretching and deformation vibration, respectively, indicating the participation of NH group in chemical bonding.
2. Appearance of a new absorption band in the region 1600–1620 cm^{-1}, which may be assigned to ν C=N stretching mode. The appearance of a new absorption band in the region 480–490 cm^{-1}, which may be assigned for ν Bi-N stretching absorption band. The absorption band observed in the region 375–430 cm^{-1}, which may be attributed to

TABLE I IR Spectral Data of 2,3-dihydro-2,2-disubstituted Benzothiazole and Its Organobismuth (III) Complexes (Cm^{-1})

	Ligand(a) and Corresponding Complexes(b)									
S. No.	R	R′	ν NH (Stretching)	νNH (Deformation) νN =C< str.	νC—H (Stretching)	νC—C (Stretching) (Skeltal Ring of Phenyl)	νC—N	νBi—N (Stretching)	νBi—S (Stretching)	νBi—C (Stretching)
1										
(a)	C_2H_5	C_2H_5	3375	1680	3070	1585	1070	—	—	—
(b)	C_2H_5	C_2H_5	—	1600	3070	1580	1030	480	375	380
2										
(a)	CH_3	CH_3	3385	1680	3070	1585	1020	—	—	—
(b)	CH_3	CH_3	—	1610	3070	1600	1020	485	410	385
3										
(a)	CH_3	C_6H_5	3360	1690	3070	1606	1020	—	—	—
(b)	CH_3	C_6H_5	—	1620	3070	1585	1030	480	410	385
4										
(a)	CH_3	$C_6H_5CH_3$-4	3360	1691	3030	1600	1020	—	—	—
(b)	CH_3	$C_6H_5CH_3$-4	—	1620	3070	1610	1020	485	428	384
5										
(a)	CH_3	C_6H_5Cl-4	3380	1680	3076	1590	1040	—	—	—
(b)	CH_3	C_6H_5Cl-4	—	1620	3060	1590	1030	485	430	385
6										
(a)	H	C_6H_5	3370	1680	3050	1600	1040	—	—	—
(b)	H	C_6H_5	—	1620	3070	1610	1030	490	410	380

ν Bi-S stretching absorption band. On the basis of the previously discussed observations, the formation of Bi-S chemical bond and bidentate nature of the ligand have been postulated.

^{1}H NMR

The ^{1}H NMR spectra of these derivatives have been recorded in $CDCl_3$ solutions, and the observed chemical shifts values have been summarized in Table II.

No PMR signal has been observed in the range δ 3.30–4.05 ppm, which was assigned to NH protons in the ligand. This disappearance of the NH proton signal in the PMR spectra of the product indicates the deprotonation of N-H proton and the formation of substituted derivatives.

TABLE II ^{1}H NMR Spectral Data of 2,3-dihydro-2,2-disubstituted Benzothiazole and Its Organobismuth (III) Complexes (δ ppm)

	Ligand (a) and Corresponding Complexes (b)					
S. N.	R	R′	NH (in bs)	R	R′	C_6H_4/C_6H_4 Bi + $SC_6H_4N{=}C$
1						
(a)	C_2H_5	C_2H_5	3.77	1.20(q) CH_2 0.96(t) CH_3	1.87(q) CH_2 1.48(t) CH_3	6.49–7.95(m)
(b)	C_2H_5	C_2H_5	—	1.20–1.56(q) CH_2 1.07 (t) CH_3	2.65(q) CH_2 2.39(t) CH_3	6.65–7.97(m)
2						
(a)	CH_3	CH_3	3.48	1.96(s)	2.50(s)	6.02–8.52(m)
(b)	CH_3	CH_3	—	1.36(s)	2.83(s)	7.20–7.90(m)
3						
(a)	CH_3	C_6H_5	3.70	2.59(s)	6.65–8.24(m)	6.65–8.24(m)
(b)	CH_3	C_6H_5	—	2.53(s)	7.13–8.90(m)	7.13–8.90(m)
4						
(a)	CH_3	$C_6H_5CH_3$-4	4.48	2.37(s)	2.56(s) CH_3 6.54–8.17(m) C_6H_4	6.59–8.17(m)
(b)	CH_3	$C_6H_5CH_3$-4	—	1.20(s)	2.40(s) CH_3 7.25–8.90(m) C_6H_5	7.25–8.90(m)
5						
(a)	CH_3	C_6H_5Cl-4	4.27	1.29(s)	6.34–7.67(m)	6.34–7.67(m)
(b)	CH_3	C_6H_5Cl-4	—	2.59(s)	7.33–8.06(m) C_6H_5	7.33–8.06(m)
6						
(a)	H	C_6H_5	3.62	*	6.43–7.44(m) C_6H_5	6.43–7.44(m)
(b)	H	C_6H_5	—	*	6.53–8.62(m) C_6H_5	6.53–8.62(m)

*= merge with phenyl protons, (s) → singlet, (t) → triplet, (q) → quartet, (m) → multiplet, (a)→ ligands [$NHC_6H_5SCR(R')$], (b)→ $Ph_2Bi[SC_6H_4N{=}CR(R')]$.

^{13}C NMR

The ^{13}C NMR spectra of these complexes have been recorded in $CDCl_3$ and DMSO solutions, and the significant changes in carbon-13 resonance signals have been observed in these derivatives, which are discussed in this section.

^{13}C NMR spectra of the ligands exhibited a carbon signal in the range δ141.50–145.53 ppm, which was assigned for >C-NH carbon. This signal for the C=N group carbon was observed in the corresponding bismuth derivatives at δ171.03–196.31 ppm. A downfield shift in the position of this carbon signal in the spectra of complexes reflects the deprotonation of the >C-NH group and rearrangement of benzothiazole ring during the complex formation. This also supports the involvement of the C=N group in the bonding.

The carbon-13 signals for the alkyl group attached to the nitrogen atom experienced a considerable downfield shift as compared to corresponding ligand. This also supports the involvement of the nitrogen atom in chemical bonding.

In the spectra of the compounds where R=R′, two sets of resonance signals have been observed for the carbon the of alkyl groups; for example, in the compounds where $R=R'=CH_3$, two sets of signals have been observed for the alkyl groups at δ 22.09 and δ 19.68 ppm.

The chemical shift values of δ' and σ R° were found to be negative in the range δ-3.45 to 4.79 and −0.15 to 0.21, respectively. The negative values of δ' and σR° indicated the electron release from the bismuth atom toward the phenyl ring through d_{Π}-p_{Π} conjugation and poor donor capability of the bismuth atom in the complexes (Table III).

On the basis of physico-chemical and spectroscopic evidences a bidentate chelating nature of the ligand has been proposed.

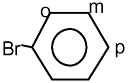
These results are in contrast to the result obtained in the case of organoaresenic (III) and –antimony (III) derivatives, reported in our earlier publication.[2] This may be due to the higher metallic character of the bismuth atom, which felicitates the ring opening. The products Ph_2BiL_2(where L = monofunctional tridentate ligands) are reported to have a tendency of disproportionation in solution according to the following equation

$$2\,Ph_2BiL \rightarrow Ph_3Bi + PhBiL_2 \tag{2}$$

EXPERIMENTAL

All reactions were carried out under anhydrous reaction conditions. The chemicals used were of reagent grade. Solvents used were dried by the

TABLE III ^{13}C NMR Spectral Data of 2,3-dihydro-2,2-disubstituted Benzothiazole and Its Organobismuth (III) complexes (δ ppm)

	Ligand (a) and Corresponding Complexes (b)								
S. N.	R	R′	NH—C< / N═C(R)R′	R	R′	C6H4		δ^1	σR^0
1									
(a)	C_2H_5	C_2H_5	141.50	14.88 (CH_3) 22.20 (CH_2)	14.00 (CH_3) 25.83 (CH_2)	139.50(C_1), 115.20(C_2): 126.60(C_3), 128.96(C_4): 117.10(C_5), 137.90(C_6)	—	—	—
(b)	C_2H_5	C_2H_5	172.42	19.90 (CH_3) 26.90 (CH_2)	16.90 (CH_3) 26.45 (CH_2)	156.79(C_1), 114.79(C_2): 128.84(C_3), 128.50(C_4): 125.89(C_5), 139.35(C_6)	149.71(δ), 116.08(o); 135.60(m), 131.07(p)	−4.53	−0.20
2									
(a)	CH_3	CH_3	145.59	26.03	30.97	136.54(C_1), 115.20(C_2): 126.60(C_3), 128.96(C_4): 117.10(C_5), 137.90(C_6)	—	—	—
(b)	CH_3	CH_3	172.39	22.09(CH_3)	19.68(CH_3)	156.6(C_1), 114.77(C_2): 128.19(C_3), 128.78(C_4): 125.82(C_5), 137.29(C_6)	138.15(δ), 116.08(o); 135.60(m), 131.07(p)	−4.53	−0.20
3									
(a)	CH_3	C_6H_5	145.53	30.03	132.77(s)114.90(o); 131.21(m) 128.99(p)	144.36(C_1), 121.45(C_2): 127.99(C_3), 129.37(C_4): 128.48(C_5), 139.10(C_6)	—	—	—
(b)	CH_3	C_6H_5	171.03	20.03	130.24(δ), 121.12(o); 127.44(m), 124.62(p)	156.67(C_1), 114.83(C_2): 129.30(C_3), 128.34(C_4): 125.84(C_5), 140.19(C_6)	144.77(δ), 116.13(o); 135.57(m), 131.11(p)	−4.46	−0.20

(*Continued on next page*)

TABLE III ^{13}C NMR Spectral Data of 2,3-dihydro-2,2-disubstituted Benzothiazole and Its Organobismuth (III) complexes (δ ppm) (*Continued*)

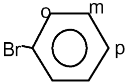
	Ligand (a) and Corresponding Complexes (b)								
S. N.	R	R′	NH—C< / N=C(R)R′	R	R′	C6H4		δ^1	σR^0
4									
(a)	CH_3	$C_6H_5CH_3$-4	145.03	30.72	35.68(CH_3); 136.35(δ), 125.15(o); 126.69(m), 117.83(p)	144.36(C_1), 121.45(C_2): 127.99(C_3), 129.37(C_4): 128.48(C_5), 139.10(C_6)	—	—	—
(b)	CH_3	$C_6H_5CH_3$-4	196.31	21.04	21.02(CH_3); 129.80(δ), 123.05(o); 129.10(m), 125.22(p)	156.61(C_1), 114.16(C_2): 128.21(C_3), 128.82(C_4): 125.35(C_5), 137.28(C_6)	141.20(δ), 116.14(o); 135.03(m), 130.24(p)	−4.79	−0.21
5									
(a)	CH_3	C_6H_5Cl-4	145.31	31.08	136.85(δ), 114.89(o); 128.87(m), 136.32(p)	134.47(C_1), 118.16(C_2): 128.07(C_3), 129.38(C_4): 128.60(C_5), 132.58(C_6)	—	—	—
(b)	CH_3	C_6H_5Cl-4	196.17	26.09	132.59(δ), 125.10(o); 127.38(m), 126.95(p)	154.96(C_1), 115.1(C_2): 128.48(C_3), 128.00(C_4): 125.42(C_5), 139.07(C_6)	140.27(δ), 121.41(o); 135.03(m), 131.58(p)	−3.47	−0.19
6									
(a)	H	C_6H_5	153.85	—	135.11(δ), 126.15(o); 133.31(m), 130.78(p)	153.05(C_1), 120.47(C_2): 134.70(C_3), 134.8(C_4): 128.52(C_5), 135.74(C_6)	—	—	—
(b)	H	C_6H_5	186.03	—	131.20(δ), 125.03(o); 129.12(m), 126.23(p)	155.96(C_1), 114.32(C_2): 128.32(C_3), 128.11(C_4): 1125.12(C_5), 140.11(C_6)	140.23(δ), 116.23(o); 135.03(m), 131.58(p)	−3.45	−0.15

TABLE IV Synthetic and Analytical Data of 2,3-dihydro-2,2-disubstituted Benzothiazole (Ligands)

	[NHC$_6$H$_4$SC(R)R′]		Reactant g (mM)		Mol. Formula	Found (Calcd.)	% Found (Calcd.)
S. No.	R	R′	Ketonealdehyde	2-aminothiopphenol	(%Yield)	S	N
1	C_2H_5	C_2H_5	6.88(79.87)	10.00(79.87)	$C_{11}H_{15}NS$ (90)	16.40(16.58)	7.14(7.27)
2	CH_3	CH_3	4.63(79.87)	10.00(79.87)	$C_9H_{11}NS$ (95)	16.64(16.40)	8.30(8.47)
3	CH_3	C_6H_5	9.59(79.87)	10.00(79.87)	$C_{14}H_{13}NS$ (80)	14.43(14.10)	6.01(6.16)
4	CH_3	$C_6H_4CH_3$—b	10.71(79.87)	10.00(79.87)	$C_{15}H_{15}NS$ (80)	13.43(13.28)	5.76(5.80)
5	CH_3	C_6H_4Cl—b	12.34(79.87)	10.00(79.87)	$C_{14}H_{12}NSC$ (85)	12.38(12.24)	5.23(5.34)
6	H	C_6H_5	8.47(79.87)	10.00(79.87)	$C_{13}H_{11}NS$ (85)	15.18(15.00)	6.43(6.56)

*After recrystallization

TABLE V Synthetic and Analytical Data of Diphenylbismuth(III) Derivatives of 2,3-dihydro-2,2-disubstituted Benzothiazole

	$Ph_2bBi[SC_6H_4\ N{=}C(R)R']$							Analysis/Found (Calcd.) (in %Age)		
S. No.	R	R′	M.P.	Nature	Reactant g (mM) ligand	Ph_3Bi	Mol. Formula (% Yield)	Bi	S Found	N Found
1	C_2H_5	C_2H_5	165	Yellowbrown	0.48(2.49)	1.10(2.49)	$C_{23}H_{24}SNBi$ (95)	37.60 (37.66)	5.67 (5.77)	2.14 (2.52)
2	CH_3	CH_3	180	Yellow	0.35(2.11)	0.93(2.11)	$C_{21}H_{20}SNBi$ (95)	38.95 (39.32)	6.01 (6.03)	2.53 (2.63)
3	CH_3	C_6H_5	181	Brown	0.53(2.33)	1.03(2.33)	$C_{26}H_{22}SNBi$ (97)	34.98 (35.45)	5.49 (5.43)	2.31 (2.37)
4	CH_3	$C_6H_4CH_3$-4	179	Brown	0.45(2.08)	0.92(2.08)	$C_{27}H_{24}SNBi$ (87)	34.18 (34.62)	5.36 (5.31)	2.28 (2.28)
5	CH_3	C_6H_4Cl-4	183	Light cream	0.57(2.18)	0.96(2.18)	$C_{26}H_{21}SNBi$ (85)	35.10 (35.51)	5.41 (5.44)	2.31 (2.38)
6	H	C_6H_5	186	Grey green	0.36(1.68)	0.74(1.68)	$C_{25}H_{20}SNBi$ (82)	36.18 (36.31)	5.16 (5.57)	2.34 (2.43)

*After recrystallization.

standard methods.[18] The ligands 2, 3–dihydro-2, 2-disubstituted benzothiazole were prepared by methods reported in the literature.[15,18] Elements Bi, S, and N were analyzed by the literature methods.[19] IR absorption spectra were recorded as a nujol mull on CSI pallets in the region 4000–200 cm^{-1}. The NMR spectra were recorded in $CDCl_3$ solutions, respectively, on bruckes 270 MHz. Brukes DPX 300 MHz and jeol Fx 90 Q(MHz) using TMS as an internal reference. All the derivatives were prepared by the same method. The preparative method of complexes and the addition complexes are described in the next section, and the results for the rest are summarized in (Table V).

Synthesis of Triphenylbismuth (III) Derivatives with 2,3-dihydro-2,2-disubstituted Benzothioazole

A weighed amount of triphenylbismuth (III) (1.01 g, 2.30 mM) was added to the benzene solution (30 mL) of 2,3-dihydro-2,2-dimethylbenzothioazole (0.38 g, 2.32 mM), and the reaction mixture was refluxed for 5 h. After completion of the reaction, the solvent was evaporated under reduced pressure. A yellowish–brown solid was obtained. All the other products were obtained by similar methods.

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