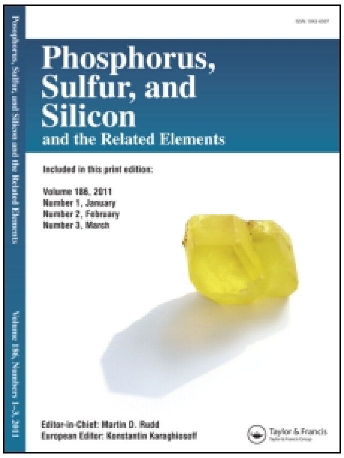

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SYNTHESIS AND CHARACTERIZATION OF SOME NEW ORGANIC DERIVATIVES OF ORGANOBISMUTH(III) WITH 2-AMINOCYCLOPENTENE 1-CARBODITHIOIC ACID AND THEIR N-/S-ALKYL DERIVATIVES

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SYNTHESIS AND CHARACTERIZATION OF SOME NEW ORGANIC DERIVATIVES OF ORGANOBISMUTH(III) WITH 2-AMINOCYCLOPENTENE 1-CARBODITHIOIC ACID AND THEIR N-/S-ALKYL DERIVATIVES

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Reactions of 2-aminocyclopentene-1-carbodithioic acid and its N-alkyl derivatives were carried out with Ph_3Bi *in 1:2 molar ratio in refluxing benzene yield the compounds having general formula* $[R(H)NC(CH_2)_3CC(S)S]_2BiPh$, *where* $R = -H(1)$, $-CH_3(2)$, $-C_2H_5(3)$, $-C_4H_9(4)$. *However, the reaction of* Ph_3Bi *and S-alkyl derivatives of 2-aminocyclopentene-1-carbodithioic acid in 1:1 as well as 1:2 molar ratio leads to the formation of addition product of the type* $[H(H)NC(CH_2)_3CC(S)SR]BiPh_3$, $R = -CH_3(5)$, $-CH_2N(C_2H_5)_2(6)$. *All of these compounds have been characterized on the basis of elemental analysis and spectral (IR and NMR) studies.*

Keywords: 1-Carbodithioic acid; 2-aminocyclopentane; -N/-S alkyl derivatives substitution product addition products; organobismuth; spectral studies

INTRODUCTION

The metal complexes of 2-aminocyclopentene-1-carbodithoic acid and their N-/S-alkyl derivatives have attracted considerable attention due to their different modes of bonding, which depend upon the nature of central metal atom.$^{1-6}$

Authors are thankful to University Grants Commission, New Delhi for financial support and Central Drug Research Institute, Lucknow for spectral studies (^{1}H and ^{13}C NMR).

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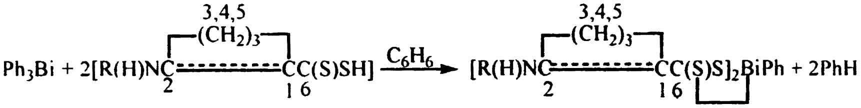
Earlier indium(III),[7] -antimony(III),[8,9] arsenic(III),[8] and -bismuth-(III),[10] complexes with 2-aminocyclopentene 1-carbodithioic acid and its N-/S-alkyl derivatives have been reported. A survey of literature reveals that no attempt has been made to prepare the analogous derivatives of organobismuth(III) with these ligands. In view of this, it has been considered worthwhile to prepare some new derivatives of these ligands with organobismuth(III) moiety. In the present communication we describe the synthesis and characterization of some organobismuth(III) complexes of 2-aminocyclopentene-1-carbodithioic acid and their N-/S-alkyl derivatives. The N-alkyl derivatives form substituted product, whereas S-alkyl leads to addition products.

RESULTS AND DISCUSSION

Since two different types of compounds, substitution and addition, have been obtained, these results are being presented under two different heads.

Substitution Products with 2-Aminocyclopentene-1-carbodithioc Acid and Its N-alkyl Derivatives

The interaction of Ph_3Bi with 2-aminocyclopentene-1-carbodithioic acid and its N-alkyl derivatives (methyl, ethyl, and butyl derivatives of 2-aminocyclopentene-1-carbodithioic acid) in 1:2 molar ratio leads to the formation of the corresponding substituted compounds in benzene solution.



$$Ph_3Bi + 2[R(H)N\underset{2}{C}\overset{\overset{3,4,5}{(CH_2)_3}}{\cdots\cdots\cdots}\underset{1\,6}{C}C(S)SH] \xrightarrow{C_6H_6} [R(H)N\underset{2}{C}\overset{\overset{3,4,5}{(CH_2)_3}}{\cdots\cdots\cdots}\underset{1\,6}{C}C(S)S]_2BiPh + 2PhH$$

where R = $-H(1)$, $-CH_3(2)$, $-C_2H_5(3)$, $-C_4H_9(4)$.

After removing the solvent under reduced pressure, these compounds are found to be yellow to dark brown solids. These compounds are found to be sparangly soluble in common organic solvents.

IR Spectra

A broad band observed in the IR spectra of the complexes in the region 3340–3350 cm^{-1} may be assigned to νNH stretching mode.[11] The band observed in the region 1615–1620 cm^{-1} may be assigned to νNH bending mode.[10] No significant shift has been observed in the position of $\nu NH(R)/NH_2$ mode in comparison to its position in parent ligands

(3344–3355 & 1615 cm^{-1}). This indicates that the NH(R)/NH_2 group is not involved in bonding. Disappearance of SH band[10] (~2550 cm^{-1}) in the spectra of phenylbismuth(III) complexes reflects the deprotonation of SH group. This has been further supported by the appearance of new bands in the region 375–418 and 380–385 cm^{-1}, which may be assigned to νBi-S[12] and νBi-C[12] stretching modes, respectively.

The strong bands observed in the spectra of the complexes of 2-aminocyclopentene-1-carbodithioic acid and its N-alkyl derivatives in the range 1615–1626, 1470–1476, 1340–1380, and 1270–1295 cm^{-1} may be assigned to a combination of νNH + C=C νCH_2 + C=C, νC=N + C=S, modes and mixing of νC=S + C=N modes, respectively.[10]

A single band for ν assym CSS mode[13–14] was observed at 870 cm^{-1} in the spectra of ligands. The appearance of single band in the region of 820–840 cm^{-1} in the spectra of their phenylbismuth(III) complexes indicates the symmetrical nature of C(S)S groups. This may be due to the involvement of both the sulphur atoms of dithiocarboxylate group in bonding. This shows the bidentate nature of the ligand involving the C(S)S group in bonding.

The bands due to the aromatic ring appeared at their usual positions.[9]

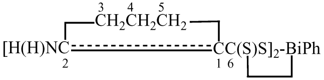
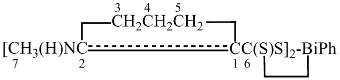
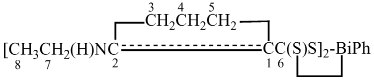
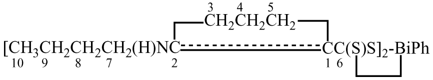
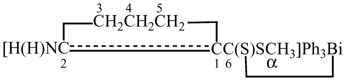
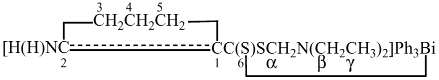
^{1}H NMR Spectra

The ^{1}H NMR spectra of the ligands exhibit a broad signal in the region δ 2.13–4.86 ppm, which is assigned to SH proton. This signal is found to be absent in the spectra of the corresponding phenylbismuth(III) metal complexes (Table I, compounds **1–4**). This shows the deprotonation of SH group and the bonding of the bismuth atom with the ligand through sulphur atom.

The two broad signals at δ 11.20 and δ 9.00 ppm observed in the ^{1}H NMR spectra of 2-aminocyclopentene-1-carbodithioic acid in dimethylsulfoxide (DMSO)-d_6 solution are being assigned to the free and hydrogen-bonded N—H protons. In the complexes, hydrogen-bonded NH proton appears between δ 9.20 and 10.42 ppm. The position of the signal at δ 9.00 ppm remains unaltered, whereas the signal at δ 11.20 ppm in ligands shows an upfield shift in its position. This shift may be due to the breaking of hydrogen bonding in free ligand on complexation. However, the existence of two signals for the —NH_2 protons, even on complexation, indicates the probability of some weak interaction between one of the –NH_2 protons and sulphur atom of the dithiocarboxylate group.

In compounds **2–4** the signal for NH (chelated) appears at δ 10.42 (bs), 10.23, and 10.39 ppm (in ligand at δ 11.21, 12.20, 12.65, and 12.55 ppm). In comparison to ligand, these show an upfield shift in their positions,

TABLE I ^{1}H NMR Spectral Data of Organobismuth(III) Derivatives of 2-Alkylaminocyclopentene-1-carbodithioic Acid and Its Esters (δ ppm) in $CDCl_3$ Solvent (Only Compound No. 1 in DMSO-d_6 Solvent)

S. no.	Compound	Assignments
1		2.20–2.75 (m) CH_2 (3 & 5), 1.61 (m) CH_2 (4), 10.42 (bs) NH (chelated), 9.20 (bs) NH free, 7.26–8.11 (m) Bi—C_6H_5
2		3.07–3.52 (m) CH_2 (3 & 5), 2.74–2.81 (m) CH_2 (4),10.42 (bs), NH (chelated), 2.36 (s) CH_3, 7.27–8.86 (m) Bi—C_6H_5
3		3.32–3.48 (m) CH_2 (3 & 5), 2.50–2.51 (m) CH_2 (4), 10.23 (bs) NH (chelated), 2.80 (q)-CH_2(7), 1.21 (t) —CH_3(8), 7.27–7.77 (m) Bi—C_6H_5
4		2.68–2.94 (m) CH_2 (3 & 5), 1.34–1.44 (m) CH_2 (4), 10.39 (bs) NH (chelated), 3.40 (q)-CH_2(C_7), 1.34–1.44 (m) —CH_2(C_8 & C_9) 0.30–0.91 (m)CH_3–(C_{10}), 7.10–7.76 (m) Bi—C_6H_5
5		2.24–3.56 (m) CH_2(3 & 5), 1.47–2.13 (m) CH_2 (4), 11.20 (bs) NH (cheleated), 5.95 (bs) (NH free), 7.24–8.00 (m) $(C_6H_5)_3$-Bi, 1.12(s) $CH_3(\alpha)$
6		2.40–3.40 (m) CH_2(3 & 5), 1.46–2.00 (m) CH_2 (4), 11.20 (bs) NH (chelated), 5.90 (bs) (NH free), 7.20–8.90 (m) $(C_6H_5)_3$-Bi, 4.00 (m) CH_2 (α), 3.00 (m) CH_2 (β), 0.90 (t) CH_3 (γ)

s, singlet; t, triplet; q, quartet; m, multiplet; bs, broad singlet.

which may be due to the breaking of hydrogen bonding in free ligand in complexation. However, existence of NH protons even on complexation indicates the nonparticipation of the amino group in bonding.

The alkyl protons attached to nitrogen atom of N-alkyl derivatives of 2-aminocyclopentene-1-carbodithioic acid (compounds **2–4**) do not show any appreciable shift in their position and appear on their expected positions at δ 0.99–3.40 ppm (in ligand at δ 0.95–3.56 ppm). This also indicates noninvolvement of NH(R) group.

The signals for $CH_2(4)$ and $CH_2(3\&5)$ were observed in the range of δ 1.34–2.81 ppm as quartet and multiplet at δ 2.20–3.52 ppm, respectively (in ligands at δ 1.66–2.28 and δ 2.53–3.18 as quartet and multiplet). No significant shift was observed in these signals in complexes in comparison to their position in free ligand.

Phenyl protons were observed in the region of δ 7.10–8.86 ppm as multiplet.

^{13}C NMR

^{13}C NMR chemical shift data observed for phenylbismuth(III) complexes of 2-alkylaminocarbodithioic acid and of their esters are summarized in Table II. The signal observed in the spectra of ligands in the region δ.191.50–197.30 ppm was earlier assigned to C(6) carbon atom.[9] This signal was observed in the region of δ 205.20–216.40 ppm in the spectra of corresponding complexes of organobismuth(III) in Table II (S. No. 1–4).

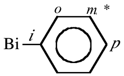
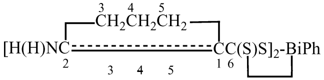
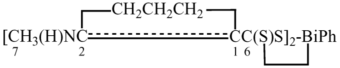
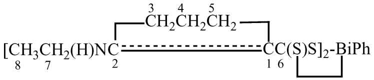
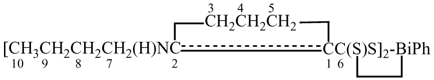
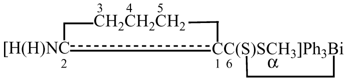
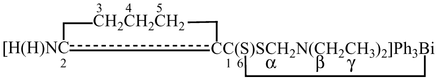
This remarkable downfield shift ($\sim$10–20 ppm) observed in the position of C(6) carbon atom signal in the spectra of the complexes in comparison to its position in ligands may be due to the involvement of both sulphur atoms in the bonding, and the deshielding of C(6) carbon atom on metallation of SH group and coordination through C=S group.

The carbon signals for C(1), C(2), C(3), C(4), and C(5) were observed at δ 115.40–116.80, δ 160–172.00, δ 33.20–33.80, δ 24.40–25.30, and δ 32.06–32.80 ppm, respectively, in complexes. No significant shift was observed in these signals in complexes in comparison to their position in free ligand.

The alkyl group carbon signals also do not show any shift in their positions and were observed in the range of δ 13.60–46.20 ppm (in ligands in the range of δ 13.50–45.20 ppm). The absence of any shift in the position of alkyl carbon attached to nitrogen atom rules out the noninvolvement of nitrogen atom in the bonding.

Phenyl group attached to bismuth atom gives a set of four ^{13}C NMR signals in the range of δ 142.20–125.38 ppm assigned to carbon atoms in the position *ipso*, *ortho*, *meta*, and *para* carbons.

TABLE II ^{13}C NMR Spectral Data of Organobismuth (III) Derivatives of 2-Alkylaminocyclopentene-1-carbodithioic Acid and Its Esters (δ ppm) in $CDCl_3$ Solvent

S. no.	Compound	Chemical shift values δ in ppm		δ'	σR°
1		116.80 C(1), 172.00 C(2), 33.80 C(3), 24.40 C(4), 32.80 C(5), 216.40 C(6)	142.20 C(i) 125.60 C(o) 140.10 C(m) 130.10 C(p)	−10.0	−0.45
2		115.80 C(1), 160.30 C(2), 33.20 C(3), 25.30 C(4), 32.06 C(5), 210.10 C(6), 22.30 CH_3(7)	138.30 C(i) 125.38 C(o) 137.50 C(m) 128.70 C(p)	−8.8	−0.39
3		115.60 C(1), 169.10 C(2), 33.20 C(3), 24.80 C(4), 32.50 C(5), 210.71 C(6), 39.20 CH_2 (7), 14.30 CH_3 (8)	141.00 C(i) 128.14 C(o) 139.00 C(m) 130.10 C(p)	−8.9	−0.40
4		115.40 C(1), 169.40 C(2), 33.23 C(3), 24.90 C(4), 32.30 C(5), 205.20 C(6), 46.20 CH_2(7), 31.60 CH_2 (8), 20.90 CH_2(9), 13.60 CH_3(10)	141.12 C(i) 128.27 C(o) 139.40 C(m) 130.48 C(p)	−9.0	0.40
5		111.75 C(1), 169.43 C(2), 35.35 C(3), 24.20 C(4), 42.16 C(5), 198.50 C(6), 15.93 C (α)	156.90 C(i) 127.39 C(o) 137.39 C(m) 128.79 C(p) 139.90 C(i) 128.92 C(o) 139.15 C(m) 128.79 C(p)	−11.15	−0.50
6		115.20 C(1), 169.84 C(2), 35.48 C(3), 24.42 C(4), 40.08 C(5), 205.09 C(6), 63.18 C (α), 47.90 C (β), 11.42 C (γ)	156.67 C(i) 128.52 C(o) 139.67 C(m) 129.47 C(p) 141.10 C(i) 128.81 C(o) 137.17 C(m) 126.89 C(p)	−10.28	−0.46

*Metal-phenyl proton values are given in the order *ipso. ortho. meta*, and *para*, respectively.

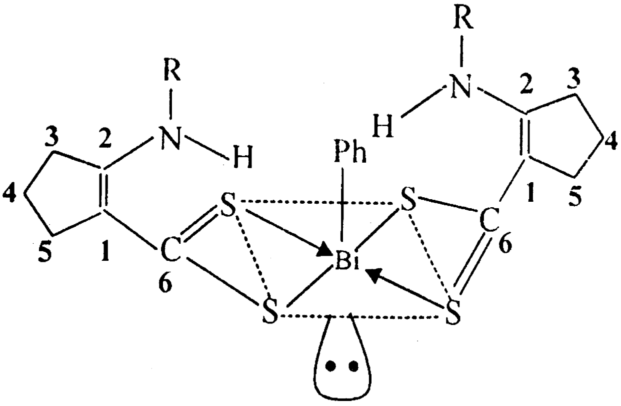
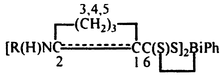


FIGURE 1 Structure of  $[R(H)N\underset{2}{C}\overset{\overset{3,4,5}{(CH_2)_3}}{=\!=\!=\!=\!=}\underset{1}{C}\underset{6}{C}(S)S]_2BiPh$, where R = H, $—CH_3$, $—C_2H_5$, and $—C_4H_9$.

The corrected chemical shift values[15,16] and Hammet Taft constant[17] were found to be in the region of δ −8.80–10.00 and δ−0.39 to −0.45 ppm for the of complexes of N-alkyl derivatives of 2-aminocyclopentene-1-carbodithioic acid (S. No. 1–4). The negative values of δ' reveal electron release from the metal atom towards phenyl ring through $d\pi$-$p\pi$ conjugation.

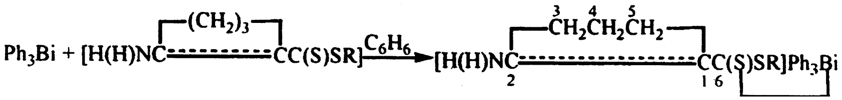
The IR and NMR studies of these compounds clearly show that the two ligand moieties bond with the phenylbismuth through bismuth sulphur bonds, and the nitrogen atom is not taking part in the bonding. The ligand behaves as monofunctional bidentate and induces a pseudo-octahedral geometry to the complex with four sulphur atoms occupying basal plane and phenyl group occupying position trans to the lone pair (Figure 1). A similar mode of bonding was reported in case of In(III),[7] As(III),[8] Sb(III),[8,9] and Bi(III).[10]

Although the definite structure may be confirmed on the basis of X-ray diffraction technique, unfortunately we could not get the good quality crystal the same.

Addition Products of S-Alkyl Ligands of 2-Aminocarbodithioic Acid

The interaction of Ph_3Bi with S-alkyl derivatives of 2-amino-cyclopentene-1-carbodithioic acid in 1:1 molar ratio leads to the formation of corresponding addition compounds in benzene solution

(Table III, S. No. 5–6).



$$Ph_3Bi + [H(H)N\overset{(CH_2)_3}{C{=}{=}{=}C}C(S)SR] \xrightarrow{C_6H_6} [H(H)N\overset{\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2}{\underset{2}{C}{=}{=}{=}\underset{1}{C}}\underset{6}{C}(S)SR]Ph_3Bi$$

where $R = \underset{\alpha}{-CH_3}(5), -\underset{\alpha}{CH_2}N(\underset{\beta}{CH_2}\underset{\gamma}{CH_3})_2(6)$.

After removing the excess solvent under reduced pressure, these compounds are found to be brownish yellow to dark maroon solid in appearance and are sparingly soluble in common organic solvents.

IR Spectra

A broad band is observed in the spectra of the compounds at 3350 cm^{-1}, and it was assigned to νNH_2 stretching mode.[11] The band observed at 1605 and 1600 cm^{-1} may be assigned to νNH bending mode.[10] No significant shift was observed in the position of νNH_2 absorption band compared to its position in the spectra of the ligands (~3400 cm^{-1}). This observation leads to the conclusion that amino group of ligand does not take part in bonding. The appearance of a new band in the region 405–410 cm^{-1} and 380 cm^{-1} may be assigned to νBi-S and vBi-C stretching mode[12]. This confirms the coordination of sulphur atom of the ligand with bismuth atom.

The strong bands have been observed in the spectra of the compounds of S-alkyl esters of 2-aminocyclopentene-1-carbodithioic acids in the range 1465–1470, 1260–1270, and 1150 cm^{-1}, and they may be assigned to the combination of νCH_2 + C=C, νC=N + C=S modes and νC=S + C=N modes respectively.[10]

The bands due to the aromatic ring appeared at their usual positions.[9]

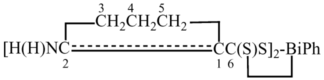
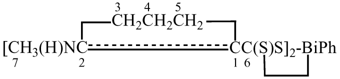
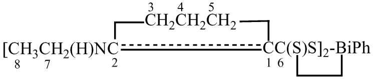
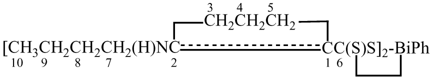
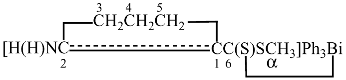
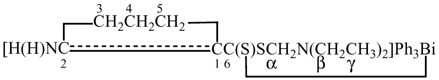
The appearance of two bands for ν assym CSS modes[10] in the range 940–970 cm^{-1} indicates the participation of only one sulphur atom of the C(S)SR group in bonding. This shows the monodentate nature of the ligand moiety in the complexes.

^{1}H NMR Spectra

^{1}H NMR spectra of triphenylbismuth(III) S-alkyl esters of 2-aminocyclopentene-1-carbodithioic acid adducts depict two broad signals at δ 6.00 ppm and 10.20 ppm for nonequivalent NH_2 protons. In the spectra of ligands, these signals are observed at δ 6.20 and 11.20 ppm. The absence of an appreciable shift in the position of these signals indicates noninvolvement of NH_2 group in bonding.[10]

An upfield shift has been observed in compound **5** in the position of SMe, a proton that was observed in the spectra of ligands at δ 2.12 ppm

TABLE III Synthetic and Analytical Data of Organobismuth(III) Derivatives of 2-Alkylaminocyclopentene-1-carbodithioic Acid and Its Esters

S. no.	Compound	Reactancts g (mM)		Molecular formula (% yield*)	S% found (calcd.)	N% found (calcd.)	Bi % found (calcd.)
		Ligand	Ph_3Bi				
1	 $[\mathrm{H(H)NC{=}CC(S)S}]_2\text{-BiPh}$ (ring $\mathrm{CH_2CH_2CH_2}$)	1.08 (6.76)	1.49 (3.38)	$C_{18}H_{21}S_4N_2Bi$ (90)	21.01 (21.28)	4.01 (4.64)	33.99 (34.68)
2	 $[\mathrm{CH_3(H)NC{=}CC(S)S}]_2\text{-BiPh}$ (ring $\mathrm{CH_2CH_2CH_2}$)	1.40 (8.03)	1.78 (4.01)	$C_{20}H_{25}S_4N_2Bi$ (85)	21.94 (20.79)	4.01 (4.44)	32.06 (33.13)
3	 $[\mathrm{CH_3CH_2(H)NC{=}CC(S)S}]_2\text{-BiPh}$ (ring $\mathrm{CH_2CH_2CH_2}$)	0.81 (4.36)	0.96 (2.18)	$C_{22}H_{29}S_4N_2Bi$ (80)	19.96 (19.46)	4.01 (4.25)	31.06 (31.72)
4	 $[\mathrm{CH_3CH_2CH_2CH_2(H)NC{=}CC(S)S}]_2\text{-BiPh}$ (ring $\mathrm{CH_2CH_2CH_2}$)	1.84 (6.81)	1.88 (3.40)	$C_{26}H_{37}S_4N_2Bi$ (85)	17.30 (17.90)	3.90 (3.92)	29.22 (29.23)
5	 $[\mathrm{H(H)NC{=}CC(S)SCH_3}]\mathrm{Ph_3Bi}$ (ring $\mathrm{CH_2CH_2CH_2}$)	0.08 (0.47)	0.20 (0.47)	$C_{25}H_{26}S_2NBi$ (95)	10.40 (10.45)	2.27 (2.28)	34.05 (34.06)
6	 $[\mathrm{H(H)NC{=}CC(S)SCH_2N(CH_2CH_3)_2}]\mathrm{Ph_3Bi}$ (ring $\mathrm{CH_2CH_2CH_2}$)	0.22 (0.90)	0.40 (0.90)	$C_{29}H_{35}S_2N_2Bi$ (80)	9.35 (9.36)	4.08 (4.09)	30.50 (30.51)

*Yield obtained after recrystallization.

and in the spectra of triphenylbismuth(III) complex at δ 1.12 ppm. This further supports that the coordination of the ligand moiety takes place with triphenylbismuth(III) through sulphur atom.

In the spectra of compounds **5** and **6**, a multiplet was observed in the range of δ 2.24–3.56 ppm (m) due to the CH_2 **3** and CH_2 **5** protons, and quintet was observed in the range of δ 1.46–2.13 ppm (m) for CH_2 **4** protons. In compound **5**, the singlet for CH_3 **7** was observed at δ 1.12 ppm and in compound **6**, and CH_2 (α), CH_2 (β), and CH_2 (γ) were observed at 4.00, 3.00, 0.90 ppm, respectively (Table I, S. No. 5–6).

Signals for phenyl groups attached to bismuth atom were observed in the region of δ 7.20–8.90 ppm in the spectra of compounds **5** and **6**.

^{13}C NMR Spectra

In the ^{13}C NMR spectra of addition compounds (Table II, S. No. 5–6), the resonances for C(6), C(2), and C(1) carbon signals have been observed at δ 198.50–205.09, 169.43–169.84, and 111.75–115.20 ppm, respectively. An upfilled shift was observed in the position of C(6) carbon atom in comparison to its position in free ligands (2–4 ppm). This favors the coordination between free sulphur atom of dithiocarboxylate group of ligand moiety with bismuth atom. Two sets of signals were observed for phenyl carbons attached with bismuth atom in compounds **5** and **6**, whereas only one set of signals are observed for compounds **1–4**. These signals are being assigned to *ipso*, *ortho*, *meta*, and *para* carbons. The appearance to two set of signals for *ipso*, *ortho*, *meta*, and *para* carbons in compounds **5** and **6** clearly indicates that the phenyl groups are not in the same environment and supports the formation of addition product of S-alkyl derivatives of 2-aminocyclopentene-1-carbodithioic acid with triphenylbismuth.

The corrected chemical shift values δ'[15,16] and Hammet Taft Constant σR°[17] for compounds **5** and **6** were found to be in the region of δ −10.28 to −11.15 and δ −0.46 to −0.50, respectively, in the triphenylbismuth(III) S-alkyl esters of 2-aminocyclopentene-1-carbodithioic acid addition complexes. These negative values indicate an electron release from bismuth atom towards phenyl ring through $d\pi$-$p\pi$ conjugation and poor donor capability of bismuth atom in these compounds. Also, a perusal of IR and NMR spectral data clearly shows the monodentate nature of the ligand moiety in compounds **5** and **6**. These two complexes appear to have to follow distorted trigonal bipyramidal geometry with two phenyl groups occupying apical positions trans to one another, and the ligand moiety along with one phenyl group and the lone pair occupying trigonal basal plane. A similar mode of bonding was reported in case of In(III),[7] As(III),[8] Sb(III),[8,9] and Bi(III).[10]

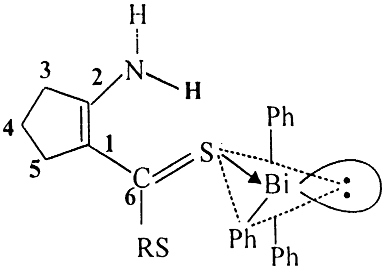
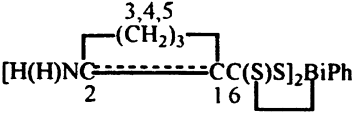


FIGURE 2 Structure of $[H(H)N\overset{\overbrace{\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2}}{\underset{2}{C}{=\!=\!=}\underset{1}{C}}\underset{6}{C}(S)SR]Ph_3Bi$, where R = $\underset{\alpha}{-CH_3}$ (5), $-\underset{\alpha}{CH_2}N(\underset{\beta}{CH_2}\underset{\gamma}{CH_3})_2$ (6).

EXPERIMENTAL

Precautions were taken to exclude moisture throughout the experiment. All the chemicals used were of reagent grade and were purified before use. The ligands[18] and triphenylbismuth[19] were synthesized by the literature method. Bismuth was estimated by literature method.[20] Nitrogen and sulphur was determined[20] by Kjeldhal's[20] and Massenger's methods,[20] respectively. IR spectra were recorded as nujolmull or CSI pallets on a Perkin-Elmer-577 and Nicolet DX-FTIR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions using tetramethylsilane (TMS) as an internal reference on a JEOL FX-90Q or Bruker DPX-300 MHz NMR spectrometer.

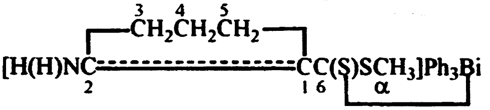
Synthesis of Phenylbismuth(III) 2-Aminocyclopentene-1-carbodithioic Acid and Its N-alkyl Derivatives: Synthesis of



$$[H(H)N\overset{\overbrace{(CH_2)_3}^{3,4,5}}{\underset{2}{C}{=\!=\!=}\underset{1}{C}}\underset{6}{C}(S)S]_2BiPh$$

A benezene solution of triphenylbismuth(III) (1.49 g, 3.38 mM) in 20 ml benezene and 2-aminocyclopentene-1-carbodithoic acid (dissolved in 20 ml benzene) (1.08 g, 6.76 mM) was mixed and refluxed for ~4 h. After the completion of the reaction, the excess of solvent was removed under reduced pressure. The crude product was recrystallized from benzene/pet. ether (40–60°C) mixture, yielding brown solid compound (yield 90%). The compound on analysis was found to have Bi = 33.99, N = 4.01, and S = 21.01% calculated for $C_{18}H_{21}S_4N_2Bi$, Bi = 34.68, N = 4.64, and S = 21.28%.

Synthesis of 1:1 Adduct of Triphenybismuth(III) with S-Methyl Ester of 2-Aminocyclopentene-1-carbodithioic Acid: Synthesis of



$$[\mathrm{H(H)N\underset{2}{C}\overset{3\;\;4\;\;5}{(CH_2CH_2CH_2)}\underset{1\,6}{C}C(S)SCH_3]Ph_3Bi}\;(\alpha)$$

A benzene solution of triphenylbismuth(III) (0.20 g, 0.47 mM) was added to a benzene solution of calculated amount of $[H(H)NC(CH_2)_3(S)SCH_3]$ (0.08 g, 0.47 mM) in stiochiometric ratio. The reaction mixture was stirred for ~3 h at room temperature. On removing the excess solvent under reduced pressure a solid product was obtained, which was purified by precipitating from chloroform/n-hexane mixture. The compound on analysis was found to have Bi = 34.05%, N = 2.27%, and S = 10.40%, calc. for $C_{25}H_{26}NS_2Bi$, Bi = 34.06, N = 2.28%, and S = 10.45%.

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