ANTIMONY TRICHLORIDE MEDIATED TRIMERIZATION OF BENZOTHIAZOLE: CRYSTAL STRUCTURE OF 2,2-BIS[BENZOTHIAZOLYL]BENZOTHIAZOLE.

J. Vela-Becerra, P. Sharma*, A. Cabrera, C. Álvarez, A. Toscano and G. Penieres.
Instituto de Química, UNAM. Circuito Exterior, Coyoacan 04510 Mexico D. F. Mexico.
Tel/Fax: (52) 5622 4515 E-mail: pankajsh@servidor.unam.mx

Abstract

The reaction of three equivalents of antimony trichloride with 2-lithium benzothiazole leads to a trimeric, coupling product. This reaction is similar to those in which PCl_3 leads to heterocycle dimerization. The monomeric, molecular structure of the title compound was determined by X-ray crystallography. The crystal is monoclinic, a=14.681(1) Å, b=8.491(2) Å, c=15.966(6) Å, β=108.00(2)°; space group $P2_1/n$, Z=4 for $C_{21}H_{13}N_3S_3$, and $\rho_{calcd}=1.416$ g/cm^3.

Introduction

In continuation to our interest on new tertiary stibines containing heterocyclic aromatic rings (1, 2), the reaction of three equivalents of 2-lithiumbenzothiazole with antimony trichloride was tried. Surprisingly, a trimeric, coupling product (2,2-Bis[Benzothiazolyl]Benzothiazole), $C_{21}H_{13}N_3S_3$, was obtained after workup.

Only dimeric coupling products of benzothiazole and other heteroaromatic compounds have been obtained in a similar way by either using PCl_3 instead of $SbCl_3$ or by reaction of the corresponding heteroarylphosphine with aryl- or heteroaryllithium derivatives (3) . Nonetheless, a trimeric species is formed in the presence of $SbCl_3$. To best of our knowledge, this is the first example of trimerization of benzothiazole promoted by $SbCl_3$. Studies are in progress to generalize this procedure.

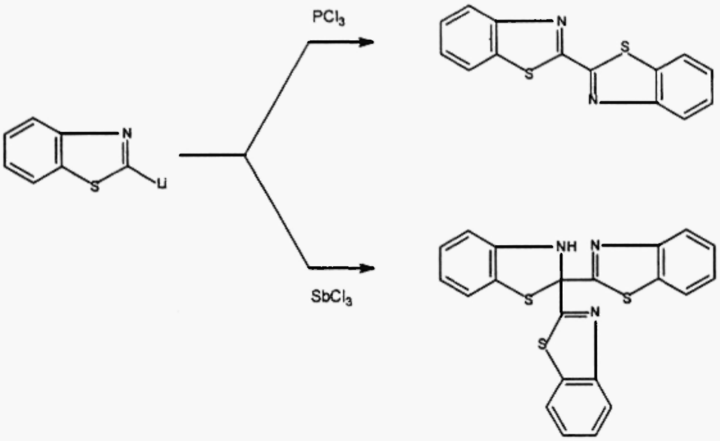
Experimental

2-Lithiumbenzothiazole was prepared as described in the literature (10). A solution of $SbCl_3$ (3.3 g, 14.7 mmol) in diethyl ether was added dropwise to a cold (-70 °C) solution of 2-lithiumbenzothiazole (44 mmol) in diethyl ether-hexane. The mixture was further stirred for 30 min and then allowed to reach ambient temperature. Treatment with cold water and extraction in hexane, followed by drying over anhydrous Na_2SO_4 afforded the product. Slow crystallization from dichloromethane-pentane solution yielded single crystals suitable for X-ray structure determination. Data for $C_{21}H_{13}N_3S_3$, pale orange crystals, mp 184-191 °C (dec.), 63% yield. Mass spectrum (EI MS) $[M]^+$ 403, $[M-\{C_7H_4NS\}]^+$ 269, $[M-\{C_{14}H_8N_2S_2\}]^+$ 135. The mass spectra were recorded in a Hewlett-Packard Model 5985 B GCMS mass spectrometer. X-Ray diffraction studies were done by the direct method on a Siemens P4/PC diffractometer, with the w-2θ scan type and using Mo-Kα radiation.

Results and Discussion

A hypervalent intermediate mechanism has been proposed by Uchida and Takaya (3) to account for ligand exchange and ligand coupling at phosphorus atom. The difference between dimeric and trimeric coupling products at phosphorus and antimony centers, respectively, might therefore arise from the increased coordinative ability of the latter due to its bigger size and its better Lewis acidic character (scheme 1).

Crystal structures for other benzothiazole derivatives (4-8) and their complexes (9) are known. Figure 1 shows the molecular structure of 2,2-Bis[BenzothiazolyI]Benzothiazole, and selected geometric parameters are shown in table 1.



Scheme 1. Coupling reaction between 2-lithiumbenzothiazole and PCl_3 or $SbCl_3$ leading to dimeric or trimenc species, respectively.

The bond distances are much as expected. The C-C bond lengths within the phenyl rings range from 1.367 to 1.408 Å with an average of 1.388 Å. For the two benzothiazolyl substituents, the $N3_x$-$C2_x$, $N3_x$-$C9_x$, $S1_x$-$C2_x$, and $S1_x$-$C8_x$ bond lengths, where x = a or b, are in well agreement with those reported in the literature (4-9).

The bond distances between the central carbon atom and its substituents are: C2-N3, 1.466 Å, C2-C2b, 1.513 Å, C2-C2a, 1.522 Å, and C2-S1, 1.855 Å. The bond distances observed for N3-C9, 1.412 Å, and S1-C8 1.779 Å, are longer than those reported for similar benzothiazole rings (6, 9).

Table 1 Selected geometric parameters (Å, °) for $C_{21}H_{13}N_3S_3$

C2-N3	1.466 (6)	S1a-C2a	1.748 (4)
S1-C2	1.855 (4)	C2a-N3a	1.291 (5)
C2-C2a	1.522 (6)	N3b-C9b	1.409 (6)
C2-C2b	1.513 (6)	S1b-C8b	1.737 (5)
N3-C2-S1	104.3 (3)	C9-N3-C2	112.9 (3)
C2b-C2-C2a	109.9 (3)	C8-S1-C2	90.6 (2)
N3-C2-C2a	112.2 (4)	C8a-S1a-C2a	88.9 (2)
C2b-C2-S1	111.6 (3)	C8b-S1b-C2b	88.2 (2)

The bond angles are unexceptional, with a slightly distorted tetrahedral geometry around the central C2 atom. The intra-ring N3-C2-S1 bond angle is 104.3; the C2b-C2-S1, C2b-C2-C2a, and N3-C2-C2a bond angles are 108.6 109.9, and 112.2°, respectively. The angles made at sulphur atoms are, as expected, lower at 88.2 and 88.9° within the two 2-benzothiazolyl substituents.

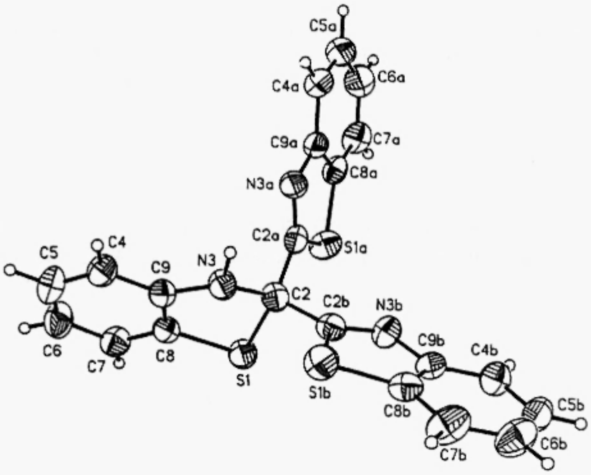


Figure 1. Structure and atom labelling for 2,2-Bis[Benzothiazolyl]Benzothiazole.

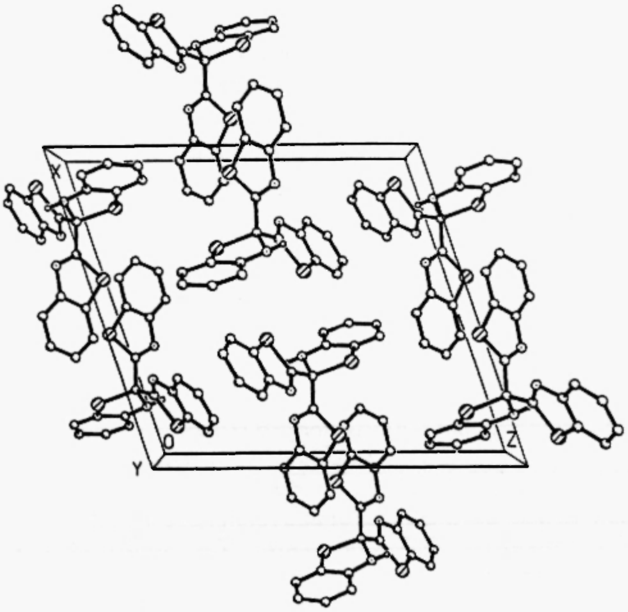


Figure 2. Unit cell packing of 2,2-Bis[benzothiazolyl]Benzothiazole, showing a monomeric nature without inter ring π-π and N-H produced interactions

In the three six-membered rings, angles range from 118.0 to 121.7°. In the partially reduced, main ring there is no planarity, with the C8-S1-C2, C9-C8-S1, C8-C9-N3, and C9-N3-C2 bond angles being, 90.6, 110.0, 113.6 and 112.9°, respectively.

The monoclinic unit cell is presented in figure 2, showing a $P2_1/n$ space group. The molecule is monomeric, with no observed interactions due to the N-H polar bond.

Conclusion

The coupling of benzothiazole leads to a trimeric product when its 2-lithium derivative is treated with $SbCl_3$. This contrasts to the dimeric species formed when PCl_3 is used. This behavior might stem from the higher coordination ability of antimony relative to phosphorus. Work is in progress in order to clarify the difference between the Vth group trihalides.

Acknowledgements

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Table 2 Crystal data and structure refinement for 2,2-Bis[Benzothiazolyl]Benzothiazole

Crystal data	
$C_{21}H_{13}N_3S_3$	Z = 4
M_r = 403.52	ρ_{calcd} = 1.416 g/cm^3
Monoclinic, $P2_1/n$	Mo Kα radiation
a = 14.681 (1) Å	θ = 1.65-24.99°
b = 8.491 (2) Å	μ = 0.402 mm^{-1}
c = 15.966 (6) Å	T = 293 (2) K
β = 108.00 (2)°	Orange plate, 0.40 x 0.287 x 0.20 mm
V = 1892.9(15) Å^3	
Data collection and refinement	
Siemens P4/PC diffractometer	Weighting squeme:
w-2θ scan type	calc $w=1/[\sigma^2(Fo^2) + (0.0632P)^2$
System solution: SHELXL-97	$+ 0.00P]$
3468 collected reflections	where $P = (Fo^2 + 2Fc^2)/3$
3329 independent reflections	Goodness-of-fit on F^2 = 1.019
3 standard reflections every 97	Final R indices $[I>2\sigma(I)]$:
reflections	R1 = 0.0589, wR2 = 0.1263
Refinement method:	Largest diff. peak and hole:
Full-matrix least squares on F^2	0.286 and –0.365 eÅ^{-3}

References

(1) P. Sharma and N.K. Jha, *J. Organomet. Chem.* 506, 19 (1996).
(2) J. Vela-Becerra, P. Sharma, A. Cabrera, C. Alvarez and S. Hernandez. (To be communicated).
(3) Y. Ukida and Y. Takaya, *Heterocycles.* 30 , 347 (1990).
(4) P. Sténson, *Acta Chem. Scand.* 24, 3729 (1970) and references therein.
(5) N.A. Mukmeneva, E.N. Cherezova, O.A. Cherkasova, V.K. Kardyrova, A.V. Il'yasov, *J. Org. Chem. USSR (Engl. Transl.)* 26, 2158 (1990).
(6) G. Trapani, A. Latrofa, A. Reho, M. Franco, G. Liso and F. Stasi, *J. Chem. Soc. Perkin Trans.1* 1505 (1991).
(7) P.C. Yates, C.J. McCall, and F.G. Stevens, *Tetrahedron*, 47, 6493 (1991).
(8) C.J. Matthews, W. Clegg, M.R.J. Elsegood, T.A. Leese, D. Thorp, P. Thornton and J.C. Lockhart, *J. Chem. Soc. Dalton Trans.* 1531 (1996).
(9) A. McCleverty, N.J. Morrison, N. Spencer, C.C. Ashworth, N.A. Bailey, M.R. Johnson, J.M.A. Smith, B.A. Tabbiner and C.R. Taylor, *J. Chem. Soc. Dalton Trans.* 1945 (1980).
(10)E.J. Corey and D.L. Boger, *Tetrahedron Lett.* 1, 5 (1978).

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