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A [1,2,3]Benzothiadiphospholo[3,2-*b*]-[1,2,3]benzothiadiphosphole as a Further Product from the Reaction of Aryl Methyl Thioethers with PCl_3 and $AlCl_3$

Graziano Baccolini* and Carmine Antonio Mosticchio

Dipartimento di Chimica Organica, Università, Viale Risorgimento 4, I-40136 Bologna, Italy

Elisabetta Mezzina

Dipartimento di Chimica Organica, Università, Via S. Donato 15, I-40127 Bologna, Italy

Corrado Rizzoli and Paolo Sgarabotto*

Istituto di Strutturistica Chimica, Università degli Studi di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. I-43100 Parma, Italy

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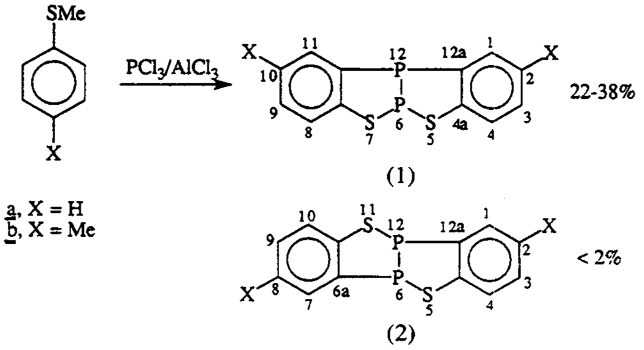
ABSTRACT

The title compound **2b** *was obtained as a minor product in the reaction between a thioanisole and* $PCl_3/AlCl_3$. *The crystal and molecular structure has been determined by single crystal X-ray techniques. The compound crystallizes in the space group* $P\ 2_1/c$, *with* $a = 9.004(2)$, $b = 13.416(3)$, $c = 11.662(3)$ Å, *and* $\beta = 93.1(1)°$. *The molecule adoptes a "butterfly" arrangement.*



SCHEME 1

INTRODUCTION

A few years ago we reported [1] the first example of a new fused heterocyclic system containing the P-P-S unit, namely, [1,2,3]benzothiadiphospholo[2,3-*b*][1,2,3]benzothiadiphosphole (**1**), starting from aryl(methyl) thioethers and $PCl_3/AlCl_3$ (Scheme 1)

In this facile synthesis, the breaking of the S–Me bond and the concomitant formation of two new C–P bonds, two P–S bonds, and one P–P bond are involved.

The X-ray crystal structure [1] of compound **1b** showed a *cis* configuration of the two phosphorus lone pairs and a "butterfly" arrangement of the entire molecule.

The separation method did not allow for work on a large scale. As these products could have some application as industrial additives, we tried to simplify the separation procedure in order to ob-

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*To whom correspondence should be addressed.

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tain larger amounts of **1**. In this article, we report an improved workup, and the separation and crystal structure determination of isomeric compounds **2**, which represent a new heterocyclic system.

RESULTS AND DISCUSSION

Treatment of the mixture obtained from the reaction of thioanisole with $PCl_3/AlCl_3$ with aqueous NaOH until neutrality has been achieved and fast extraction with methylene dichloride gives a crude product containing fused benzothiadiphospholes **1a,b** as the main products, together with small amounts of thiophenol or *p*-methyl thiophenol and unidentified products. Crystallization from CH_2Cl_2-light petroleum ether (40–60°C) gave compounds **1** in almost pure form.

GC-MS analysis of the mother liquor showed the presence of an isomer of **1b**, presumably compound **2b**, in small amount, together with the predominant **1b**. Subsequent crystallizations and separations of **1b** allowed enrichments of isomer **2b**, which was at last recovered in a 1:1 ratio with compounds **1b**. Flash chromatography of this mixture gave the new product **2b** in a pure form (in about 2% total yield). In a GC-MS analysis of the initial reaction mixture compound **2b** was not detected, and this fact explains its nonobservation in a previous report [1b].

Products **2** were characterized by spectroscopic and analytical data; in particular, their mass spectra presented the same fragmentation pattern as compound **1**.

The ^{31}P $\{^1H\}$ NMR spectra of compound **1** showed an AB spin system corresponding to the presence of nonequivalent phosphorus atoms [1,2], while the same spectra of **2** exhibited a single peak, indicating that the two phosphorus atoms are equivalent. For this reason, the structure reported in Scheme 1 was unambiguously assigned to the compounds **2**, excluding a possible *trans* isomer of **1**.

In the ^{13}C NMR spectrum of **2b**, C-1, C-2, C-4a, and C-12a signals were apparent triplets (X-part of AA′X spin systems), while the corresponding spectrum of **1b** showed doublets for the same carbon atoms except for the C-4a signal, which appeared as a singlet (X-part of AB′X spin systems).

An X-ray single crystal diffraction of compound **2b** was performed in order to confirm its structure. Figure 1 shows the molecule; Table 1 lists bond distances and angles.

The bond lengths, in line with the hybridization expected for the atoms involved, provide evidence that the skeleton of the double thiadiphospholic ring system is of the butterfly type, comparable to that found in **1b** [1a], as shown by the averaged values of S-P 2.100(1) and 2.129(2) Å, S-C 1.776(2) and 1.776(4) Å, and P-C 1.827(2) and 1.829(4) Å, in **2b** and in **1b** respectively. However, the small variations observed concerning the corresponding values of internal angles P-S-C 100.2(1) and 105.2(1)°, S-P-P 94.3(1) and 96.8(1)°, P-P-C 96.3(1) and 97.9(1)°, S-C-C 119.7(2) and 120.5(4)°, and P-C-C 118.9(1) and 120.0(3)° are indicative of a not equal conformation of the heterocyclic five-membered rings in **2b** and **1b**.

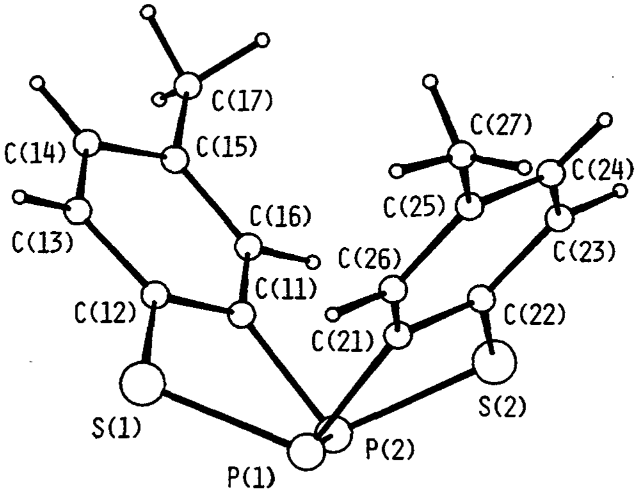

FIGURE 1 Perspective view of cis-2,8-dimethyl-[1,2,3]benzothiadiphospholo[3,2-b] [1,2,3]benzothiadiphosphole (**2b**).

The analysis that the two five-membered rings in **1b** are in different but nearly planar conformations, that containing S(2) [P(2) being out of the plane of the other four atoms by 0.091(3) Å] and that containing S(1) [S(1) being out of the plane of the other four atoms by −0.158(2) Å] with a pseudosymmetry plane through S(1). On the other hand, the two condensed rings in **2b** are in the same envelope conformation with a pseudosymmetry plane through P(1) for the ring containing S(1) and through P(2) for that containing S(2). The butterfly angles between the mean planes of the two condensed rings are 74.71(1) and 75.01(1)° in **1b** and **2b**, respectively.

EXPERIMENTAL

Methods and Materials

^1H, ^{13}C, and ^{31}P $\{^1H\}$ NMR spectra were recorded at 300.00, 75.50, and 120.75 MHz, respectively, with a Varian Gemini 300 instrument. ^1H and ^{13}C NMR chemical shifts are given in ppm from Me_4Si and ^{31}P NMR chemical shifts from H_3PO_4 85% (external standard) in $CDCl_3$ solutions. Mass spectra were recorded with a VG 7070 spectrometer or with an HP 59970 workstation formed by an HP-5890 gas chromatograph equipped with a methyl silicone capillary column and by an HP-5970 mass detector. Commercial aryl(methyl) thioethers were used without purification.

TABLE 1 Selected Bond Distances (Å), Angles (°), and Torsion Angles (°) for (2b) (Esd's are in parentheses)

S(1)-P(1)	2.116(2)		
S(1)-C(12)	1.781(3)		
S(2)-P(2)	2.096(1)		
S(2)-C(22)	1.771(3)		
P(1)-P(2)	2.219(2)	C(21)-C(22)	1.398(4)
P(1)-C(21)	1.829(3)		
P(2)-C(11)	1.824(3)		
C(11)-C(12)	1.400(3)		
P(1)-S(1)-C(12)	100.3(2)		
P(2)-S(2)-C(22)	100.1(2)		
S(1)-P(1)-C(21)	104.7(1)		
S(1)-P(1)-P(2)	93.9(1)		
P(2)-P(1)-C(21)	96.2(1)	P(1)-C(21)-C(26)	121.4(3)
S(2)-P(2)-P(1)	94.6(1)	P(1)-C(21)-C(22)	118.6(2)
P(1)-P(2)-C(11)	96.4(1)	C(22)-C(21)-C(26)	119.7(3)
S(2)-P(2)-C(11)	103.5(1)	S(2)-C(22)-C(21)	120.5(3)
P(2)-C(11)-C(16)	121.4(2)	C(21)-C(22)-C(23)	119.9(3)
P(2)-C(11)-C(12)	119.2(2)	S(2)-C(22)-C(23)	119.6(3)
C(12)-C(11)-C(16)	119.2(3)		
S(1)-C(12)-C(11)	119.4(2)		
C(11)-C(12)-C(13)	119.8(2)		
S(1)-C(12)-C(13)	120.7(2)		
S(1)-P(1)-P(2)-C(11)	28.4(2)	S(2)-P(2)-P(1)-C(21)	27.3(2)
P(1)-P(2)-C(11)-C(12)	−23.4(3)	P(2)-P(1)-C(21)-C(22)	−21.7(3)
P(2)-C(11)-C(12)-S(1)	3.4(4)	P(1)-C(21)-C(22)-S(2)	2.3(4)
C(11)-C(12)-S(1)-P(1)	19.9(3)	C(21)-C(22)-S(2)-P(2)	20.0(4)
C(12)-S(1)-P(1)-P(2)	−27.9(2)	C(22)-S(2)-P(2)-P(1)	−27.1(2)
S(1)-P(1)-P(2)-S(2)	132.6(2)	C(21)-P(1)-P(2)-C(11)	−76.8(2)

Reaction of Thioanisoles with $PCl_3/AlCl_3$

General Procedure. *p*-Tolyl(methyl)sulfide (0.2 mol) was added dropwise to a suspension of $AlCl_3$ (0.15 mol) in PCl_3 (0.6 mol) without a solvent and under a nitrogen atmosphere. The mixture was refluxed for 2 hours. TLC and GC-MS analyses revealed the presence of isomer **1b**. Treatment of the reaction mixture with aqueous NaOH solution until neutrality was achieved, extraction with CH_2Cl_2, and subsequent crystalizations of the crude product from CH_2Cl_2-Et_2O gave pure **1b**. The residue mother liquor contained products **2b** and **1b** in about a 1:1 ratio. Flash chromatography over silica gel column of this mixture with eluting by light petroleum ether (bp 40–60°C) gave compound **2b** (R_f 0.09). In a similar manner, compound **2a** was detected by GC-MS analysis, but it was not possible to isolate it in pure form.

Compound **1a** δ_{P-6} 85.1, δ_{P-12} 65.7, J_{PP} 212 Hz [2,3]. Compound **1b** δ_{P-6} 88.3, δ_{P-12} 65.4 J_{PP} 211 Hz [2,3]. Compound **2a** selected δ_C 125.2 (C-4), 129.3 (C-3), 130.6 (at C-1, J_{CP} 10.6 Hz); $^{31}P\{^1H\}$ NMR: δ = 56.6; m/z 277.9545, (M^+, calcd for $C_{12}H_8P_2S_2$, 277.9542) 215 (base-peak), 189, 139, 107, 63; (found: H, 2.9; C, 51.75; P, 22.35; S, 23.0; $C_{12}H_8P_2S_2$ requires: H, 2.9; C, 51.8; P, 22.26; S, 23.04%).

Compound (**2b**), δ_H 2.27 (s, 6H, Me), 6.90 (d, 2H, H-3 and H-9, $J_{HH'}$ 7.8 Hz), 7.10 (d, 2H, H-4 and H-10, $J_{HH'}$ 7.8 Hz), and 7.40 (bs, 2H, H-1 and H-7); δ_C 20.6 (Me), 125.4 (C-4), 130.5 (C-3), 131.2 (at C-1, J_{CP} 10.5 Hz), 136.1 (at C-2, J_{CP} 2.0 Hz), 136.6 (at C-12a, J_{CP} 14.8 Hz), and 142.9 (at C-4a, J_{CP} 2.8 Hz); $^{31}P\{^1H\}$ NMR: δ = 56.9; m/z 305.9857, (M^+, calcd for $C_{14}H_{12}P_2S_2$, 305.9855), 243 (base-peak), 211, 153, 152, 121, 63; (found: H, 4.00; C, 54.4; P, 20.26; S, 20.9; $C_{14}H_{12}P_2S_2$ requires: H, 3.95; C, 54.9; P, 20.25; S, 20.9%).

X-ray Crystal Structure Determination for **2b**

Crystals, obtained from petroleum ether solution, were yellow flattened prisms. Lattice constants were determined repeatedly, rectifying on the diffractometer the values of $(\theta, \chi, \phi)_{hkl}$ angles by 30 reflections to have the maximum of the peak when the angles were moving by 0.01° as a maximum. The compound (**2b**) $C_{14}H_{12}P_2S_2$ crystallizes in the space group $P\,2_1/c$, with a = 9.004(2), b = 13.416(3), c = 11.662(3) Å, and β = 93.1(1)°, V = 1406.7(6) Å^3, Z = 4, D_c = 1.45 g cm^{-3}; Cu-K_α radiation λ = 1.5418 Å, μ = 54.0 cm^{-1}, $F(000)$ = 632.

X-ray measurement was performed at T = 294 K on a Siemens AED single crystal diffractometer on line to an IBM PS/2 computer, in the range $3 < \theta < 70°$ using Ni-filtered Cu-K_α radiation. The diffraction angle θ for every reflection was determined on the basis of the orientation matrix, and

TABLE 2 Fractional Atomic Coordinates (× 10^4) and Equivalent Isotropic Thermal Parameters (× 10^4 Å^2) for Non-H atoms of **2b**, (Esd's are in parentheses)

	$U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (a_i \cdot a_j)$			
	x	y	z	U_{eq}
S(1)	−29(1)	−487(1)	1617(1)	534(2)
S(2)	4532(1)	571(1)	3125(1)	566(2)
P(1)	1815(1)	426(1)	1284(1)	499(2)
P(2)	2240(1)	847(1)	3112(1)	463(2)
C(11)	1492(2)	−289(2)	3717(2)	388(6)
C(12)	456(2)	−854(2)	3056(2)	421(6)
C(13)	−217(3)	−1671(2)	3538(2)	488(7)
C(14)	163(3)	−1944(2)	4661(2)	503(7)
C(15)	1213(3)	−1401(2)	5334(2)	450(7)
C(16)	1843(2)	−567(2)	4847(2)	417(7)
C(17)	1649(4)	−1704(3)	6543(3)	585(9)
C(21)	3379(3)	−439(2)	1220(2)	451(7)
C(22)	4572(3)	−342(2)	2030(2)	477(8)
C(23)	5845(3)	−921(2)	1932(3)	612(10)
C(24)	5890(3)	−1597(2)	1042(3)	653(10)
C(25)	4725(3)	−1719(2)	235(2)	598(9)
C(26)	3466(3)	−1120(2)	324(2)	534(8)
C(27)	4799(5)	−2471(3)	−718(4)	831(14)

the outline of the diffraction peaks was collected in the θ-2θ scanning mode using a scan width from $(\theta - 0.60)°$ to $(\theta + 0.60 + \Delta\lambda/\lambda tg\theta)°$. The intensities I_{hkl} were determined by analyzing the reflection profiles with the Lehmann and Larsen procedure [4]. A total of 2929 of reflections ($-10 < h < 10$, $0 < k < 16$, $0 < l < 14$), measured with 2179 having $I_{hkl} > 2\sigma(I_{hkl})$, $\sigma(I)$ based on statistical counting, were used in the refinement. One standard reflection, measured every 100 collected reflections to monitor crystal decomposition and instrumental linearity, showed no significant variation. The dimensions of the crystal roughly in the x, y, and z directions were 0.21, 0.26, and 0.38 mm, respectively. Corrections for Lorentz and polarization effects were performed, with no absorption corrections being applied.

The structure was solved by direct methods by use of SHELXS86 [5] and refined by SHELX76 [6], with cycles of full-matrix anisotropic least-squares (hydrogen atoms isotropically) up to $R = 0.034$ and $R_w = 0.040$; the weighting function was of the form $w = 0.484/(\sigma^2_{|F|} + 0.0027|F_0|^2)$. All the hydrogen atoms were located in the difference Fourier map. Positional parameters for nonhydrogen atoms with their standard deviations are given in Table 2.

Atomic scattering factors were taken from the *International Tables for X-ray Crystallography* [7]. All the calculations were carried out on the GOULD 6040 POWERNODE computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. di Parma. Bibliographic searches were carried out using the Cambridge Structural Database Files through the Servizio Italiano di Diffusione Dati Cristallografici, Parma.

Supplementary Material Available

Tables of H-atom coordinates, anisotropic thermal parameters, and observed and calculated structure factors are available. Ordering information is given on any current masthead page.

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