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A NEW ORGANODITHIOPHOSPHORIC DERIVATIVE; SYNTHESIS AND STRUCTURAL CHARACTERISATION OF BIS(DIPHENYLBORANO)DITHIOPHOSPHORIC $[(C_6H_5)_2BO]_2P(S)SH$

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ABSTRACT. A new organoderivative of dithiophosphoric acid $(RO)_2P(S)SH$ has been obtained by the reaction of phosphorus pentasulfide (P_4S_{10}) with diphenylborinic acid. IR, ^1H, ^{13}C, ^{11}B and ^{31}P NMR spectra of intermediates and the main product are discussed. Geometrical parameters (distances in Å, angles in degrees) for the minimum energy structure have been studied by ab initio RHF/3-21G* using Spartan version 5.0 installed on a SGI Octane.

INTRODUCTION

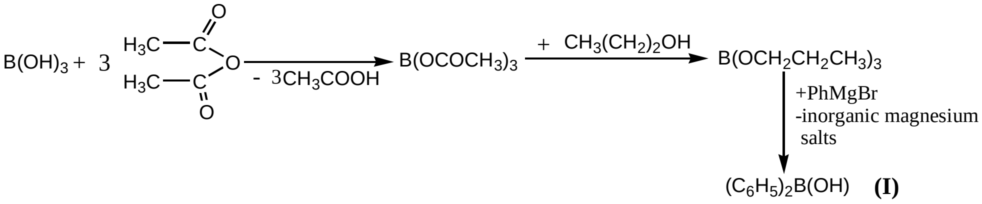
Diorganodithiophosphoric acids and their derivatives $(RO)_2P(S)SH$ $(R=(C_6H_5)_2B)$ have a very reach chemistry which has been reviewed several times in the last years [1-3]. These acids are obtained by the reaction of phosphorus pentasulfide with alcohols (**1**).

$$P_4S_{10} + 8\ ROH \longrightarrow 4\ (RO_2)P(S)SH + 4\ H_2S \quad \mathbf{(1)}$$

Boronic acids R_2BOH due to their polar OH group should react in a similar manner. In this paper, we investigate the reaction of diphenylborinic acid Ph_2BOH with phosphorus pentasulfide (***1***, $R=Ph_2B$-) which leads to bis(diphenylborano)ditiophosphoric acid. Such reactions afford an alternative route to new boron/phosphorus containing materials.

RESULTS AND DISCUSSION

Diphenylborinic acid has been synthesized following the general scheme ***(2)*** [4,5] with a few modifications (as described in the experimental part) which assure a better control of the product.



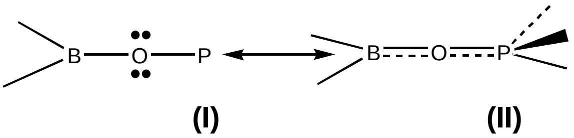
(**2**)

Reaction of diphenylborinic acid with phosphorus pentasulfide, P_4S_{10} (***1***, R=$(C_6H_5)_2B$), in 8:1 molar ration proceeds around at 36^{0}C in diethylether and the corresponding boron derivative of dithiophosphoric acid ***$[(C_6H_5)_2BO]_2P(S)SH$ (II)*** results in a good yield.

Infrared spectral data for the new compound are collected in table 1. Table 2 contains NMR chemical shifts for ^{1}H, ^{11}B, ^{13}C and ^{31}P.

The IR spectra for bis(diphenylborano)ditiophosphoric acid show the bands due to BO, SiO, PO, and PS group vibrations in their characteristic regions [6,7]. The BO band in the IR spectra of diphenyl borinic acid is situated at 1371 cm^{-1}compared to 1350-1380 cm^{-1}, the range found for $B(OR)_3$ and $RB(OR)_2$ [6].

The stretching frequency of B-O bond in ***(II)*** (1346 cm^{-1})is slightly than in diphenylboronic acid ***(I)***, (1371 cm^{-1}). This shift is due to the presence of phosphorus atom that decreases the electron density on the bridging oxygen

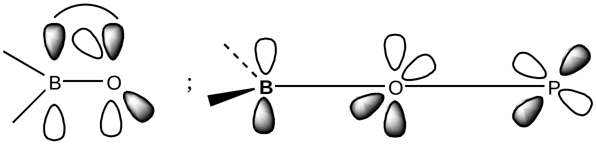


(**3**)

The characteristic bands for the PO stretching group in compound ***(II)*** are situated in the range 980-1022 cm^{-1}, in agreement with the literature data [3]. The P-O bond stretching in ***(II)*** appears at high values than in classical dithiophosphates $R_2P(S)SH$.

The P-S bonds give the symmetric and antisymetric stretching at 450 cm^{-1} and 600 cm^{-1} respectively [3].

A possible explication of the B-O stretching frequencies might be described by the simple valence scheme ***(3)***. The electron pairs of oxygen are delocalised both to boron and phosphorus, which means that to B-O bond order in (II) can be lower than in $(C_6H_5)_2BOH$ ***(4)***.



(**4**)

Table 1

Caracteristic vibration in infrared spectra of diphenylborinic, bis(diphenylborano)ditiophosphoric and bis(triphenylsilano)ditiophosphoric acids.

Compound	**ν(P-O) cm^{-1}**	**ν(B-O) cm^{-1}**	**ν(P-S) cm^{-1}**	**ν(S-H) cm^{-1}**
$[(C_6H_5)_2BOH$ (**I**)	-	1371	-	-
$[(C_6H_5)_2BO]_2P(S)SH$ (**II**)	1000-980	1346	600-555	2419

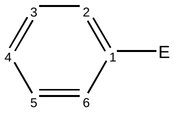
The ^1H, ^{13}C, ^{31}P, ^{11}B NMR studies has been effected. The results are shown in table 2.

Table 2

The chemical shifts (δ, ppm) in ^1H, ^{13}C, ^{31}P, ^{11}B NMR spectra, for diphenylborinic bis(diphenylborano)ditiophosphoric and bis(triphenylsilano)ditiophosphoric acids

COMPUS	**^{1}H aliphatic**	**^{1}H aromatic**	**^{13}C**	**^{31}P**	**^{11}B**
Ph_2BOH	2,2	7,37-7,39d (4) 7,44-7,49t (3,5) 7,61-7,63d (2,6)	138,2 (1) 128,2 (2,6) 136 (3,5) 129,4 (4)	-	29.45
$[Ph_2BO]_2P(=S)SH$	2,28	7,32-7,36m (4) 7,41-7,46m (3,5) 7,58-7,61dd (2,6)	141,65 (1) 127,65 (2,6) 129,2 (3,5) 127,75 (4)	130 s	29,80

See (**5**) for the atom numbering scheme.



(**5**)

E=B, Si

In the ^1H RMN spectra of $(C_6H_5)_2BOH$ the OH proton appears at δ(ppm) = 2.2(s), which reflects the greater acidity of this group than in alcohols (δ=3,15 ppm) [8] or in Me_2BOH (δ=6.65 ppm) [9].

In the ^1H NMR for bis(diphenylborano)ditiophosphoric acid appears one signal at 2,28 ppm for P(S)SH proton, comparable with the values in $(RO)_2P(S)SH$ [7], and the aromatic protons give a multiplet signal in the range 7.37-7.63 ppm (table 2).

The ^{13}C NMR spectra show four signals in normal range for phenyl group (table 2).

For the assignment of the protons attached to the phenyl groups we has used a 2D homocorrelation experiment COSY-45. This bidimensional experiment shows the coupling of the aromatic protons.

By ab initio RHF/3-21G* calculations using Spartan version 5.0 have been determined the geometrical parameters for the minimum energy structure of the bis(diphenylborano)ditiophosphoric acid. Some of the distances and angles for optimized geometry are comprised in table 3.

Table 3

Geometrical parameters (distances in Å, angles in degrees) for the minimum energy structure of bis(diphenylborano)ditiophosphoric acid

Distances (Å)		Angles and Torsiona Angles (degrees)	
B7-C11	1.546	P1-O5-B7	137.5
B7-C12	1.551	P1-O6-B8	136.98
B8-C9	1.547	C9-B8-C10	122.37
B8-C10	1.549	C11-B7-C12	121.97
B7-O5	1.361	O5-P1-S3	118.02
B8-O6	1.367	O5-P1-S2	106.71
P1-O5	1.585	O5-P1-O6	97.31
P1-O6	1.586	O6-P1-S3	120.94
P1-S2	2.106	O6-P1-S2	97.51
P1-S3	1.847	H-S2-P1	101.96
S2-H	1.336	B8-O6-P1-O5	72.98
		O6-P1-O5-B7	177.28

Since oxygen has lone pairs of electrons available for back donation into the formally empty p_z orbital of boron, the shortening of the bonds may be ascribed to partial double bond character, $p\pi$-$p\pi$ interactions. The values (table 3) obtained are very similarly whit that described in literature [10].

The obtained molecular model with numbering of atoms is shown in fig.1.

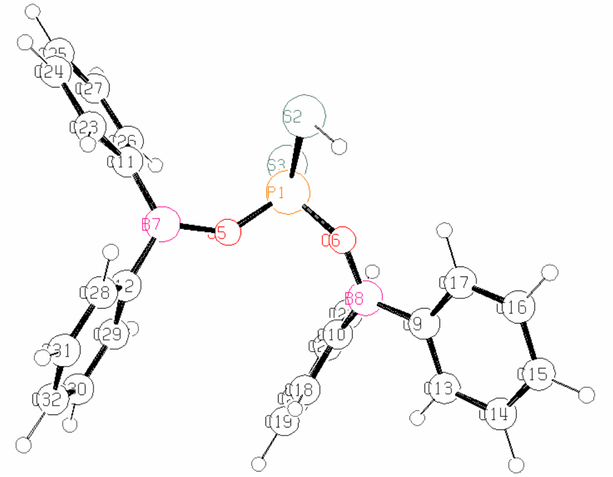


Fig. 1. Atomic numbering for the optimised structure of bis(diphenylborano)ditiophosphoric acid (depicted in ORTEP)

EXPERIMENTAL

Diphenylborinic acid has been synthesized [4] according to Scheme ***(2)****.* All the reactions with the modification given in [11] have been carried out under inert atmosphere using anhydrous solvents. ^{1}H, ^{13}C, ^{31}P, ^{11}B NMR spectra were recorded on Varian Unity Plus instrument, 500 MHz. Melting points were measured on a Leitz microscope.

Ab initio RHF/3-21G* molecular orbital calculation have been carried out by using Spartan version 5.0 [12] installed on a SGI Octane

1. Diphenyl borinic acid $(C_6H_5)_2B(OH)$ (I)

To a 2.25 mol (255 g) of acetic anhydride is added to 0.75 mol (46,5 g) of boric acid. The mixture was warmed gradual on the water bath until the temperature arrived at 60-65^{0}C (the temperature of reaction mixture is 47^{0}C). At this point the boric acid passes in solution, the reaction starts and the temperature increases to 100-120^{0}C. Tri-acetyl borate precipitates on cooling as a white solid (m.p=120-124^{0}C, η=82%).

2.5 moli of n-propanol (220 ml) (50% excess) is added to 0,46 mol (97 g) $B(OAc)_3$. After two hour of stirring at reflux temperature the excess of alcohol is removed and than tri-n-propyl borate distils at 175-176^{0}C (18 ml, η=42%). Because of the sensitivity to water the product is used immediately.

Dropwise addition of the two equivalents tri(n-propilborate) in diethylether to one equivalent of Grignard reagent (4.6 g magnesium and 20 ml bromobenzenein diethylether) [13] leads to the diphenylborinic acid (scheme 2) which distils at 175-190^{0}C, and which turns on staying into a white solid (m.p.=52-54^{0}C, η=88%) IR: 3250 (νOH), 1385 (νBO), 1410 (νBPh), 1600, 1472, 700-730 (νPh).

2. Bis(diphenylborano)ditiophosphoric acid $[(C_6H_5)_2BO]_2P(S)SH$ (II)

To a diethylether solution of diphenyl borinic acid (0.08, 14.56 g moli in 20 ml diethyl ether) 0.01 moli (0.44 g) P_4S_{10} was added. After stirring at reflux temperature for 4 hours, the solvent was removed in vacuum resulting white solid. This precipitate is redissolved in the minimum pentane/ether mixture and after cooling at O^{0}C, $[(C_6H_5)_2BO]_2P(S)SH$ as a white solid (m.p.=46-48^{0}C, η=87%).

IR: 3029 (νPh), 1460 (B-Ph); 1366-1340 (B-O), 1000-980(P-O), 600 (P=S), 555(P-S), 1550(ν_{CC}Ph) 750-720 (Ph)

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