



Note

Bis(*o*-trifluoromethylphenyl)dithiophosphinic methyl esterJohn R. Klaehn^{a,*}, Dean R. Peterman^a, Mason K. Harrup^a, Thomas A. Luther^a, Lee M. Daniels^b^a Idaho National Laboratory, P.O. Box 1625, Idaho Falls, ID 83415-2208, USA^b Rigaku Americas Corporation, 9009 New Trails Dr., The Woodlands, TX 77381, USA

ARTICLE INFO

Article history:

Received 13 September 2010

Received in revised form 22 December 2010

Accepted 9 January 2011

Available online 21 January 2011

Keywords:

Synthesis

Characterization

Dithiophosphinic acid

Dithiophosphinic ester

X-ray crystal determination

ABSTRACT

When bis(*o*-trifluoromethylphenyl)dithiophosphinic acid (**1**) is dissolved in methanol, crystals of bis(*o*-trifluoromethylphenyl)dithiophosphinic methyl ester (**2**) are formed. The structure of dithiophosphinic methyl ester (**2**) has been characterized *via* single-crystal X-ray diffraction and multinuclear NMR studies. Compound **2** is remarkable in that the dithiophosphinic (PS₂) core is preserved during this transformation. The transformation to **2** suggests that the *o*-trifluoromethylphenyl groups on phosphorus assist in retaining the PS₂ core, possibly by steric hindrance.

Published by Elsevier B.V.

1. Introduction

Dithiophosphinic acid compounds are well-known for their ability to selectively bind/chelate certain metal ions from aqueous solutions. The most cited dithiophosphinic acid is Cyanex 301[®] for the extraction and separation of many different metals [1–13]. Cyanex 301[®] is primarily used as an industrial metal extractant for the first row transitional elements [1–6]; however, it has been tested for the separation of actinides from lanthanides [7–13]. There are other dithiophosphinic acid derivatives that show complexation behavior with metals [14–22], where some exhibit selective extraction of actinides(III) over lanthanides(III) [18–22]. Recently, a report has shown that an aromatic dithiophosphinic acid, bis(*o*-trifluoromethylphenyl)dithiophosphinic acid, **1** (Fig. 1), is capable of extracting actinides(III) over lanthanides(III) with high selectivity [22]. Understanding how **1** maintains the phosphorus–sulfur core provide clues to producing better dithiophosphinic acid extractants in the future.

Aromatic dithiophosphinic acid derivatives can be prepared by several pathways: Higgins synthetic route [23], modified Kosolapoff reactions [24–31], or phosphorus–halide nucleophilic additions [22]. Compound **1** was synthesized by nucleophilic addition at phosphorus [22], and this route provides the capability to maintain substituent (ligand) regiochemistry. Compound **1** can be isolated in good yields and can be recrystallized in hot hexanes. From these crystals, the X-ray structure of **1** was determined. In this paper,

we describe the addition of a methyl to the structure of **1** after it has been recrystallized from methanol.

2. Results and discussion

From the synthetic method, compound **1** is isolated as the ammonium salt for long term storage; however, the ammonium salt can be easily converted into **1** by hydrochloric acid. Compound **1** has been recrystallized from tetrahydrofuran and hexanes previously without any observable changes in structure. The best solvent for recrystallization of **1** is from hexanes, and the isolated free acid gives light green crystals with little odor. Typically, tetrahydrofuran gives an opaque crystalline solid, not suitable for X-ray diffraction. However, prismatic crystals are formed from methanol when the solvent is slowly evaporated at room temperature. A few of these crystals were used for NMR spectroscopy, and a downfield shift was observed, relative to **1**, in the ³¹P NMR spectra as a singlet at 69.3 ppm. The acidic proton resonance for **1** was not seen in the ¹H NMR spectrum; however, a resonance corresponding to three protons was observed as a singlet at 2.15 ppm. In addition, the ¹³C NMR spectrum exhibited an additional singlet at 14.2 ppm. The remaining aromatic peaks did not show any significant shifts in the ¹H and ¹³C NMR spectra. Overall, the ¹H and ¹³C NMR spectra indicated that **1** changed from the original free acid to a substituted methyl group. The unexpected reactivity between the dithiophosphinic acid and methanol produces a new dithiophosphinic ester, **2** (Fig. 2).

The single crystal X-ray determination provided the structure of the new product, bis(*o*-trifluoromethylphenyl)dithiophosphinic

* Corresponding author. Fax: +1 208 526 8541.

E-mail address: john.klaehn@inl.gov (J.R. Klaehn).

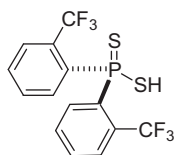


Fig. 1. Bis(*o*-trifluoromethylphenyl)dithiophosphinic acid, (**1**).

methyl ester (**2**; Fig. 3). The structure of **2** was remarkable, because the dithiophosphinic core (PS_2) remained unchanged. Another interesting feature of the structure, previously noted with **1**, is the relative orientation of the *o*-trifluoromethyl groups. Two fluorines, each from a different *o*-trifluoromethyl group, are in close proximity to the phosphorus at a distance of 2.923(3) Å (P1–F3) and 3.220(3) Å (P1–F5). These distances are close enough to suggest electronic interactions between the fluorines and the phosphorus center. However, the ^{31}P NMR of **2** (singlet) implies that this interaction is not observable in solution at room temperature. Crystal data and refinement parameters are given in Table 1, and the relevant bond angles and bond lengths are given in Tables 2 and 3. The phosphorus–sulfur bond distances in **2** are found to be 2.0929(8) Å (P1–S1) and 1.9483(8) Å (P1–S2), which is remarkably close to **1** [P1–S1 = 1.9566(8) Å and P1–S2 = 2.0885(8) Å]. However, the ammonium salt of **1** showed different phosphorus–sulfur bond distances [P1–S1 = 2.0018(5) Å and P1–S2 = 1.9942(5) Å], because the ionic charge is delocalized nearly equally between the sulfurs. This suggests that **2**'s methyl group on sulfur does not influence the phosphorus–sulfur bonds, when compared to **1**. The bond angles around the phosphorus are distorted [114.75(10)° for C–P–C and 113.58(4)° S=P–S] from the typical tetrahedral arrangement, and these angles differ with those in **1** [113.53(10)° for C–P–C and 113.05(4)° S=P–S] and in the ammonium salt of **1** [113.29(7)° for C–P–C and 113.20(2)° S=P–S]. The C–P–C bond angles show the greatest differences among the three compounds, and **2** shows the largest distortion around phosphorus (over 1°). This suggests that **2**'s methyl group on sulfur and the *o*-trifluoromethyl groups might contribute to the observed distortion through steric encumbrance, but electronic effects or crystal packing forces are possible, also.

Dithiophosphinic esters are not common in literature; however, the formation of the dithiophosphinic ester [R_2PS_2R' ($R, R' =$ alkyl, aromatic)] is obvious when the reactions involve reactive groups [32–35], like phosphorus–chloride with mercaptans or silicon–chloride with dithiophosphinic acid. These reactive compounds easily form dithiophosphinic ester products. However, the formation of the dithiophosphinic ester with organic alcohols has not been previously observed. Dithiophosphinic acids are not expected to react with organic alcohols, since many of the dithiophosphinic acids are recrystallized from these solvents. In this case, the reaction with methanol was unexpected, and isolating crystals of **2** was even more remarkable. The proposed transformation suggests that **1** is intimate with methanol (Scheme 1), and it will protonate methanol at the hydroxyl position. One of the sulfurs on **1** then displaces water on the protonated alcohol and bonds with the methyl group giving **2**. The described mechanism in Scheme 1 suggests a stepwise reaction (S_N1 type); however, a concerted (S_N2 type) mechanism cannot be

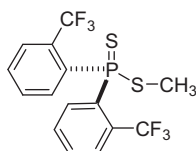


Fig. 2. Bis(*o*-trifluoromethylphenyl)dithiophosphinic methyl ester, (**2**).

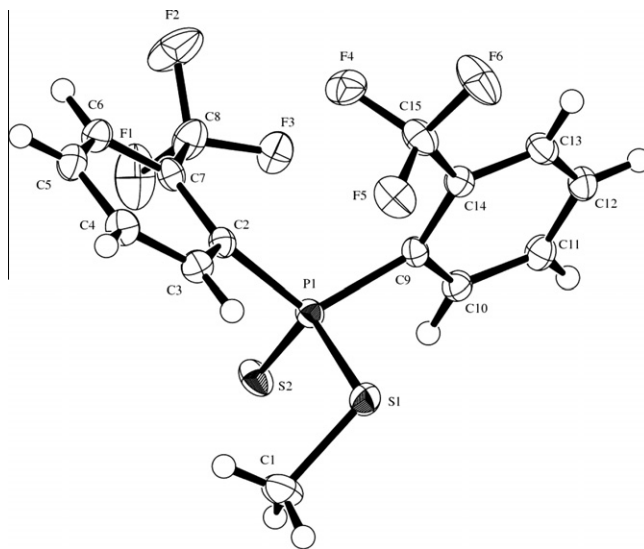


Fig. 3. View of the structure of bis(*o*-trifluoromethylphenyl)dithiophosphinic methyl ester, (**2**). Ellipsoids are drawn at the 50% probability level.

Table 1

Crystal data and structure refinement for bis(*o*-trifluoromethylphenyl)dithiophosphinic methyl ester, (**2**).

Empirical formula	$C_{15}H_{11}F_6PS_2$
Formula weight	400.33
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	14.1767(9)
<i>b</i> (Å)	8.8669(8)
<i>c</i> (Å)	15.1837(5)
α (°)	90.00
β (°)	119.9540(10)
γ (°)	90.00
Volume (Å ³)	1653.70(19)
<i>Z</i>	4
D_{calc} (mg/m ³)	1.608
Absorption coefficient (mm ^{−1})	0.475
$F(0\ 0\ 0)$	808
Crystal size (mm ³)	$0.49 \times 0.34 \times 0.21$
θ Range for data collection (°)	3.10–27.48
Index ranges	$-18 \leq h \leq 14$ $-11 \leq k \leq 11$ $-14 \leq l \leq 19$
Reflections collected	11322
Independent reflections	3719 [$R_{int} = 0.0454$]
Completeness to $\theta = 27.48^\circ$	98.0%
Maximum and minimum transmission	0.9069 and 0.8007
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3719/0/219
Goodness-of-fit on F^2	1.033
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0427$, $wR_2 = 0.0964$
<i>R</i> indices (all data)	$R_1 = 0.0603$, $wR_2 = 0.1050$
Largest differences in peak and hole (e Å ^{−3})	0.374 and −0.385

excluded. Due to the aromatic *o*-trifluoromethyl groups, the authors postulate that steric encumbrance is one of the principal factors that preserve the PS_2 core of **2**. Observance of this transformation suggests that **1** is a strong acid, and dithiophosphinic acids that have strong acid behavior towards organic alcohols have not been thoroughly studied. However, it is apparent that mixing organic alcohols (like methanol) with **1** should be explored further, and it is feasible that these dithiophosphinic acids can form other new dithiophosphinic ester derivatives.

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