International Journal of Advance Research in Science and Engineering
Vol. No.6, Issue No. 09 , September 2017
www.ijarse.com

IJARSE
ISSN (O) 2319 - 8354
ISSN (P) 2319 - 8346

Synthesis and Spectroscopic Characterization of Disulfide of di(4-chloro-3-Methylphenyl)Dithiophosphate, $[(4\text{-Cl-3-}CH_3C_6H_3O)_2PS_2]_2$

Atiya Syed

Department of Chemistry, University of Jammu, Baba Saheb Ambedkar Road, Jammu, J&K-180006

ABSTRACT

The disulfide corresponding to $[(4\text{-Cl-3-}CH_3C_6H_3O)_2PS_2]_2$ *has been synthesized by oxidation of sodium salt of di(4-chloro-3-methylphenyl)dithiophosphate,* $[(4\text{-Cl-3-}CH_3C_6H_3O)_2PS_2Na]$ *by iodine in chloroform. This disulfide has been characterized by elemental analyses, IR, ESI-Mass, heteronuclear NMR (*^{1}H*,* ^{13}C *and* ^{31}P*).*

Keywords**: *Disulfide, Phosphorus, NMR***

I. INTRODUCTION

Dithiophosphates and their derivatives have been extensively employed both as antioxidant and antiwear additives in rubber and as lubricating oils [1, 2]. The literature reports of dithiophosphate ligand and their metal derivatives are very diverse and almost each compound has found its significant role to play in either industrial, agricultural or biomedical fields [3—5]. Bis(dialkyldithiophosphate)disulfides are highly effective in breaking the dormancy of plant seeds, bulbs and tubers. These disulfides can be used as herbicides or applied to the cultivation of crop plants[6] . Gasoline storage units contain blended disulfides (0.001%-0.500%, by weight), for a long term storage without sludge deposition [7]. Disulfide are added to electrolytes as additives for secondary lithium batteries in order to increase life of the batteries [8]. Herein, the synthesis and spectroscopic characterization of $[(4\text{-Cl-3-}CH_3C_6H_3O)_2PS_2]_2$ has been reported.

II. EXPERIMENTAL

The entire synthetic process is conducted using Schlenk line techniques. 4-chloro-3-methylphenol (Himedia) was used as received. The solvent chloroform was purified and dried by standard methods before use. The ligands were synthesized by the reported literature procedure [9]. Elemental analyses of C, H and S were done on Vario EL III and CHNS-932 Leco elemental analyzer and their results were in good agreement (±0.3%) with the calculated values. The mass spectra were recorded on ESQUIRE3000_00037 spectrophotometer. IR spectra were recorded using KBr pellet in the range of 4000-200 cm^{-1} on a Perkin Elmer Spectrum 400-I FTIR spectrophotometer. The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ on Bruker Avance II and III 400 (400 MHz) spectrometer using TMS as internal reference for ^{1}H and ^{13}C NMR and H3PO4 as external reference for ^{31}P NMR.

Synthesis of disulfide of di(4-chloro-3-methylphenyl)dithiophosphate, $[(4\text{-Cl-3-}CH_3C_6H_3O)_2PS_2]_2$

The title compound was prepared by dropwise addition of chloroform solution (10 ml) of iodine, I_2 (0.38 g, 1.50 mmol) to a chloroform solution (30 ml) of (1.00 g, 3.00 mmol) sodium 4-chloro-3-methylphenyl)dithiophosphate with constant stirring at room temperature. As soon as the iodine solution was added the dark pink colour of the disappeared due to the oxidation of sodium salt of 4-chloro-3-methylphenyl)dithiophosphate. The iodine solution was added continuously till a light pink colour appeared in the reaction. The reaction mixture was then stirred for 4-5 hours at room temperature for the sake of completion of the reaction. The precipitates of sodium iodide were filtered off using alkoxy funnel fitted with G-4 sintered disc and volatiles were removed from the filtrate under reduced pressure and the desired product $[(4\text{-Cl-3-}CH_3C_6H_3O)_2PS_2]_2$ was obtained from the filtrate as yellow viscous compound. Yield: 77 %; *Anal*. Calcd. for $C_{28}H_{24}Cl_4O_4P_2S_4$: Calculated (%): C, 44.45; H, 3.20; S, 16.95; Cl, 18.75; Found (%): C, 44.23; H, 3.11; S, 16.87; Cl, 18.81; FTIR (cm^{-1}): 3031, b [*v*(C–H)], 1211, s [*v*(P)–O–C], 1005, s, [*v*P–O–(C)], 951, m, [*v*(P–S)], 597, m, [*v*(P=S)], 503, m, [*v*(S–S)], ^1H NMR ($CDCl_3$): 2.0 (s, 12H), 6.6, s, 4 $H_{(ortho)}$; 6.5, d, 4 $H_{(meta)}$; (*J* = 8.0 Hz); 7.0, d, 4 $H_{(ortho')}$ (*J* = 8.0 Hz) ppm; ^{31}P NMR ($CDCl_3$): 93.5 ppm; ^{13}C NMR ($CDCl_3$): 19.6 ($3\text{-}CH_3$), 115.8 (C_6), 127.5 (C_5), 114.2 (C_2), 124.3 ($C_3\text{-}CH_3$), 136.7 (C_4-Cl), 157.4 (C_1-O) ppm. ESI-MS: m/z (%) = $[M^+]$ 756.51 (13) $[(4\text{-Cl-3-}CH_3C_6H_3O)_2PS_2]_2]$; $[M^+]$ 554.56 (13) $[(C_6H_3O)_2PS_2]_2$; $[M^+]$ 141.57 (10) $[4\text{-Cl-3-}CH_3C_6H_3O]$; $[M^+]$ 106.12 (20) $[CH_3C_6H_3O]$.

III. RESULTS AND DISCUSSION

Oxidation of the sodium salt of di(4-chloro-3-methylphenyl)dithiophosphate with iodine in chloroform resulted in the formation of disulfide corresponding to $[(4\text{-Cl-3-}CH_3C_6H_3O)_2PS_2]_2$ in fairly good yield as yellow solid compound under anhydrous conditions as shown in **Scheme 1.**

$$2\ (ArO)_2PS_2Na\ +\ I_2\ \xrightarrow[\text{-2NaI}]{CHCl_3}\ (ArO)_2P(S)S{-}S(S)P(ArO)_2$$

$$Ar = 4\text{-Cl-3-}CH_3C_6H_3$$

Scheme 1: Synthesis of disulfide of di(4-chloro-3-methylphenyl)dithiophosphate

Pure disulfide was isolated after the isolation of sodium iodide thus formed during the course of reaction under anhydrous conditions. The compound is soluble in common organic solvents *viz.* benzene, toluene, chloroform, acetone, dichloromethane *etc.*, but is insoluble in *n*–hexane and carbon tetrachloride. This disulfide was obtained in sufficient purity as revealed by spectral studies. The elemental analyses of all the disulfides were found consistent to their molecular formula.

Infrared

The tentative assignments of IR spectral data (4000–400 cm^{-1}) were interpreted on the comparison basis with the literature reports []. The IR spectrum shows the characteristic sharp band for *v*[(P)─O─C] at 1211 cm^{-1} and *v*[P─O─(C)] at 1005 cm^{-1} and medium intensity bands at 951 cm^{-1} ascribed to [*v*(P–S)] and at 597 cm^{-1} ascribed to [*v*(P=S)]. The appearance of new band of medium intensity for v(S–S) in the region 503 cm^{-1} is indicative of the formation of new bond between sulfur atoms of the two ligands in the compound.

^{1}H NMR

In the ^{1}H NMR spectrum (in $CDCl_3$), the chemical shift for the $-CH_3$ protons was observed at 2.0 ppm as singlet whereas the protons of the aryl ring gave the chemical shift in the range 6.5–7.0 ppm with their usual splitting pattern. The 4-chloro-3-methylphenyl ring shows three signals one singlet at 6.6 and one doublet at 7.0 ppm for *ortho* protons. Another doublet for *meta* protons is observed at 6.5 ppm.

^{13}C NMR

The ^{13}C NMR spectrum of the disulfide has shown the appearance of the chemical shift for all the carbon nuclei in their characteristic region. The chemical shift for methyl ($-CH_3$) carbon occurred at 19.6 ppm. The carbon nuclei of aryl ring have displayed their resonance in the region 114.2-157.4 ppm. The carbon attached to the methyl resonated at 124.3 ppm. The peak at 157.4 was due to the carbon attached to the oxygen atom.

^{31}P NMR Spectra

The ^{31}P NMR spectrum of the compound depicted the chemical shift for the phosphorus atom as singlet at 93.5 ppm. Furthermore, occurrence of a downfield shift in comparison to the parent dithiophosphate ligands is indicative of the linkage of both the sulphur atoms of the two dithiophosphate ligands. The appearance of a singlet is a confirmation of equivalent nature of the phosphorus atoms and symmetric structure of compound.

Mass

Mass spectral analytical data as interpreted from the mass spectrum showed characteristic molecular ion peak [M^+] at m/z = 756.51. In addition to molecular ion peak several other peaks were also observed which are corresponding to the fragmented species m/z = 554.56, $[(C_6H_3O)_2PS_2]_2$, m/z = 141.57, $[4\text{-}Cl\text{-}3\text{-}CH_3C_6H_3O]$, m/z = 106.12, $[CH_3C_6H_3O]$ after the consecutive removal of different groups. The occurrence of molecular ion peak in the compound supported its monomeric nature. The fragments containing chlorine atom exhibited the peak in accordance to the isotopic effect of chlorine (calculated as 35.5 a.m.u.) and M and M+2 peaks were observed.

Structural Features

On the basis of analytical studies like elemental analyses, mass, IR and multinuclear NMR (^{1}H, ^{31}P and ^{13}C), a probable geometry may be assigned to the disulfides. In the IR spectrum the appearance of new band for νS─S vibration supported the formation of this compound. In conjunction with the literature reports[6,9-10] the following structure is assigned (**Figure 1**).

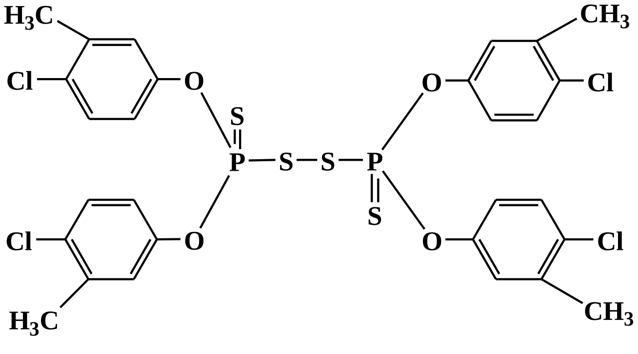

Figure 1: Proposed structure of $[(4\text{-}Cl\text{-}3\text{-}CH_3C_6H_3O)_2PS_2)_2]$

REFERENCES

[1] A. Ghanbarzadeh, E. Piras, I. Nedelcu, V. Brizmer , M. C. T. Wilson, A. Morina, D. Dowson, A. Neville (2016) Zinc dialkyl dithiophosphate antiwear tribofilm and its effect on the topography evolution of surfaces: A numerical and experimental study. Wear, 362-336, 186-198.

[2] D. Mahipal, P. Krishnanunni, P.M. Rafeekh, N. H. Jayadas (2014) Analysis of lubrication properties of zinc-dialkyl-dithio-phosphate (ZDDP) additive on Karanja oil (Pongamia pinnatta) as a green lubricant, International Journal of Engineering Research, 3, 494-496.

[3] C. Lai, B. Xie, C. Liu, W. Gou, L. Zhou, X. Su and L. Zou (2016) A Study of N,N-Diethylammonium O,O'-Di(*p*-methoxyphenyl)dithiophosphate as New Corrosion Inhibitor for Carbon Steel in Hydrochloric Acid Solution, 2016, 1-8

[4] P. Bhatnagar, N. K. Pokhriyal, N. Sivasurian, A. K. Tiwari, V. P. Deshmukh, J. C. Kandisseril, B. R. Tyagi, R. K. Malhotra, R. P. Verma and N. R. Raje, (2005) Composition of an Agricultural Spray Oil. U.S. Patent Application 11/912,204.

[5] N. D. Abeydeera, M. Egli, N. Cox, K. Mercier, J. N. Conde, P. S. Pallan, D. M. Mizurini, M. Sierant, F. E Hibti, T. Hassell, T. Wang, F.W. Liu, H. M. Liu, C. Martinez, A. K. Sood, T. P. Lybrand, C. Frydman, R. Q. Monteiro, R. H. Gomer, B. Nawrot, X. Yang, (2016) Evoking picomolar binding in RNA by a single phosphorodithioate linkage, Nucleic Acids Research, 44, 8052–8064.

[6] H-K. Fun, S. Chantrapromma, I. A. Razak, F. Bei, F. Jian, X. Yang, L. Luc and X Wang, (2001) Bis(N-methyl-N-phenylthiocarbamoyl) disulfide, Acta Cryst. E57, o717-o718.

[7] B. Rahimi, A. Semnani, A. Nezamzadeh-Ejhieh, H. S. Langeroodi and M. H. Davood (2012) Monitoring of the Physical and Chemical Properties of a Gasoline Engine Oil during Its Usage, Journal of Analytical Methods in Chemistry, 2012, 1-8.

[8] Zhe Chen, Xiangwen Liu, Yuhong Liu, Selda Gunsel & Jianbin Luo, (2015) Ultrathin MoS_2 Nanosheets with Superior Extreme Pressure Property as Boundary Lubricants, Scientific Reports, 5:12869, 1-7.

[9] A. Kumar, K. R. Sharma and S. K. Pandey, (2007) Synthesis and characterization of *O,O'*-(*o*-, *m*-, or *p*-ditolyl) dithiophosphate ligands, Phosph., Sulf., and Silicon and the Related Elements, 182, 1023-1031.

[10] Z. Shu-sheng, L. Xue-mei, W. Jin-li, W. Jun and J. Kui, (2004) Crystal Structure of Bis(O,O′-diisopropyl dithiophosphate):$[(C_3H_7O)_2PS_2]_2$, Chemical Research in Chinese Universities, 20, 146-148.