Chinese Chemical Letters Vol. 11, No. 10, pp. 887–890, 2000

Synthesis and Structure of A Novel Caged Bicyclic Phosphate Flame Retardant

Xin LI* , Yu Xiang OU, Yun Hong ZHANG , Dan Jun LIAN

National Laboratory of Flame-retarded Materials,
Beijing Institute of Technology, Beijing 10008l

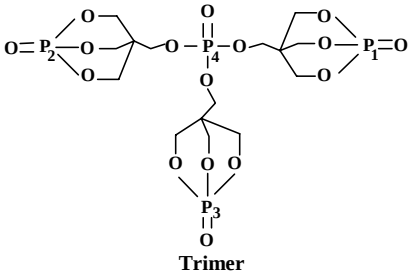
Abstract: A novel caged bicyclic phosphate flame retardant tri(1-oxo-2,6,7-trioxa-l-phosphabicyclo [2.2.2] octane-methyl) phosphate (Trimer) was synthesized from 1-oxo-4-hydroxymethyl-2,6,7-trioxa-l-phosphabicyclo [2.2.2] octane (PEPA) and phosphorus oxychloride in this paper. Its structure was characterized by elemental analysis, FTIR, ^{1}H NMR, ^{31}P NMR and X-ray diffraction analysis.

Keywords: Caged bicyclic phosphate, flame retardant, crystal structure.

Introduction

The ecological safety of polymer flame retardant has become a major subject in the modern polymer industry, and there is an international demand for the control of polymer flammability without the use of halogenated additives. Consequently, current research is mainly focused on looking for environmental friendly additives in the form of organophosphorus compounds, which are being thought as the alternatives of the halogen containing flame retardants[1]. Among the organophosphorus flame retardants, caged bicyclic phosphates have attracted many interests, and many investigations have been done about them[2]. It is found that caged bicyclic phosphates and their derivatives can serve as effective flame retardants to some polymers[3]. But they also have disadvantages in efficiency, processability, thermal stability and water absorption *etc*. Thus their applications are still limited.

We synthesized a novel caged bicyclic phosphate tri(2,6,7-trioxa-l-phosphabicyclo [2.2.2] octane-1-oxo-4-methanol) phosphate (Trimer), and characterized its structure with elemental analysis , FTIR, ^{1}H NMR, ^{31}P NMR, and X-ray diffraction analysis. As compared with other bicyclic phosphates, Trimer has an ideal symmetrical caged structure, higher phosphorous content and excellent thermal stability. It is insoluble in water and many common used organic solvents such as ethanol, acetone, ethyl acetate, dichloro methane, toluence, *etc*. The results of TG and DSC show that the initial decompose temperature of Trimer is 316℃ and the peak temperature on DSC curve is 368℃. We believed that Trimer might be a promising non-halogen flame retardant.



Trimer

Experimental

The preparation of PEPA This compound was prepared according to the reference: 3 c). The compound melts at 210-212℃. The elemental analysis and FTIR spectrum supported the structure.

The preparation of Trimer A 500 mL four-necked round bottom flask was equipped with a mechanical stirrer, reflux condenser, thermometer, and a funnel. The flask was charged with 150 mL of acetonitrile, 50mL of pyridine and 108g (0.6mol) of PEPA. The reaction mixture was heated with stirring to reflux. When the PEPA dissolved, 18.2 mL(0.2mol) of $POCl_3$ was slowly dropped in. After 12 h, the reaction mixture was cooled, filtered, and the precipitate was washed with water and then dried at 60℃ under reduced pressure, giving 94.2g (80.7%) of white powder, m.p. 349～351℃ (decomposition), density (white powder) 1.66 g/cm^3. Anal. calcd. for $C_{15}H_{24}O_{16}P_4$: C, 30.98%; H, 4.14%; P, 21.22%; Found: C, 30.87%; H, 4.15%; P, 21.05%. FTIR (KBr, cm^{-1}): 2912.7, 1311.5, 1279.4, 1027.5, 995.4, 848.9; ^{1}H NMR ($(CD_3)_2SO$, δ ppm): 4.60～4.75(18H), 3.90～4.04(6H); ^{31}P NMR ($(CD_3)_2SO$, δ ppm): $P_{1\text{-}3}$, -5.6956, P_4, -0.7063.

Colorless needle crystal used for X-ray diffraction measurement (0.40×0.35×0.30mm^3) was obtained by slowly evaporating the solution of Trimer in the mixture of formic acid and DMSO (5:1, V/V) at room temperature.

Structure Determination and Results

The data for the crystal of Trimer were collected at room temperature on a Rikaku AFC6S diffractomer with Mo-k$_\alpha$ (λ = 0.71073Å) radiation. The crystal is monoclinic, space group Cc, with unit cell dimensions a=12.754(3) Å, b=18.582(4) Å, c=11.269(2) Å, V=2324.2(8)Å^3, four molecules per unit cell ($D_{calc.}$=1.670 g/cm^3). The final R = 0.0322, R_w= 0.0907 for 2177 unique reflections.

The structure was solved by direct methods and subsequent Fourier different techniques and refined by full-matrix least squares using the SHELXL-97 program. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located theoretically and refined with riding mode position parameters and fixed isotropic thermal parameters. The final cycle of full-matrix least squares refinement was converged with $(\triangle \sigma)_{max}$=0.000, $\omega^{-1}=\sigma^2 F_o^2+(0.0905P)^2$, where P=(F_o^2 + 2 F_c^2)/3, S=0.826. The maximum and minimum residual peaks on the final difference Fourier map were 0.196 and -0.181e / Å^3, respectively.

The molecular structure and packing diagram are depicted in Figure 1 and Figure 2 respectively. It can be seen that three bicyclic cages in the molecule of Trimer are structurally equivalent, and in each cage, the corresponding average bond lengths and angles are almost equal. The structure of P_4 is a kind of metamorphous tetrahedron.

Figure 1. The molecular structure of Trimer

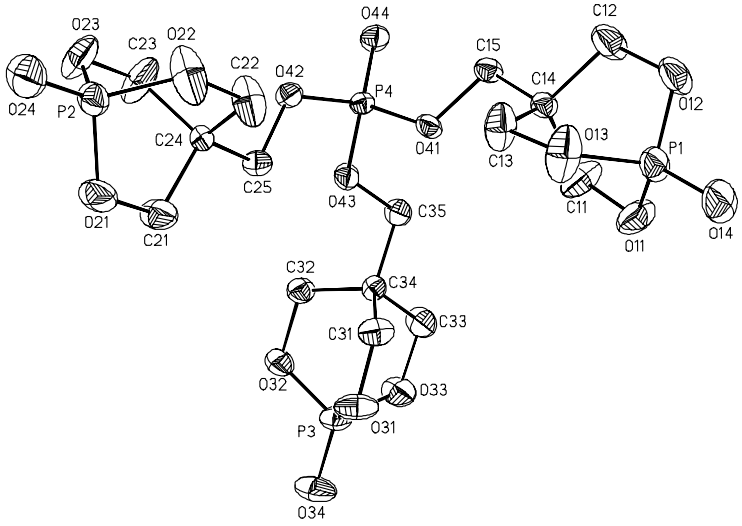
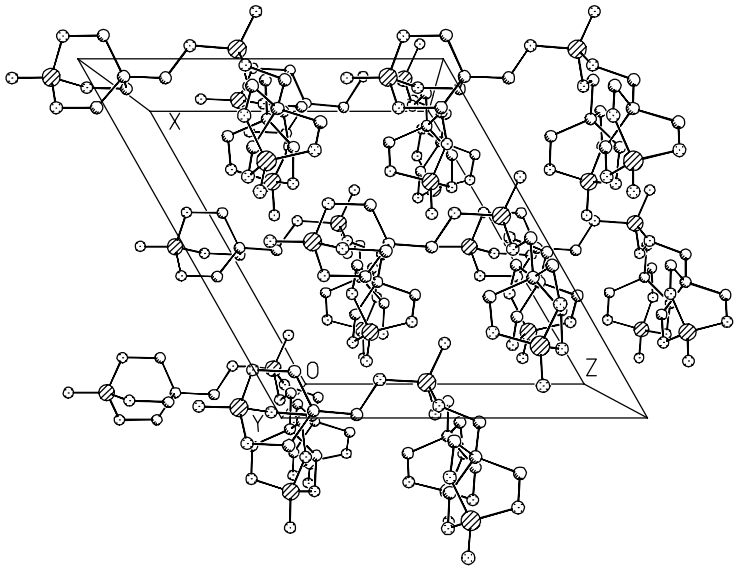


Figure 2. The packing diagram of the unit cell



References

1. J. Green, *J. Fire Science*, **1997**, *15*, 52.
2. a) Y. G. Li, J. J. Wang, *et al.*, *Acta Chimica Sinica*, **1988**, *46*, 679.
   b) Z. H. Peng, Y. X. Ou, *Chemical Aviso*, **1998**, *8*, 39.
   c) R. B. Luo, Y. X. Ou, *Chem. Eng. Fine Petroleum*, **1993**, *6*, 19.
3. a) U.S. Pat. *4341694*, **1982**.
   b) U.S. Pat. *4480093*, **1984**.
   c) Y. Halpern, M. M. Denna, R. H. Niswander, *Ind. Eng. Chem. Prod. Res. Dev.*, **1984**, *23*, 233.

Received 14 April 2000