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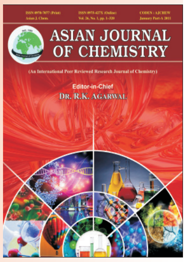

Synthesis and Crystal Structure of Diethyl Tosyloxybenzylphosphonate

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Diethyl tosyloxybenzylphosphonate was synthesized by the reaction of hydroxybenzylphosphonate with *p*-toluenesulfonyl chloride characterized by NMR spectroscopy, elemental analyses and X-ray single-crystal diffraction. The possessing parameters: m.f. $C_{18}H_{23}O_6PS$, monoclinic, P2(1)/n, a = 8.1087(9) Å, b = 20.215(2) Å, c = 12.5201(12)Å, α = 90º, β = 98.7380(10)º, γ = 90º, V = 2028.5(4) Å3, Z = 4, M_r = 398.39, Dc = 1.305 g/cm^3, μ = 0.268 mm^{-1}, F(000) = 840, T = 298(2) K, R_1 = 0.0462, wR_2 = 0.1076 for 3579 observed reflections with I >2σ(I).

Keywords: Diethyl tosyloxybenzylphosphonate, Synthesis, Crystal structure.

INTRODUCTION

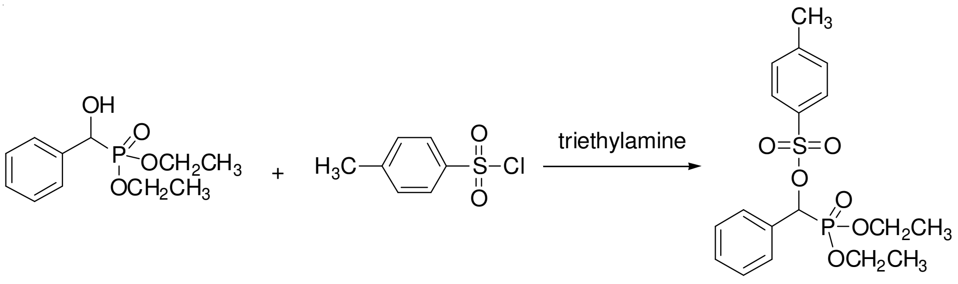
The biological importance of phosphonates was recognized in the past decade[1]. Among them, α-substituted phosphonates are particularly important in connection with their remarkable biological activities[2-4]. The widespread uses of phosphonates are as enzyme inhibitors[5-7], botryticides[8], anti-HIV agents[9-10], antibacterial agents[11] and haptens for catalytic antibodies[12].

In our recent researches, we require *p*-toluenesulfonyl chloride as the intermediate to synthesize a series of α-oxophosphonic acid derivatives in the hope of looking for new biological compounds. As an extension of the work on structure characterization of α-oxophosphonic acid derivatives, a single crystal of the title compound was subjected to X-ray diffraction experiment.

EXPERIMENTAL

Starting materials were obtained from commercial suppliers and were used without further purification. All melting points were determined on a Yanaco apparatus and they are uncorrected. NMR spectral data were collected on a Brucker 400 MHz with TMS as an internal standard.

Synthesis: To a solution cooled to 0 °C of 10 mL methylene chloride, (2.44 g, 10 mmol) diethyl hydroxybenzylphosphonate and 2.81 mL of triethylamine was added dropwise over 0.5 h a solution of *p*-toluenesulfonyl chloride (1.91 g, 10 mmol) in 10 mL of methylene chloride. The reaction temperature did not exceed 25 °C during the addition. After an additional 0.5 h of stirring the reaction was allowed to warm to room temperature and stir overnight, filtration and evaporation afforded 3.90 g (98 %) of the title compound as a white solid, as shown in **Scheme-I**. m.p. 63-65 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 01.21 (6H, m) 2.34 (3H, s), 4.03 (4H, m), 5.65 (lH, d, 1 = 16 Hz) and 7.35 (9H, m); ^{13}C NMR (50 MHz, $CDCl_3$): 016.4 (m), 21.6, 63.5 (m), 75.8, 79.2,128.0, 128.2, 128.3, 128. 4, 128. 5, 129.0, 129.1, 129.5, 131.8, 133.8 and 144.8. Anal. Calcd for $C_{18}H_{23}O_6PS$: C, 54.26; H, 5.82. Found: C, 54.12; H, 5.73.



Scheme-I

Determination of crystal structure: A colourless crystal having approximate dimensions of 0.45 mm × 0.32 mm × 0.30 mm was selected for X-ray diffraction study. Diffraction experiments were performed on a Siemens SMART CCD area-detector diffractometer with graphite-monochromatic MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å) at 298 ± 2 K, scan technique $2.60° \leq \theta \leq 25.02°$. A total of 10016 reflections were collected, of which 3579 reflections were unique with $R_{int} = 0.0292$. Lp effects and empirical absorption were applied in data corrections. The structure was solved by direct methods and expanded using Fourier techniques and SHELXS-97 program system was used in the solution and refinement of the structure. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were added according to theoretical model. The final full-matrix least-squares refinement including 258 variable parameters for 3579 reflections with $I > 2\sigma(I)$ and converged with unweighted and weighted agreement factors of $R_1 = 0.0462$ and $wR_2 = 01076$, where $w = 1/[\sigma^2(F_0^2) + (0.0466P)^2 + 1.0491P]$ and $P = (F_0^2 + 2F_C^2)/3$. The maximum and minimum peaks on the final difference fourier map are corresponding to 0.264 and -0.264e/A^3, respectively.

RESULTS AND DISCUSSION

Figs. 1 and 2 show the molecular structure and packing diagram of the title compound, respectively. Selected bond distances and angles are listed in Table-1. In the title compound, the dihedral angle formed by the two benzene planes is 6.1 (1)° The atom P(1) has a distorted tetrahedral configuration. The widening of angle O(3)-P(1)-O(1)(115.76(13)°) and narrowing of angle O(1)-P(1)-C(1)(101.62(12)°) from the ideal tetrahedral value are attributed to the Thrope-Ingold effect . The bond P(1)-O(3) (1.454(2)Å) of is much shorter than P(1)-O(1) (1.561(2)Å) and P(1)-O(2)(1.562(2)Å). This is result of the (d-p)π bonding between 3d vacant orbital of the P atom and the lone electron pair of the O(2) atom. These values are basically identical with that of the reference[13]. The two ethoxy groups on the phosphorus atom were unequivalent symmetry. The angular disposition of the bond about atom S(1) shows a significant deviation from that of a regular tetrahedron, with the largest deviation for the O-S-O angle. The widening of the O(5)-S(1)-O(6) angle, to 120.43(16) in the title compound, from the ideal tetrahedral value is presumably the result of the repulsive interaction between the short S=O bonds, similar to that observed in related structures[14-15]. The bond length of S(1)-C(12)(1.749(3)Å) is shorter than that of general S-C(1.81Å), which may be attributed to the conjugation of all carbon-carbon bonds in benzene ring and exocyclic sulfur-oxygen double bonds. The orientation of the benzene ring substituent is

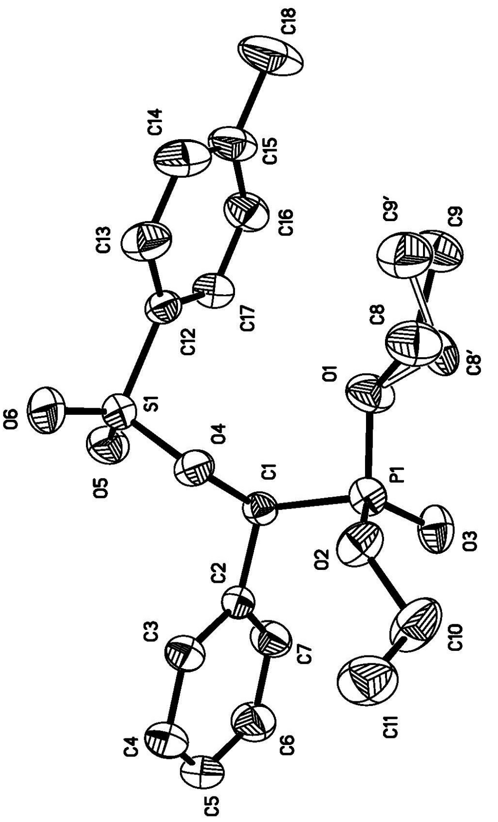


Fig. 1. Molecular structure of the title compound

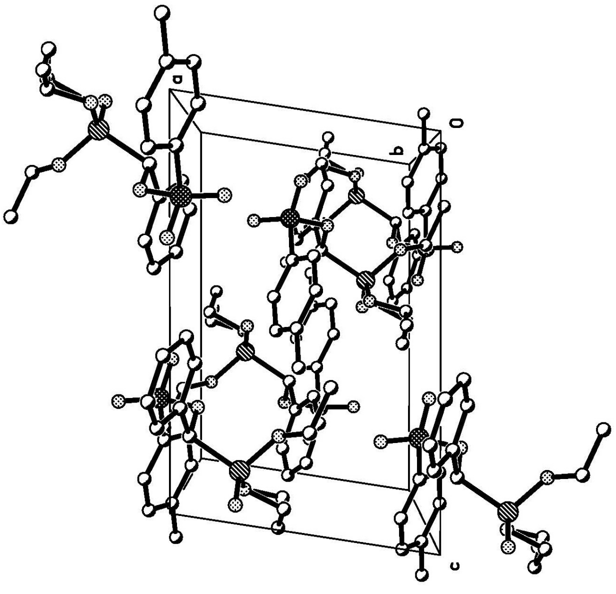


Fig. 2 Packing diagram of the title compound

TABLE –1
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE COMPOUND

Bond	Lengths	Bond	Lengths	Bond	Lengths
O(1)-C(8)	1.41(3)	O(4)-S(1)	1.5863(19)	P(1)-C(1)	1.822(3)
O(1)-P(1)	1.561(2)	O(5)-S(1)	1.419(2)	S(1)-C(12)	1.749(3)
O(2)-C(10)	1.431(4)	O(6)-S(1)	1.421(2)	C(1)-C(2)	1.512(3)
Bond	Angles	Bond	Angles	Bond	Angles
C(8)-O(1)-P(1)	127.9(13)	O(4)-C(1)-H(1)	109.4	C(4)-C(3)-H(3)	119.5
C(8')-O(1)-P(1)	120.3(14)	C(7)-C(2)-C(3)	118.7(3)	C(2)-C(7)-C(6)	120.2(3)
O(4)-C(1)-C(2)	110.3(2)	C(3)-C(2)-C(1)	121.8(2)	O(1)-C(8)-C(9)	116(2)

influenced by a weak C(2)-H(2)…O(5) interaction, defined by the torsion angle S(1)-O(4)-C(1)-C(2), while the orientation of the phenyl ring bound to the sulfonyl group is governed by a C(13)-H(13)...O(6) interaction, defined by the O(4)-S(1)-C(12)-C(13) torsion angle.

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REFERENCES

1. M. Horiguchi and M. Kandatsu, *Nature*, **184**, 901 (1959).
2. S. Bhagat and A.K. Chakraborti, *J. Org. Chem*., **72**, 1263 (2007).
3. K. Ando and T. Egami, *Heteroatom Chem*., **22**, 358 (2011).
4. M. Hosseini-Sarvari, *Tetrahedron*, **64**, 5459 (2008).
5. M.C. Allen, W. Fuhrer, B. Tuck, R. Wade and J.M. Wood, *J. Med. Chem*., **32**, 1652 (1989).
6. E.W. Logusch, D.M. Walker, J.F. McDonald, G.C. Leo and J.E. Franz, *J. Org. Chem*., **53**, 4069 (1988).
7. P.P. Giannousis and P.A. Bartlett, *J. Med. Chem*., **30**, 1603 (1987).
8. L. Maier, *Phosphorus Sulfur Silicon*, **53**, 43 (1990).
9. E. Alonso, E. Alonso, A. Solís and C. del Pozo, *Synlett*, 698 (2000).
10. N.P. Camp, P.C.D. Hawkins, P.B. Hitchcock and D. Gani, *Bioorg. Med. Chem. Lett*., **2**, 1047 (1992).
11. F.R. Atherton, C.H. Hassall and R.W. Lambert, *J. Med. Chem*., **29**, 29 (1986).
12. R. Hirschmann, A.B. Smith, C.M. Taylor, P.A. Benkovic, S.D. Taylor, K. Yager, P. Sprengeler and S. Benkovic, *J. Sci*., **265**, 234 (1994).
13. Z.Q. Shang, R.Y. Chen and Y. Hang, *Chinese J. Struct. Chem*., **25**, 1453 (2006).
14. R.L. Beddoes, L. Dalton, J.A. Joule, O.S. Mills, J.O. Street and C.I.F. Watt, *J. Chem. Soc. Perkin Trans. II*, 787 (1986).
15. J.G. Rodriguez, F. Temprano, C. Esteban-Calderon, M. Martinez-Ripoll and S. Garcia-Blanco, *Tetrahedron*, **41**, 3813 (1985).