



Crystal Structures of Two Homologues: Diethyl (Benzo[D][1,3]Dioxol-5-Yl((4-Bromophenyl)Amino)Methyl)Phosphonate And Dibutyl(Benzo[D][1,3] Dioxol-5-Yl((4-Bromophenyl)Amino)Methyl)Phosphonate

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Abstract: The title compounds, C₁₈H₂₁BrNO₅P (I) and C₂₂H₂₉BrNO₅P (II) form a homologous series, the structures determinations confirm the nature of the products. The compounds all crystallize in Space group C2/c for compound I and P-1 for compound II. Differ by the presence of a Phosphonate atom instead of a dibutyl atom in the para position of two benzo atom of compound (II). Bond lengths and angles may be considered normal for these compound types. The dioxole rings in both structures similar planar conformations. Intra- and Intermolecular C-H...O and N-H...O hydrogen bonds are responsible for the consolidation of the crystal packing of both molecules. In addition to this, weak C-H...π interactions are also observed.

Index Terms: single-crystal X-ray study; T = 296 K; mean (C-C) = 0.006 Å; R-factor = 0.0550 in I and 0.0699 in II; wR factor = 0.1429 in I and 0.1869 in II; data-to-parameter ratio 25.9.

I. INTRODUCTION

In recent years, epidemiological studies confirmed the significant negative impact of infections caused by pathogenic bacteria and fungi against human health. Large-scale surveillance revealed increasing incidence of drug-resistance that had compromised the efficacy of antimicrobial therapy. The increased emergence of multidrug-resistant pathogenic bacteria has called for exploration of alternative drug therapies ^[1]. As such, research is now focused towards new antimicrobial agents with expansion of bioactivity of existing drugs and also with novel target so as to address the problem of resistance ^[2]. It has been long since researchers show special interest in heterocyclic compounds that possess sulphur and nitrogen atom ^[3, 4]. Tiazole, for instance, exhibit widespread biological activities like antibacterial ^[5, 6], antimycobacterial ^[7], antileishmanial ^[8], anticancer ^[9] and antifungal ^[10]. A similar co-ordination in hydrogen bonding, diethyl[(5-chloro- 2-hydroxyanilino)(4-chlorophenyl)methyl]phosphonate has been reported by us ^[11].

II. Experimental

The diethyl (benzo[d][1,3]dioxol-5-yl((4-bromophenyl)amino)methyl)phosphonate compound **I**(C₁₈H₂₁BrNO₅P) / dibutyl(benzo[d][1,3] dioxol-5-yl((4-bromophenyl)amino)methyl)phosphonate compound **II**(C₂₂H₂₉BrNO₅P) was prepared by treating triethyl phosphite / tributylphosphite (0.001 mmol) and N-(benzo[d][1,3]dioxol-5-ylchloromethyl)-4-bromoaniline (0.0015) in toluene at reflux temperature according to a previously reported method [16]. The chemical structure of the compound is shown in **Figure 1**.

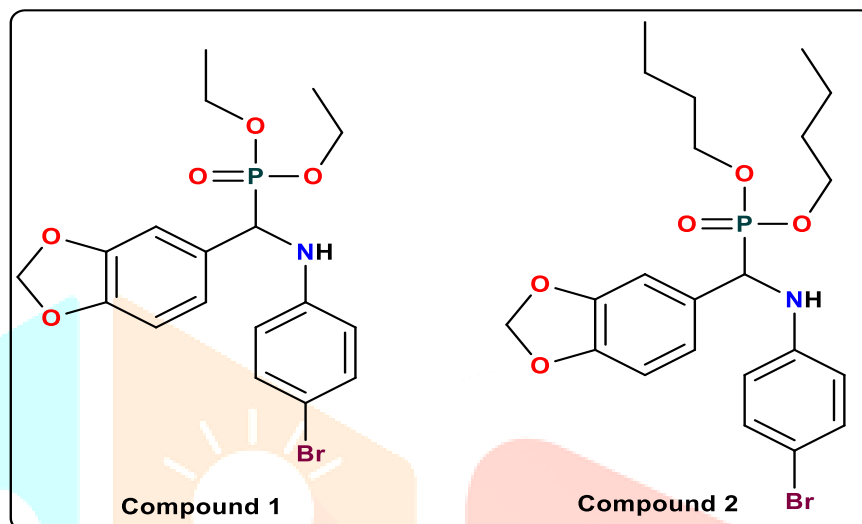


Fig.1 Chemical structure of compounds I and II

III. Data collection

CryAlis Pro (Oxford Diffraction, 2007)^[12]; cell refinement: CryAlis Pro; data reduction: CryAlis RED (Oxford Diffraction, 2007); program(s) used to solve structure: SHELXS86 (Sheldrick, 2008)^[13]; program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ZORTEPII (Zsolnai, 1997)^[14]; software used to prepare material for publication: PARST (Nardelli, 1995)^[15].

IV. Refinement

H atoms bonded to N and O atoms were located in a difference map and refined with distance restraints of O—H = 0.82 and N—H = 0.86 Å, and with $U_{iso}(H) = 1.2U_{eq}(N,O)$. Other H-atoms bound to carbon were positioned geometrically and refined using a riding model with $d(C—H) = 0.93\text{Å}$ $U_{iso}=1.2_{eq}(C)$ for aromatic, $C—H = 0.980\text{Å}$ $U_{iso}=1.2_{eq}(C)$ for methine, 0.97Å $U_{iso} = 1.2_{eq}(C)$ for CH₂ group and 0.96Å $U_{iso} = 1.5_{eq}(C)$ for CH₃ group.

V. Structural Commentary

The structure determinations confirm the nature of the products compound I (Fig.1) and II (Fig.2). In both compounds, the bond angles for compound I, O2-P1-O4 and O2-P1-O5 are larger than C5'-P1-O2 and C5'-P1-O4 and compound II, O2-P2-O4 and O2-P2-O5 are larger than C5'-P2-O4 and C5'-P2-O2 bond angles indicate a distorted tetrahedral around the phosphorus atom. The P=O bond length is in good agreement with related structures (Krishnai et al., 2009). The P-O-C-C groups are in Trans configuration avoiding steric interactions. The compounds C5'-P1-O5-C16 group is nearly planar unlike the C5'-P2-O5-C18 group the end atoms C17-C19 are completely out of plane due to more thermal vibrations. The dihedral angles between the dioxole ring and the almost planar di-methyl-amino-methyl (r.m.s deviation = 0.042Å). 1,3-benzodioxole fragment is nearly planar [the maximum deviation being 0.057Å]. The planar benzene rings are nearly perpendicular to each with dihedral angle of 78.1(1)°. In both compounds, the bromophenyl ring system (C1-C6) is essentially planar with maximum deviations of 0.026(1)Å and 0.016(1)Å for atom Br in compound I and II, respectively. The mean planes of the dioxole ring system make dihedral angles of 2.1(1)°, 19.0(1)° and 33.9(1)° respectively, in compound I and 0.7(1)°, 38.1(2)° and 87.6(2)° respectively, in compound II. In both compounds, the tetrahedral configuration is distorted around the atom P1 and P2. The increase in the O4-P1-O5 and O4-P2-

O5 angle $[120.0(1)^\circ$ in I and $119.9(2)^\circ$ in II], with simultaneous decrease in the $C5'-P1-O2$ and $C5'-P2-O2$ angle $[108.5(1)^\circ$ in I and $107.6(1)^\circ$ in II], from the ideal tetrahedral value (109.5°) are attributed to the Thorpe-Ingold effect (Bassindale, 1984). The widening of the angles may be due to the repulsive interaction between the two short P=O bonds.

VI. Supramolecular features

In compounds I, the molecules are held together by an intermolecular interactions of the types N1-H1...O2 and C8-H8...O5 (Table 2), enclosing an $R^2_2(10)$ closed ring motif, propagating along the $[101]$ direction (Figs. 4 and 5). Fig.6 packing of the molecule in the unit cell, viewed down 'a'-axis. In compounds II, the molecules are held together by an intermolecular interactions of the types N1-H1...O2 and C13-H13...O2 (Table 2), enclosing an $R^2_2(12)$ closed ring motif, propagating along the $[101]$ direction (Figs. 7 and 8). Fig.9 packing of the molecule in the unit cell, viewed down 'c'-axis. The C-H...O intermolecular hydrogen bonds, acts as a bridge between N-H...O intermolecular bonds, intra and intermolecular N-H...O hydrogen bonds. Here the phosphonate double bonded oxygen atom, which behaves as an acceptor participates in C-H...O intermolecular hydrogen bonding, whereas, the hydroxyl oxygen, which acts as both donor and acceptor, participates in the N-H...O intra and intermolecular hydrogen bonding. The hydrogen bond forms chains along $[010]$.

In the crystal of I, weak $\pi \dots \pi$ interactions are present $Cg2-Cg3 = 3.766(2)\text{\AA}$ where Cg2 and Cg3 are the centroids of rings (C1-C6) and (C7-C13) respectively. Symmetry code: $[1-x, 2-y, 1-z]$. No significant intermolecular interactions or C-H... π interactions with centroid distances of less than 4\AA are observed in the structure.

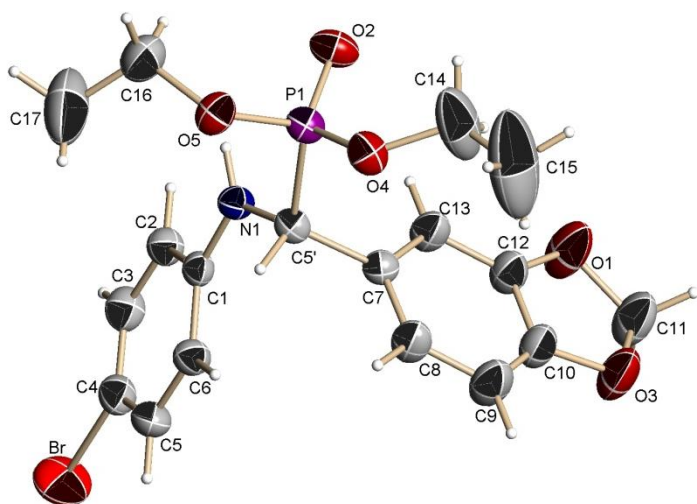


Fig.2. ORTEP diagrams are drawn at 30% probability

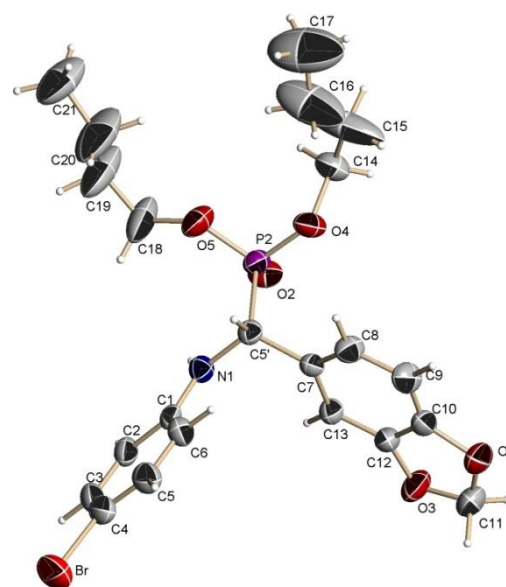


Fig.3. ORTEP diagrams are drawn at 30% probability

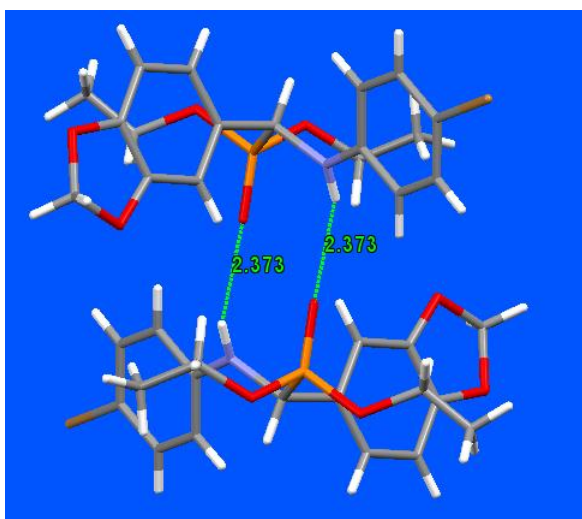


Fig. 4. For compound I packing of the molecules dimer via N-H...O Hydrogen bond, showing the $R^2_2(10)$ ring motif.

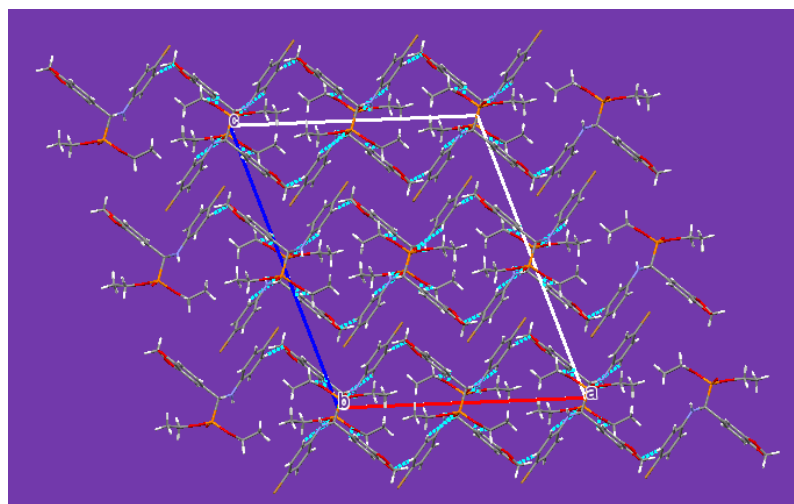


Fig.5. For compound I the intermolecular interactions enclosing the $R^2_2(10)$ ring motif propagating along the $[101]$ direction.

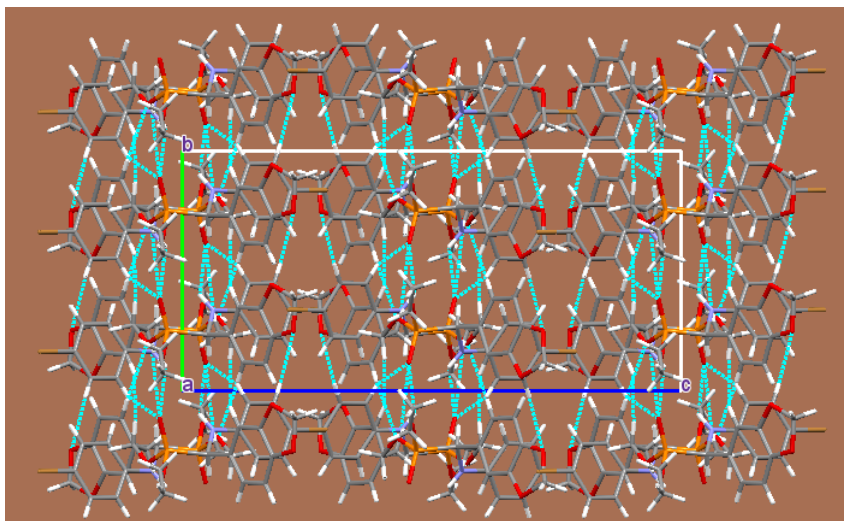


Fig.6. For compound I packing of the molecule in the unit cell, viewed down 'a'-axis

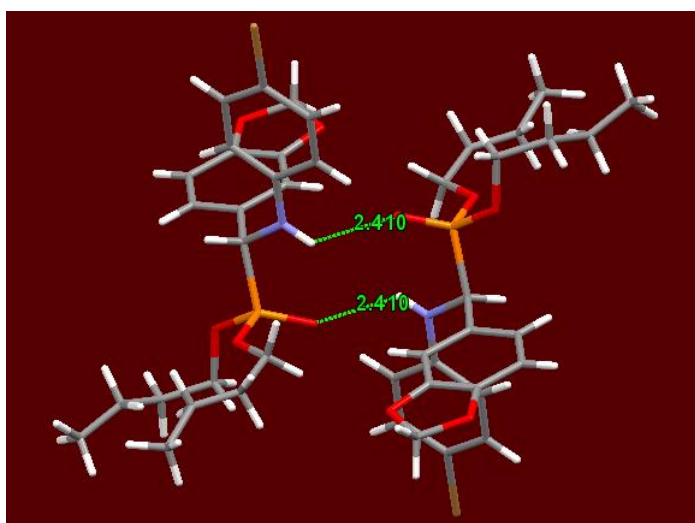


Fig. 7. For compound II packing of the molecules dimer Via N-H...OHydrogen bond, showing the $R^2_2(10)$ ring motif.

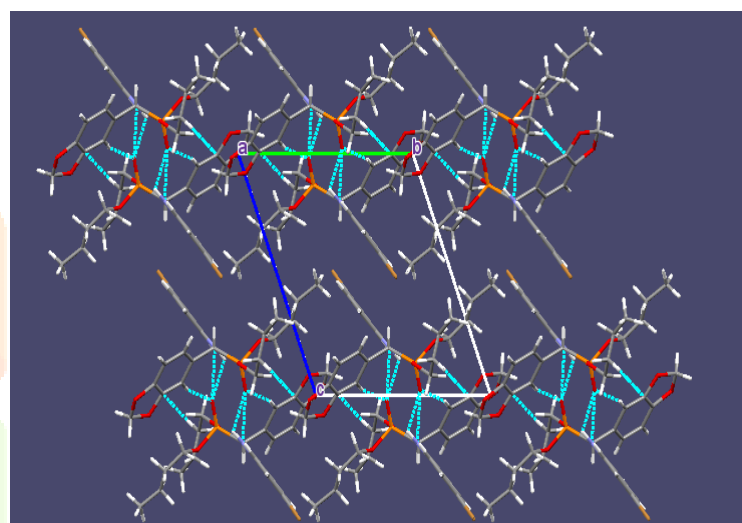


Fig.8. For compound II the intermolecular interactions enclosing the $R^2_2(10)$ ring motif propagating along the [001] direction.

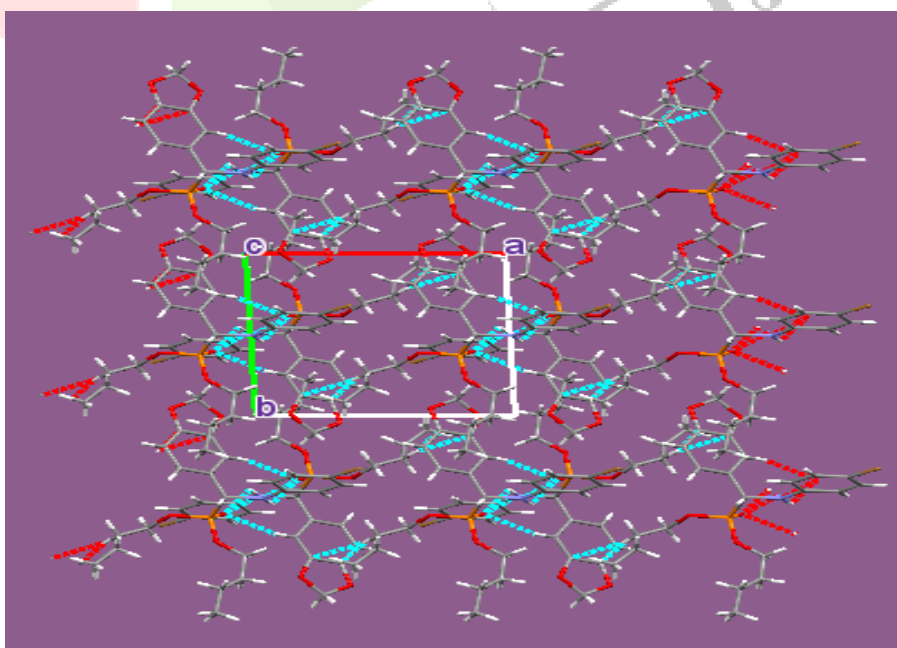


Fig.9. For compound I packing of the molecule in the unit cell, viewed down 'c'-axis

VII. Table: 1

Crystal Data and Details of the Structure Determination

Crystal data	Compound I	Compound II
Empirical formula	C18 H21 Br N O5 P	C22 H29 Br N O5 P
Formula weight	442.24	498.34
Temperature	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P-1
Unit cell dimensions	a = 18.480(3) Å $\alpha = 90^\circ$	a = 10.1380(9) Å $\alpha = 68.726(6)^\circ$
	b = 10.227(2) Å $\beta = 108.650(9)^\circ$	b = 10.144(1) Å $\beta = 86.845(6)^\circ$
	c = 22.540(5) Å $\gamma = 90^\circ$	c = 12.568(1) Å $\gamma = 86.598(6)^\circ$
Volume	4036.0(15) Å ³	1201.4(2) Å ³
Z	8	2
Density (calculated)	1.456 g/cc	1.378 g/cc
Absorption coefficient	2.143 mm ⁻¹	1.808 mm ⁻¹
F(000)	1808	516
Crystal size	0.40 x 0.23 x 0.02 mm ³	0.44 x 0.27 x 0.09 mm ³
Theta range for data collection	1.91 to 25.00°	2.16 to 24.99°
Index ranges	-21<=h<=21, -12<=k<=12, -26<=l<=26	-12<=h<=12, -12<=k<=12, -14<=l<=14
Reflections collected	55622	17236
Independent reflections	3569 [R(int) = 0.0762]	4226 [R(int) = 0.0245]
Completeness to theta = 25.00°	100.00%	99.90%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9524 and 0.4826	0.8542 and 0.5068
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	3569 / 4 / 237	4226 / 0 / 273
Goodness-of-fit on F ²	1.021	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0550, wR2 = 0.1429	R1 = 0.0699, wR2 = 0.1869
R indices (all data)	R1 = 0.0869, wR2 = 0.1670	R1 = 0.0912, wR2 = 0.2048
Largest diff. peak and hole	0.521 and -0.627 e.Å ⁻³	1.254 and -1.083 e.Å ⁻³

VIII. Table 2

Hydrogen-bond geometry for Compound I and II(Å, °).

	D-H...A	D-H	H...A	D...A	D-H...A
I	N1-H1...O2 ⁱ	0.86	2.37	2.977(2)	128
	C8-H8...O5 ⁱⁱ	0.93	2.57	3.396(5)	148
II	N1-H1...O2 ⁱⁱⁱ	0.86	2.41	2.955(2)	122
	C13-H13...O2 ⁱⁱⁱ	0.93	2.58	3.489(6)	165

Symmetry codes: (i) 1-x,2-y,1-z
(ii) 1-x,1-y,1-z
(iii) 2-x,1-y,2-z

IX. ACKNOWLEDGMENT

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X. References

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