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### Symmetric Quaternary Phosphonium Cation and Perchlorate/Chlorate Anions:

# Crystal Structure, Database Study and Hirshfeld Surface Analysis

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#### Abstract

Two new quaternary phosphonium salts of 1,2-ethandiylbis(triphenylphosphonium) Diperchlorate (**I**), 1,2-ethandiylbis(triphenylphosphonium) Dichlorate (**II**) were prepared and used for oxidation of different benzylic alcohols to afford their corresponding carbonyl compounds. These new compounds were characterized by **IR**, NMR spectroscopy and single crystal X-ray analysis. The crystal structure and Hirshfield surface analysis of titled compounds revealed that the change of accompanying anionic moiety can affect the directional interactions of CH···O hydrogen bonds between anionic and cationic units which lead to various supramolecular aggregations on the crystal packing. In order to exploring the influence of crystal environment of anionic moieties on the geometry of main symmetric cationic unit, the relative contribution of various close contacts and 2D fingerprint plots of title compounds and twenty three analogous structures retrieved from Cambridge Structural Database (CSD) were investigated through the distortion of tetrahedral coordination geometry of P center of main cationic unit based on  $\tau_4$  indices.

*Keywords:* Quaternary phosphonium salt; Accompaning anions; Crystal structure analysis; Oxidation agent; Hirshfeld surface analysis.

#### Introduction

The quaternary phosphonium cations which can be able to transfer the anionic reactants from aqueous media into organic media (as phase transfer catalysis) have received great interest with their structures and properties as room-temperature ionic liquids.<sup>1-3</sup> The results of studies have shown to increase the rate of the organic reaction by enhancing the reactivity of the ionic species and increasing the encounter rate with the organic substrate. The chlorate and perchlorate species are strong oxidant, and their salts such as some phosphonium chlorates and perchlorates compounds are frequently used to oxidize a variety of functional groups;<sup>4-10</sup> so, the application of chlorate and perchlorate-based compounds in organic synthesis has been extensively reviewed.<sup>11-13</sup> Oxidation of benzylic alcohols is one of the significant reactions in organic chemistry and up to the present moment a variety of reagents has been introduced this subject ionic liquids terms for such as in of methoxymethyltriphenylphosphonium halochromates,<sup>14</sup> triphenylphosphine surface-modified iron oxide nanoparticles,<sup>15</sup> benzyltriphenylphosphonium chlorate.<sup>16</sup> Although a wide variety of methods have been reported for oxidation of benzylic alcohols to the corresponding carbonyl compounds, some of them encounter disadvantages such as use of expensive oxidizing agents, low yields of the oxidized species and causing side products and harsh condition reaction. Eventually of these characteristics, introduce of methods and oxidizing agents for such functional group transformations is still in demand.

As part of our current study concerning the structural characteristics of bis triphenylphosphonium moiety, we have synthesized and characterized two new oxidation agents as 1,1'-(1,2-ethanediyl)bis[1,1,1-triphenyl]phosphonium diperchlorate (**I**) and 1,1'-(1,2-ethanediyl)bis[1,1,1-triphenyl]phosphonium dichlorate (**II**). The results of oxidation reactions by title compounds are very satisfactory and showed that these new reagents have valuable additions in comparison to existing oxidizing agents. We described the crystal

structure of titled compounds as well as the intermolecular interactions between bistriphenylphosphonium cationic and perchlorate and chlorate anionic moieties by Hirshfeld surface analysis. In fact, Hirshfeld surface analysis represents unique quantitative and qualitative tools to decode intermolecular interactions and offer a facile way of obtaining information from comparable structures.<sup>17-24</sup> In order to evaluate the role of various anionic moieties on the packing of cationic unit, the CSD search was performed for the analogous structures. The relative contribution of different intermolecular contacts of the main unit in these structures was investigated by Hirshfeld surfaces over a d<sub>norm</sub> and the 2D fingerprint plots.

#### **Results and Discussion**

#### Crystal structure description

The asymmetric unit of compound I contains the 1:2 ratio of cationic unit and discrete ClO<sub>4</sub><sup>-</sup> anionic unit. One of perchlorate anions was disordered over two positions with the occupancy ratio of 0.9 to 0.1 in which the moiety with major site occupation factor was considered in the structural investigations. The asymmetric unit of II contains half of cationic unit and one ClO<sub>3</sub><sup>-</sup> anionic unit. The bond angles around the P atoms are in the range of 107.8(2)° to 112.1(3)° in compound I and 107.6(2)° to 111.3(2)° in compound II. The torsion angles of P-C-C-P for dications is  $-134.35(13)^{\circ}$  and 131.78(12). The geometry of dications (bond lengths and angles) are general and comparable with our previously reported periodate salt.<sup>25, 26</sup> The arrangement of the phenyl rings in the –PPh<sub>3</sub> moieties diverged from planarity with the mean deviations of 0.184 and 0.122 Å for the phenyl rings around P<sub>1</sub> and 0.070 and 0.122 Å for the phenyl rings attached to P<sub>2</sub> of compounds I and II, respectively.

The 3D supramolecular networks of these compounds are dominated by the variety of C-H···O and C-H··· $\pi$  hydrogen bonds. According to the supramolecular aggregations of these structures, the  $\pi$ -system of benzene rings of cationic unit and also oxygen atoms of anionic

units play key role in packing them in all directions. Changing accompanying anionic moiety effects directional interactions between anionic and cationic units and therefore different supramolecular aggregation can be observed for these structures, including weak hydrogen bonding C–H···O and C–H···Cl which their structural parameters were listed in Table 1. Obviously, one of the main interactions in these compounds, which can play the important role in the crystal packing of title structures, is C–H···O interaction which is illustrated in c and d parts of Figures 1 and 2.

The results showed that the special direction of aromatic rings around the P centers in I and II prepare the suitable arrangement of cationic units alongside each other through the formation of C-H… $\pi$  interactions of benzene rings which illustrated in b part of Figures 1 and 2, respectively. Geometrical parameters of these interactions were presented in Table 2. One of three phenyl rings around the P-center interestingly engaged in  $\pi$ … $\pi$  intramolecular interactions while the other phenyl rings contribute in formation of effective C–H… $\pi$  interactions. Regarding to the recent studies of  $\pi$ … $\pi$  stacking interactions <sup>27-32</sup>, the geometrical parameters of aromatic phenyl interactions were distance of ring centroids as C-C distances of 3.795 Å and 4.246 Å and the angles between two ring planes 13.90° and 17.31° and also normal distance of centroid to ring planes as P–CC distances of 3.535 Å and 3.573 Å for compounds I and II, respectively.

# Hirshfeld surface analysis

Intermolecular interactions of the main unit functionality of the [EDBTPP]<sup>2+</sup> cation in the different crystalline environments of title compounds were mapped by the Hirshfeld surface analysis which is an extremely useful method for visualizing molecular contacts. The Hirshfeld surfaces were generated using Crystal Explorer 3.1 <sup>33</sup> based upon the X-ray structure analysis. Since, the internal consistency is important for comparison of

intermolecular contacts in different structures, the bond lengths of C–H, O–H and N–H have been normalized to standard neutron diffraction values which equals to 1.083, 0.983 and 1.009 Å, respectively. The red and blue colors in the Hirshfeld surface, mapped with  $d_{norm}$ , are associated with distances that are shorter and longer than van der Waals intermolecular contacts, respectively. Similarities and differences in behavior of hydrogen bond donor and acceptor was compared based on careful evaluation of the normalized contact distance ( $d_{norm}$ ) (-0.283–1.367 Å), and the decomposed fingerprint plots for close contacts of each unit have been prepared from compounds I, and II (Figures 3 and 4).

The comparison of these surfaces, despite differences in anionic fragments and different crystal structures, reveals that there is similarity between the treatment of the hydrogen bond acceptor and donor groups of these compounds. Figure 3 shows the percentage of participation of close contact between different atoms of the main unit, with the decomposed 2D fingerprint plots. Brief overview at the decomposed 2D fingerprint plots of title compounds, shows a considerable contribution of O···H/H···O, C···H/H···C, and H···H contacts in these compounds. Considering species of cationic moiety, investigated, the less contribution of other contacts such as C···O, C···C, C···Cl, and Cl···H. One of the main interactions in these compounds, which play an important role in their stacked structures, is C-H···O interactions, which are shown as O···H/H···O contacts in the decomposed 2D fingerprint plots. Most parts of red circular depressions with a range of different intensity, on these d<sub>norm</sub> surfaces, are due to the C-H···O interactions, which created between oxygen atoms of anionic moiety and hydrogen atoms of main unit. These contacts, with a range of different energies, appear as a sharp spike in the 2D fingerprint plots with points with minimum di + de values equals to 2.2 and 2.1 Å, respectively. The percentage of contribution of O…H/H…O contacts is 28.2% for compound I, and 21.3% for compound II of the total surfaces, which the more the proportion of O···H contacts in compound I revealed because of

the presence of more oxygen atoms in the anionic moiety ClO<sub>4</sub>.

On the other hand, the C–H··· $\pi$  interactions can be mentioned as one of the dominant interactions of these structures that are shown as C···H/H···C contacts and includes 25%, and 30.4% of the Hirshfeld surfaces for compounds I and II, respectively. The significant contribution of these surfaces is related to H···H interactions, which covers a vast range of surfaces in the center of the plots with proportions of 41.3% and 43.6% for compounds I and II, respectively. These contacts illustrated as sharp peaks with minimum di + de values in the 2D fingerprint plots (Figure 4). As it was previously mentioned about  $\pi$ ··· $\pi$  stacking interactions in titled compounds, the low contribution of C···C contact was expected with proportions of 2.7% and 0.8% for I and II, in which minimum di + de values equals to 3.6 and 3.5 Å, respectively.

Shape index and curvedness surfaces of cationic units as an interesting features of Hirshfeld surface analysis were prepared to compare the arrangement of  $[EDBTPP]^{2+}$  moiety against  $ClO_4^-$  and  $ClO_3^-$  anionic units in compounds I and II, respectively (Fig. S1). Features on these surfaces indicate to the intermolecular contact areas by identical pattern with various colors which show the complementarity between constituent moieties in the title molecules. This complementarity helps to better understand the packing arrangement of ionic moieties in the crystal structures.

#### Database study

In order to evaluate the performance of the main unit on the relative contribution of different intermolecular contacts to the Hirshfeld surfaces and its impact on the packing of the similar structures, the Cambridge Structural Database (CSD)  $^{34}$  search was performed on the compounds including the [EDBTPP]<sup>2+</sup> cationic unit, which led to 23 cases. In this regard, the

Hirshfeld surfaces of the main unit over a  $d_{norm}$  and the 2D fingerprint plots have been also studied, that represented in Figure 5 and Table 3.

The comparison of the relative contribution of various contacts shows that C…C, C…H/H…C, and H…H contacts exist in all of them, so that the contribution of C…H/H…C, and H…H contacts, apart from the role of anionic moiety, are significant. Furthermore, the highest contribution in all of the structures is relevant to the H…H contacts, which is changed from 18.9 to 78.3 Å. Indeed, C…H/H…C contacts which assigned to C-H… $\pi$  interaction have variety of contributions to the Hirshfeld surface from 11.2% to 30.7% in DUGKOG and AZUZIG refcodes, respectively. In these cases, the smallest contribution of C…C contacts demonstrating little effect of  $\pi$ … $\pi$  interactions in crystal packing of these structures.

Analysis of the crystalline environment of these structures demonstrates little effect of  $\pi \cdots \pi$  interactions in their crystal packing because of special direction of aromatic rings around the phosphor centers which confirmed by the little contribution of C…C contacts in the decomposed Hirshfeld surfaces. In this regard, relationship between the relative contribution of various close contacts in the crystal packing and the amounts of  $\tau_4$  parameter for P centers of main unit were investigated and also their decomposed 2D fingerprint plots analyzed separately. The geometry index for four-coordinated complex as  $\tau_4$  parameter was developed by Yang *et al.* to distinguish whether the geometry of the coordination center is square planar or tetrahedral. In this equation,  $\alpha$  and  $\beta$  are the two largest  $\theta$  angles in the four-coordinate species.<sup>35</sup>

$$\tau_4 = \frac{360^\circ - (a + \beta)}{141^\circ}$$

The results indicated to the special direction of aromatic rings around the P centers, which can decrease the possibility of formation the effective  $\pi \cdots \pi$  interactions between the aromatic moieties. However, C–H $\cdots \pi$  interactions based on  $\pi$ -system of benzene rings as well as the

other interaction, such as H···H and Cl···H become dominant in the stability of [EDBTPP]<sup>2+</sup> cationic unit in their crystal structures.

#### Oxidation reagent activity

The reagent of I as a white powder which is prepared by addition of an aqueous solution of NaClO<sub>4</sub> to an aqueous solution of 1,2-Ethandiylbis(triphenylphosphonium) dibromide <sup>8</sup> at room temperature. The white precipitate of I was filtered and dried in vacuum (95% yield, m.p:258-260°C). This powder recrystallized in chloroform to obtain suitable single crystals which are shown in Figure S2 and it could be stored for several months without losing its oxidation ability and so it has high efficiency. Similarly, the reagent of II is a white powder which is prepared by addition of an aqueous solution of NaClO<sub>3</sub> to an aqueous solution of 1,2-Ethandiylbis(triphenylphosphonium) dibromide <sup>8</sup> at room temperature. (96% yield, m.p:184-186°C). After one week from the suspension formation, the salt crystals of 1,2-ethandiylbis(triphenylphosphonium) Dichlorate (II) are obtained and separated through filtration (Fig. S3). This compound was stable for several months at room temperature without loss of its activity (as bench top reagent). More ever the similar combinations, such as benzyltriphenylphosphonium chlorate<sup>16</sup>, which has already been reported show the stability of this compound. Benzylic alcohols were converted to their corresponding carbonyl compounds with I and II in good to high yields (scheme 1).

Sodium perchlorate and sodium chlorate are cheap and stable oxidizing agents. These are insoluble in non-aqueous solutions. Title reagents are quite soluble in DMF, DMSO and insoluble in nonpolar solvents such as carbon tetrachloride, n-hexane and diethyl ether. The effect of various solvents such as DMF, DCM, acetonitrile on the oxidation of 4-chlorobenzyl alcohol with I and II was examined (Table 4). DMF for I and II were found to be the best solvent. The oxidation of benzylic alcohols to their corresponding carbonyl compounds in

presence of different oxidants (I and II) were performed in good to excellent yields at the reflux condition (Table S1). All of the products were identified by the comparison of their physical and spectral data with those of authentic sample (melting and boiling point).<sup>5, 7</sup> Different benzyl alcohols were subjected to oxidations with I and II in DMF. This oxidation takes place under mild and quantitative conditions giving in good to excellent yields. The results showed that the reactivity of oxidant I is more than II. On the other hand the oxidation reactions in the presence of reagent I have high rates and accompany excellent yields under reflux conditions.

#### Conclusion

In this study, the syntheses, characterization and X-ray crystal structures of two new quaternary phosphonium salts of 1, 2-ethandiylbis(triphenylphosphonium) diperchlorate (**I**) and 1,2-ethandiylbis(triphenylphosphonium) dichlorate (**II**) have been reported with certain advantages over similar oxidizing agents in terms of stability, easy storage, short reaction time, easy preparation and high yields of the products. These reagents are stable for several months at room temperature without loss of their activities (Bench top reagents). The Hirshfeld surface analysis of crystal structures of titled compounds as well as analogous structures containing [EDBTPP]<sup>2+</sup> cationic unit obtained from CSD survey, revealed that the arrangement of aromatic rings around the P centers of cationic unit and tetrahedral geometry of phosphorous atom by  $\tau_4$  indices are related to the various intermolecular interactions of neighboring anionic moieties.

### **Experimental and methods**

#### Materials and methods

Alcohols, 1,2-dibromo ethane, triphenylphosphine, sodium perchlorate, sodium chlorate, chromium trioxide were purchased from Fluka and Merck Co and used without further purification. Solvents were purified by standard methods. Infrared spectra were recorded as KBr disk on a Shimadzu FT-IR 8440S spectrophotometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR (for products) were carried out on a Bruker AC, 300 MHZ spectrometer with tetra methyl silane as an internal reference and DMSO-d<sub>6</sub> and also CDCl<sub>3</sub> as solvents. GC spectra were recorded by a Shimadzu 17a-GC spectrometer. Elemental analysis was performed on a LECO 250 instrument. The reactions were monitored by TLC using Silica gel plates. The products were identified by comparison of their <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR and GC spectra and physical data with those of authentic samples.

# Preparation of 1, 2-Ethandiylbis(triphenylphosphonium) Diperchlorate(C<sub>38</sub>H<sub>34</sub>Cl<sub>2</sub>O<sub>8</sub>) (I)

1, 1'-(Ethane, 1, 2-Diyl)Ditriphenylphosphonium Dibromide  $(C_{38}H_{34}Br_2)^8$  (5 mmol, 3.56 g) in H<sub>2</sub>O (20 ml) was prepared in a 50 ml round bottomed flask with a magnetic stirrer. Then NaClO<sub>4</sub> (10 mmol, 1.225 g) in H<sub>2</sub>O (10 ml) was added to this solution, and the reaction was stirred at ambient temperature for 30 minute. The resulting white precipitate was filtered, washed with distilled water (2×10 ml) and dried in vacuum. (95% yields, 3.57g). m.p: 258-260 °C.

<sup>1</sup>H NMR (100 MHz, DMSO) :  $\delta$  (ppm) = 4 (d, CH<sub>2</sub>), 7.8, 7.98 (m, aromatic hydrogens) <sup>13</sup>C NMR (100 MHz, DMSO):  $\delta$  (ppm)135.8, 134.5, 129.8, 117, 15.6.

IR(KBr):  $\overline{\nu}$  (cm<sup>-1</sup>)= 689(s), 738(s), 1099(s), 1439(s), 1486,1589(m), 2917(w), 3064(w).

### Preparation of 1, 2-Ethandiylbis(triphenylphosphonium) Dichlorate(C<sub>38</sub>H<sub>34</sub>Cl<sub>2</sub>O<sub>6</sub>) (II)

1, 1'-(Ethane, 1, 2-Diyl)Ditriphenylphosphonium Dibromide  $(C_{38}H_{34}Br_2)^8$  (5 mmol, 3.56 g) in H<sub>2</sub>O (20 ml) was prepared in a 50 ml round bottomed flask with a magnetic stirrer. Then

NaClO<sub>3</sub> (10 mmol, 1.06 g) in H<sub>2</sub>O (10 ml) was added to this solution, and the reaction was stirred at ambient temperature for 1 h. The resulting white suspension was allowed to stand at room temperature for 1 week. Then the solution was filtered and dried in vacuum. (96% yields, 3.45g). m. p : 184-186  $^{\circ}$ C.

<sup>1</sup>H NMR (100 MHz, DMSO) :  $\delta$  (ppm) = 4 (d, CH<sub>2</sub>), 7.8, 7.95 (m, aromatic hydrogens).

<sup>13</sup>C NMR (100 MHz, DMSO):  $\delta$  (ppm) = 135,9, 134.5, 130.8, 117.8, 15,6.

IR(KBr):  $\overline{\nu}$  (cm<sup>-1</sup>)= 689(s), 741(s), 1110(s), 1436(s), 1482,1589(m), 2900(w), 2940 (m), 3064(w).

### Single crystal X-ray diffraction analysis

The suitable single crystals for X-ray diffraction analysis were obtained by slow evaporation at room temperature. Diffraction data for I and II crystals were collected at 100(2) K on Oxford Diffraction Excalibur PX Ultra diffractometer equipped with enhance ultra (Cu) Xray source and Onyx CCD detector. Data reduction and analysis for those structures were carried out with CrysAlisPro program v. 1.171.37.35.<sup>36</sup> X-ray The structures were solved by direct methods  $^{37}$  and subsequent different Fourier maps were used for refinement on F<sup>2</sup> by a full-matrix least-square procedure using anisotropic displacement parameters. The structures were checked for higher symmetry with the help of the program PLATON.<sup>38</sup> For title compounds, the non-H atoms were refined anisotropically and H-atoms were placed in the ideal positions. The structural resolution procedure was performed using WinGX crystallographic software package.<sup>39</sup> Summary of crystallographic data and structural refinement of titled compounds is presented in Table 5. CCDC 1577312-1577313 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, B2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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### **Figure Captions:**

**Figure 1** (a) ORTEP diagram and partial atom-numbering scheme represent asymmetric unit of I. The perchlorate anion (Cl1) with major occupation factor of 0.9 was only represented for more clarity. Displacement ellipsoids are given at 40% probability level. (b) C-H... $\pi$ interactions involving cation molecules of I along *b* direction. The intermolecular interactions are represented by dashed lines. (c) and (d) representations of selected intermolecular hydrogen bonds present in one dimensional hydrogen bonded chains in I. The hydrogen bonds are represented by dashed lines. The centroid of phenyl rings are called as Cg (No).

**Figure 2** (a) ORTEP diagram and partial atom-numbering scheme represent asymmetric unit of II. Displacement ellipsoids are given at 40% probability level. (b) C-H... $\pi$  interactions involving cation molecules of II in side view. The intermolecular interactions are represented by dashed lines. (c) and (d) representations of selected intermolecular hydrogen bonds present in one dimensional hydrogen bonded chains in compound II along *a* and *c* directions, respectively. The hydrogen bonds are represented by dashed lines. The centroid of phenyl rings are called as Cg (No).

Figure 3 Schematic illustrations of decomposed fingerprint plots of compounds I and II.

Figure 4 Representation of the Hirshfeld surfaces of compounds I and II, which mapped over  $d_{norm}$  and their related the 2D fingerprint plots. The CH···O interactions were presented by red spot in the upper section.

Figure 5 Fingerprint plots of twenty three structures obtained from the CSD analysis.

Scheme 1







Figure 2







D-HA	d(D–H)/Å	d(HA)/Å	d(DA)/Å	∠D–HA/°
Compound I				
C4-H4O2(i)	<mark>0.95</mark>	<mark>2.65</mark>	<b>3.572 (3)</b>	<mark>163.6</mark>
C8-H8O4	<mark>0.95</mark>	<mark>2.57</mark>	<mark>3.436 (2)</mark>	<mark>151.3</mark>
C19-H19AO7	<mark>0.99</mark>	<mark>2.34</mark>	<mark>3.188 (2)</mark>	<mark>143.4</mark>
C19-H19BO4	<mark>0.99</mark>	<mark>2.58</mark>	<mark>3.548 (3)</mark>	<mark>167.4</mark>
C20-H20BO5(ii)	<mark>0.99</mark>	<mark>2.42</mark>	<mark>3.396 (3)</mark>	<mark>169.6</mark>
C22-H22O3 (iii)	<mark>0.95</mark>	<mark>2.52</mark>	<mark>3.463 (3)</mark>	<mark>170.7</mark>
C24-H24O6 (ii)	<mark>0.95</mark>	<mark>2.67</mark>	<mark>3.325 (2)</mark>	<mark>126.5</mark>
C30-H30O3 (ii)	<mark>0.95</mark>	<mark>2.60</mark>	<mark>3.534 (2)</mark>	<mark>167.1</mark>
C32-H32O7	<mark>0.95</mark>	<mark>2.64</mark>	3.176 (2)	<mark>116.3</mark>
C36-H36O6 (iv)	<mark>0.95</mark>	<mark>2.43</mark>	3.380 (2)	<mark>174.9</mark>
C38-H38O3 (iii)	<mark>0.95</mark>	<mark>2.67</mark>	3.619 (3)	<mark>175.6</mark>
C24-H24Cl2(ii)	<mark>0.95</mark>	<mark>2.91</mark>	<b>3.714 (3)</b>	<mark>143.2</mark>
Compound II				
C3-H3O1(i)	<mark>0.95</mark>	<mark>2.47</mark>	<b>3.294 (2)</b>	<mark>144.9</mark>
C8-H8O2	<mark>0.95</mark>	<mark>2.55</mark>	<mark>3.314 (3)</mark>	<mark>137.5</mark>
C10-H10O1(ii)	<mark>0.95</mark>	<mark>2.59</mark>	<mark>3.281 (2)</mark>	<mark>129.8</mark>
C11-H11O3(ii)	<mark>0.95</mark>	<mark>2.60</mark>	<mark>3.547 (3)</mark>	<mark>171.4</mark>
C12-H12O3	<mark>0.95</mark>	<mark>2.46</mark>	<mark>3.339 (3)</mark>	<mark>154.1</mark>
C14-H14O1	<mark>0.95</mark>	<mark>2.49</mark>	<b>3.389 (4)</b>	<mark>158.2</mark>
C16-H16O3(iii)	<mark>0.95</mark>	<mark>2.62</mark>	3.290 (2)	<mark>127.9</mark>
C17-H17O2 (iv)	<mark>0.95</mark>	<mark>2.65</mark>	<mark>3.555 (3)</mark>	<mark>158.4</mark>
C18-H18O2 (iii)	<mark>0.95</mark>	<mark>2.52</mark>	<b>2.280 (3)</b>	<mark>137.6</mark>
C19-H19AO2	<mark>0.99</mark>	2.27	<mark>3.250 (2)</mark>	<mark>171.0</mark>

# Table 1. Selected hydrogen-bond parameters of compounds I and II

Symmetry codes, compound I: (i) -1+x, y, z ; (ii) 1/2-x,1/2+y,1/2-z; (iii) 1/2+x,1/2-y,1/2+z; (iv) -1/2+x,1/2-y,1/2+z, compound II: (i) 1-x, -y, 2-z; (ii) -1/2+x,1/2-y,-1/2+z; (iii) 1/2-x,1/2+y,1/2-z; (iv) -1/2+x,-1/2+y, z.

Table 2. CH… $\pi$  interaction geometries of I and II

CHπ Interaction	H…Cg/Å	C…Cg/Å	CH···Cg ∕°
Compound I			
C-H10…π(Cg2)*	<mark>2.720</mark>	3.427	<mark>131.77</mark>
C-H14…π(Cg4)	<mark>3.316</mark>	<mark>4.241</mark>	<mark>164.87</mark>
C-H23…π(Cg6)	<mark>3.694</mark>	<mark>4.565</mark>	<mark>153.67</mark>
C-H37…π(Cg1)	<mark>2.760</mark>	<mark>3.443</mark>	127.67
Compound II			
C-H6…π(Cg2)	<mark>3.435</mark>	<mark>4.121</mark>	<mark>130.94</mark>
C-H9…π(Cg3)	<mark>2.779</mark>	<mark>3.679</mark>	<mark>158.51</mark>

\* The centroid of phenyl rings are called as Cg (No).

No.	Refcode	[Counter anion] (solvent)	τ <sub>1</sub> (P1)	τ <sub>2</sub> (P2)	Δτ	H…H	C…C	C…H H…C	C…O O…C	O…H H…O	X…C C…X	X…H H…X	M…C C…M	M…H H…M	S…C C…S	S…H H…S	Ref
Ι	Compound I	2[ClO <sub>4</sub> ] <sup>-</sup>	0.971	0.974	- 0.003	41.3	2.7	25.0	2.8	28.2	-	-	-	-	-	-	This study
п	Compound II	$[ClO_3]^{2-}$	0.977	0.977	0.000	43.6	0.8	30.4	1.0	21.3	1.6	1.3	-	-	-	-	This study
1	BORJEX	$\frac{[C_{26}O_{24}Ru_{10}]^{2}}{2(C_{3}H_{6}O)}$	0.975	0.984	- 0.008	26.0	1.3	12.4	8.4	51.9	-	-	-	-	-	-	<mark>40</mark>
2	DUGKOG	$\frac{[Cl_8O_3Re_2]^2}{4(CHCl_3)}$	0.992	0.992	0.000	18.9	0.1	11.2	1.2	5.2	12.2	51.1	-	-	-	-	<mark>41</mark>
3	DUGLEX	$\left[\mathrm{Cl}_{8}\mathrm{O}_{3}\mathrm{Re}_{2}\right]^{2}$	0.985	0.985	0.000	38.9	3.1	18.9	1.2	4.9	4.8	28.2	-	-	-	-	<mark>41</mark>
4	EGAVAL	$2[CH_4Cl_4O_2Re]^{-1}$	0.965	0.965	0.000	45.2	1.3	19.4	1.1	7.1	3.5	22.4	-	-	-	-	<mark>42</mark>
5	HADWIT	$2[C_4H_{22}B_{18}C_0]^{-1}$	0.979	0.992	0.013	78.3	0.2	21.5	-	-	-	-	-	-	-	-	<mark>43</mark>
6	HISPOO	$\frac{[C_{27}H_4O_{22}Ru_{10}]^2}{2(C_3H_6O)}$	0.970	0.970	0.000	32.1	1.3	15.0	6.3	45.3	-	-	-	-	-	-	<mark>44</mark>
7	HISPUU	$\frac{\left[C_{28}H_8O_{20}Ru_{10}\right]^{2}}{2(C_3H_6O)}$	0.967	0.935	0.032	33.8	1.3	15.4	6.4	43.1	-	-	-	-	-	-	<mark>44</mark>
8	JEGZEB*	$\frac{1.33(C_6H_{12}O_2)}{2(C_2H_6O)}$	-	-	-	47.8	5.8	24.9	1.2	13.4	-	6.8	-	-	-	-	<mark>45</mark>
9	JEGZIF*	$\frac{2[Br]^{-}}{2(C_{6}H_{12}O_{3})}$	-	-	-	-	-	-	-	-	-	-	-	-	-	-	<mark>45</mark>
10	MOZQAV*	2[BF <sub>4</sub> ]	0.986	0.981	0.005	46.2	0.1	22.4	-	-	3.1	28.2	-	-	-	-	<mark>46</mark>
11	NIPTUB	$\left[\mathrm{Cl}_{8}\mathrm{Re}_{2}\right]^{2}$	0.985	0.986	0.001	41.6	2.1	24.5	-	-	2.8	2.7	0.4	1.5	-	-	<mark>47</mark>
12	NIPVAJ	$\left[\mathrm{Cl}_{8}\mathrm{Os}_{2}\right]^{2}$	0.946	0.962	- 0.016	44.8	2.1	19.4	-	-	4.2	29.2	0.3	-	-	-	<mark>47</mark>
13	SONKAH	$\frac{[C_{38}H_{10}O_{22}Ru_{10}]^{2}}{2(C_{3}H_{6}O)}$	0.983	0.984	0.001	23.7	5.0	15.1	9.5	46.8	-	-	-	-	-	-	<mark>48</mark>
14	UNUREB	$2[IO_4]^{-1}$	0.988	0.975	0.013	39.8	2.3	22.5	3.8	31.4	-	0.1	-	-	-	-	<mark>49</mark>
15	IWUWAA	[O <sub>8</sub> S <sub>2</sub> ] <sup>2-</sup> 2(H <sub>2</sub> O)	0.994	0.986	0.008	48.9	3.1	25.4	1.8	20.8	-	-	-	-	-	-	26
16	UWOVOT	$2[Br_3]$	0.982	0.982	0.000	41.7	1.6	25.9	-	-	4.2	26.7	-	-	-	-	25
17	<b>SALKAU</b>	2[AuCl <sub>2</sub> ]	<mark>0.968</mark>	<mark>0.999</mark>	- <mark>0.031</mark>	<mark>52.1</mark>	<mark>0.4</mark>	<mark>18.1</mark>	·	-	<mark>3.8</mark>	<mark>17.2</mark>	<mark>3.0</mark>	<mark>5.3</mark>	•	-	<mark>50</mark>
18	AZUZOM	2[AuCl <sub>4</sub> ] <sup>-</sup>	<mark>0.991</mark>	<mark>0.992</mark>	- 0.001	<mark>39.7</mark>	<mark>2.2</mark>	<mark>19.0</mark>	-	-	<mark>4.3</mark>	<mark>31.6</mark>	<mark>2.7</mark>	<mark>0.6</mark>	-	-	<mark>51</mark>
19	AZUZIG	2[C <sub>2</sub> H <sub>6</sub> Cl <sub>3</sub> OPdS] <sup>-</sup>	<mark>0.964</mark>	<mark>0.964</mark>	0.000	<mark>47.7</mark>	<mark>1.4</mark>	<mark>30.7</mark>	<mark>1.4</mark>	<mark>4.1</mark>	<mark>0.2</mark>	<mark>13.4</mark>	<mark>0.4</mark>	<mark>0.7</mark>	•	-	<mark>52</mark>
20	AZUXUQ	(C <sub>2</sub> H <sub>6</sub> OS) 2[I <sub>3</sub> ] <sup>-</sup>	<mark>0.994</mark>	<mark>0.982</mark>	<mark>0.012</mark>	<mark>47.2</mark>	<mark>0.5</mark>	<mark>21.1</mark>	<mark>0.7</mark>	<mark>3.2</mark>	<mark>3.0</mark>	<mark>23.8</mark>	-	·	<mark>0.2</mark>	<mark>0.2</mark>	<mark>53</mark>
21	<b>AZUSEV</b>	$\frac{4(C_2H_6OS)}{[Cl_6Pt]^{2}}$	<mark>0.965</mark>	<mark>0.977</mark>	- <mark>0.012</mark>	<mark>30.7</mark>	<mark>3.3</mark>	<mark>29.1</mark>	<mark>2.4</mark>	<mark>11.6</mark>	•	<mark>14.9</mark>	<mark>1.0</mark>	H	<mark>2.5</mark>	<mark>4.6</mark>	<mark>54</mark>
22	AZOYEV	$\left[\mathrm{Ag}_{2}\mathrm{Cl}_{4}\right]^{2}$	<mark>0.969</mark>	<mark>0.969</mark>	<mark>0.000</mark>	<mark>46.7</mark>	-	<mark>28.4</mark>	-	-	<mark>1.4</mark>	<mark>18.2</mark>	<mark>1.4</mark>	<mark>3.8</mark>	-	-	<mark>55</mark>
23	BORJEX10	$\frac{[C_{26}O_{24}Ru_{10}]^{2}}{2(C_3 H_6 O)}$	<mark>0.975</mark>	<mark>0.984</mark>	- <mark>0.008</mark>	<mark>26.0</mark>	<mark>1.3</mark>	<mark>12.4</mark>	<mark>8.4</mark>	<mark>51.9</mark>	•	ł	ł	•	ł	-	<mark>56</mark>

**Table 3**. Relative contribution of various atom pair contacts to the Hirshfeld surface area compounds I and II and twenty three structures including the [EDBTPP]<sup>2+</sup> cationic unit obtained from the CSD analysis

\*disorder structure- M= Metal - X= Halogen

# Table 4. The optimized oxidation conditions of 4-chlorobenzyl alcohol by using the various

oxidants in different solvents.

Entries	Solvent	Туре о		
		Yield (		
		Ι	II	
1	DMF	98 (5min)	95 (5min)	
2	$CH_2Cl_2$	65 (70min)	10 (<5min)	
3	CHCl <sub>3</sub>	N. R.	N. R.	
4	CH <sub>3</sub> CN	90 (15min)	30 (25min)	
5	THF	N. R.	N. R.	
6	n-Hexane	N. R.	N. R.	

1:1 Molar ratio of substrate to oxidant at the reflux condition

compound	Ι	II
chemical formula	$(C_{38}H_{34}P_2) \cdot 2(ClO_4)$	$(C_{38}H_{34}P_2) \cdot 2(ClO_3)$
M <sub>r</sub>	751.49	719.49
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, C2/c
Temperature (K)	100(2)	100(2)
a (Å)	8.9446(1)	13.10880(10)
b (Å)	17.6952(1)	14.47530(10)
c (Å)	21.8856(2)	18.3261(2)
β (°)	94.301(1)	98.0420(10)
V (Å <sup>3</sup> )	3454.22(5)	3443.25(5)
Z	4	4
Radiation type	CuKa	CuKa
$\mu ({\rm mm}^{-1})$	3.024	2.963
Crystal size (mm)	$0.2 \times 0.5 \times 0.5$	$0.2 \times 0.3 \times 0.6$
Diffractometer	Xcalibur, Onyx, Ultra	Xcalibur, Onyx, Ultra
Absorption correction	Multi-scan	Multi-scan
No. of measured, unique	<mark>24228, 6332</mark>	47119, 3180
GOOF	<mark>1.040</mark>	1.057
$R_1(I>2\sigma(I))$	0.0487	<mark>0.0383</mark>
$WR_2(I>2\sigma(I))$	0.1252	<mark>0.1023</mark>
Largest diff. peak and hole $[e/Å^3]$	1.640 and -0.530	0.370 and -0.460

**Table 5.** Structural data and refinement for title compounds

- Two new quaternary phosphonium salts of perchlorate (I) and chlorate (II) have been synthesized and characterized.
- The Hirshfeld surface analysis of crystal structures of titled compounds as well as analogous structures obtained from CSD revealed that the arrangement of phenyl rings around the P centers and  $\tau_4$  tetrahedral geometry indices are related to the various intermolecular interactions of neighboring moieties.
- Crystal packing in both compounds is mostly governed by hydrogen bond which assisted by  $\pi$ -based interactions.