

Short Note

Dicyclohexylammonium *O,O'*-Diphenyl Phosphate, [(C₆H₁₁)₂NH₂][(C₆H₅O)₂P(O)(O)]: Spectroscopic Study, Crystal Structure, and Hirshfeld Surface Analysis

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Abstract: The title salt, [(C₆H₁₁)₂NH₂][(C₆H₅O)₂P(O)(O)], crystallizes in the chiral space group *P*2₁2₁2₁, composed of achiral cation and anion components. The strong charge-assisted N–H ... O hydrogen bonds build a linear assembly along the *a* axis, including a non-centrosymmetric C₂²(6) chain graph-set motif. The intra and intermolecular C–H ... O interactions as well as the C–H ... π-electron ring interactions also exist in the crystal structure. Fingerprint plots are used for a detailed investigation of intermolecular interactions participating in the crystal packing. The spectroscopic features (IR, ¹H NMR, ¹³C{¹H} NMR, ³¹P{¹H} NMR, and mass) are studied.

Keywords: phosphate; X-ray structure analysis; chiral space group; charge-assisted hydrogen bond; NMR

1. Introduction

The charge-assisted hydrogen bonds were observed in some cation–anion compounds including phosphorus–oxygen-based anions. Typical examples are the [(Cl)₂P(O)(O)][−] anion and also the anions with the (S)(O)P(O)(O), (C)₂P(O)(O), (C)(N)P(O)(O), and (O)P(O)(S)(S) skeletons [1–4]. The Cambridge Structural Database (CSD) survey was investigated to compare the hydrogen bond strengths in some phosphate-based classes of salts and neutral closely related structures [4].

The chiral crystal structures from chiral or achiral molecules/components were also studied, and the diversity of hydrogen bond motifs was investigated [5–7].

In this article, the chiral crystal structure [(C₆H₁₁)₂NH₂][(C₆H₅O)₂P(O)(O)], including achiral components, is investigated, and the synergistic cooperation of N–H ... O, C–H ... O, and C–H ... π interactions in the crystal packing is discussed. The synthesis procedure and spectroscopic characterization of the title compound are detailed. A comparison of the cation and anion components of the title salt with the structures including similar components from the CSD is presented.

2. Results and Discussion

2.1. Structure Description

The title compound crystallizes in the orthorhombic system with chiral space group $P2_12_12_1$, and the asymmetric unit is composed of one cation and one anion components (Figure 1). Selected bond distances and angles are given in Table 1. In general, all bond distances are within the characteristic values according to the atoms involved and are in the ranges of similar bonds observed in analogous structures. For example, the phosphorus–oxygen bond lengths of the $[P(O)(O)]^-$ segment are 1.469(2) and 1.459(2) Å, which are slightly more than the typical $P=O$ bond length (1.45 Å) [8].

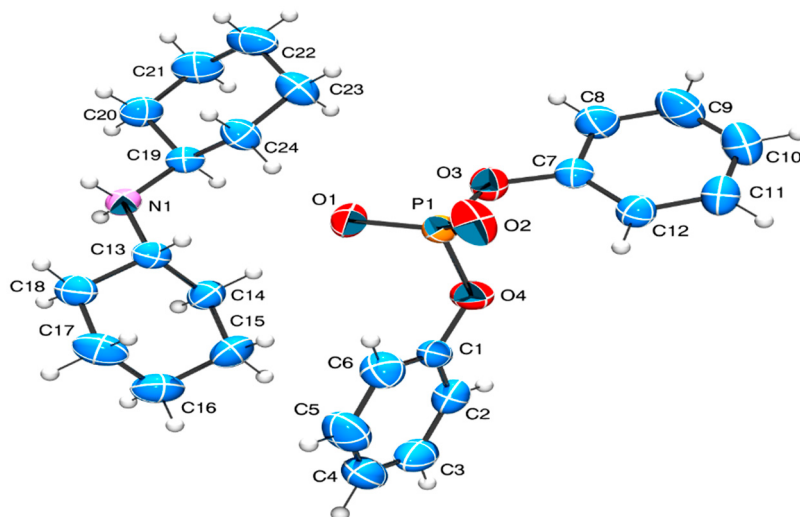


Figure 1. The structure of $[(C_6H_{11})_2NH_2][(C_6H_5O)_2P(O)(O)]$, showing the atom-numbering scheme for non-hydrogen atoms and displacement ellipsoids at the 50% probability level. Hydrogen atoms are drawn as spheres of arbitrary radii.

Table 1. Selected bond distances (Å) and angles (°).

Bond Distances			
O1–P1	1.469(2)	C1–O4	1.382(3)
P1–O2	1.459(2)	C7–O3	1.374(3)
O3–P1	1.602(2)	C13–N1	1.499(4)
O4–P1	1.623(2)	C19–N1	1.506(4)
Angles			
O2–P1–O1	119.96(12)	O3–P1–O4	96.31(11)
O1–P1–O3	106.78(12)	C7–O3–P1	126.80(18)
O2–P1–O3	111.27(13)	C1–O4–P1	124.5(2)
O1–P1–O4	109.86(12)	C13–N1–C19	118.1(2)
O2–P1–O4	110.05(15)	C2–C1–O4	115.1(3)

In the cation, the cyclohexyl rings adopt a chair conformation, and the NH_2 unit is situated in the equatorial position with respect to the rings. The large $C-N-C$ angle, of $118.1(2)^\circ$, is a result of the steric bulk of the cyclohexyl rings, as has been also observed in the structures with the same cation, typically in $[(C_6H_{11})_2NH_2][C_6H_5PO_2(OH)]$ (with CSD refcode ZARGOQ and the $C-N-C$ angle of $118.80(10)^\circ$) [9].

In the anion, the phosphorus atom has a distorted tetrahedral $(O)_2P(O)(O)$ environment, with the bond angles within $96.31(11)^\circ$ and $119.96(12)^\circ$. These extreme values correspond to the $O3-P1-O4$ and $O2-P1-O1$ angles, respectively (O1 and O2 are the atoms in the $[P(O)(O)]^-$ segment; O3 and O4 are the ester oxygen atoms). Similar trends of $O-P-O$ angles were observed in structures with

$[(C_6H_5O)_2P(O)(O)]^-$ anion, like for example the structures with the CSD refcodes PABMUA and PABNAH [10]. The P–O–C angles of $124.5(2)^\circ$ and $126.80(18)^\circ$ show a few more “s” characters with respect to the sp^2 hybridization. These values in the anion with a $(C-O)_2(O)P(O)$ core are in accordance with the previously reported P–O–C angles, typically in the $(C-O)_2P(X)(N)$ -based structures ($X = O, S$) [3] deposited in the CSD. The similarities and differences of cations and anions in the title structure with the selected related structures in the CSD are compared and discussed in Section 2.2.

In the crystal structure of the title compound, the cations and anions are hydrogen-bonded to each other, through N–H ... O hydrogen bonds ($N1 \dots O1 = 2.806(3)$ Å and $N1 \dots O2 = 2.730(3)$ Å), building a linear arrangement along the *a* axis (Figure 2, Table 2). This assembly includes the non-centrosymmetric $C_2^2(6)$ graph-set motif. The strength of N–H ... O hydrogen bonds is a result of the assistance of positive and negative charges in hydrogen bonding interactions.

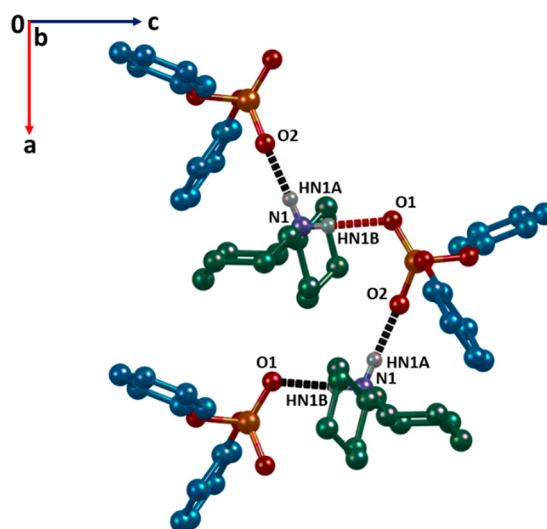


Figure 2. A view of the one-dimensional array of the title cation–anion compound built from N–H ... O hydrogen bonds. Color keys are red O, orange P, dark blue N; the C atoms of cation and anion components are shown as green and blue colors, respectively. The carbon-bonded hydrogen atoms were omitted for the sake of clarity, and the hydrogen bonds are shown as dashed lines.

Table 2. Hydrogen bond geometries (e.s.d.s are given in parentheses).

<i>D</i> –H ... <i>A</i>	<i>D</i> –H (Å)	H ... <i>A</i> (Å)	<i>D</i> ... <i>A</i> (Å)	$\angle D$ –H ... <i>A</i> ($^\circ$)
N1–HN1B ... O1#1	0.83(3)	1.97(3)	2.806(3)	177(3)
N1–HN1A ... O2#2	0.90(3)	1.84(3)	2.730(3)	176(3)
C12–H12 ... O4	0.93	2.62	3.139(4)	115.8
C24–H24B ... O2#1	0.97	2.65	3.548(4)	154.9
C11–H11 ... Cg1#3	0.93	2.80	3.629(3)	149
C15–H15B ... Cg1#4	0.97	2.97	3.664(4)	130
C15–H15A ... Cg2#4	0.97	2.95	3.765(4)	142

Symmetry codes: #1 $x - 1/2, -y + 1/2, -z + 2$; #2 $x - 1, y, z$; #3 $-x + 2, y + 1/2, -z + 3/2$; #4 $-x + 1, y - 1/2, -z + 3/2$.

In addition, the crystal packing shows one weak intermolecular C–H ... O hydrogen bond ($C24 \dots O2 = 3.548(4)$ Å), and one intramolecular C–H ... O hydrogen bond ($C12 \dots O4 = 3.139(4)$ Å) (Table 2). The C–H ... O interactions do not extend the dimensionality of hydrogen bond pattern made by N–H ... O hydrogen bonds. Figure 3 indicates a view of crystal packing with the relevant N–H ... O and C–H ... O hydrogen bonds. This assembly includes an $R_2^2(8)$ hydrogen-bonded ring motif, made by the cooperation of $N1$ – $HN1B \dots O1$ and $C24$ – $H24B \dots O2$ hydrogen bonds. The two phenyl rings of the anion also involved in the C–H ... π -electron ring interactions, as the acceptors;

the geometries are given in Table 2. The C–H ... π interactions network is also formed along the *a* axis (Figure 4). In all contacts noted, the acceptor sites (O, π) belong to the anion.

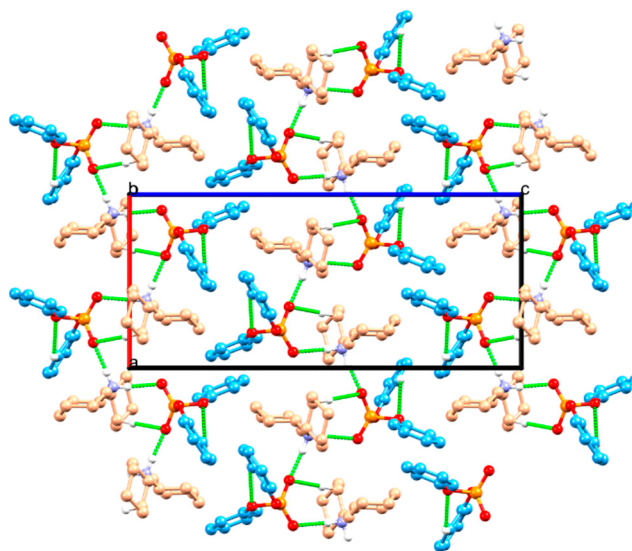


Figure 3. The molecular interactions of $[(C_6H_{11})_2NH_2][(C_6H_5O)_2P(O)(O)]$ viewed along the *b* direction. Intra and intermolecular C–H ... O interactions are shown along with the strong N–H ... O intermolecular interactions. Hydrogen atoms not involved in the interactions are omitted for the sake of clarity, and the hydrogen bonds are shown as dashed lines. Color keys are red O, orange P, blue N; the C atoms of cation and anion components are shown as gold-orange and light blue colors, respectively.

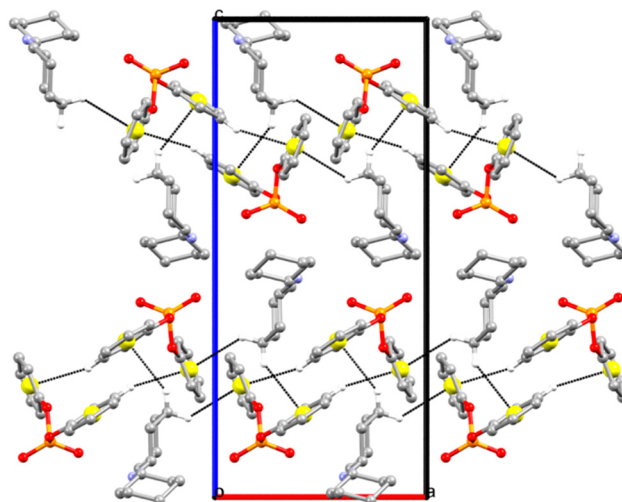


Figure 4. The C–H ... π interactions of $[(C_6H_{11})_2NH_2][(C_6H_5O)_2P(O)(O)]$ viewed along the *b* direction. Only the hydrogen atoms participating in C–H ... π interactions are shown, and the C–H ... π interactions are represented by dashed lines. Color keys are red O, orange P, blue N, gray C, and yellow for centroid of the phenyl ring.

2.2. Structural Comparison

CSD study has been carried out to understand the similarities and conformational changes of the title compound. Fourteen structures (CSD REFCODES: CADGUJ [11], EFUMEX [12], GAGQOV [13], HAXRAZ [14], JOXMAK [15], LOKGUN [16], OBOTOQ [17], TEDFIR [18], WILKOR [19], YIWXOR [20], ZALTEL [21], ZALTIP [21], ZARGOQ [9], and ZETHIP [2]) containing the cation “dicyclohexylammonium” moiety were retrieved from the CSD. The bond lengths

(Supplementary Table S1, Figure 5A), selected bond angles (Supplementary Table S2, Figure 5B), and selected torsion angles C14–C13–N1–C19 and C24–C19–N1–C13 (Supplementary Table S3, Figure 6) of the cation component are compared with the literature. From the results, it is evident that the bond lengths of dicyclohexylammonium moiety of the title compound are well-matched with the reported literature values (Figure 5A). The bond angles C13–N1–C19 (118.1°), C14–C13–N1 (111.2°), C18–C13–N1 (108.0°), C20–C19–N1 (107.1°), and C24–C19–N1 (112.3°) match the average bond angles calculated from the literature data as well (Figure 5B).

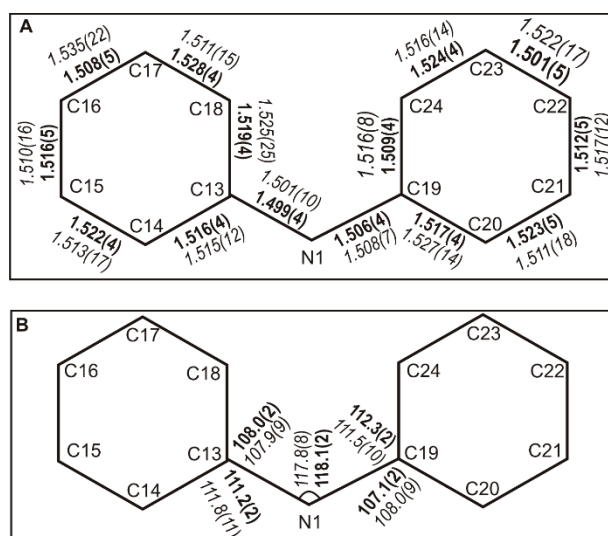


Figure 5. Structural comparison of the cation moiety of the title compound. (A) Bond lengths of the dicyclohexylammonium moiety are shown with the average literature values extracted from the Cambridge Structural Database (CSD). (B) Selected bond angles of the cation moiety of the title compound are marked with the literature values. The bond lengths and angles of the title compound are shown in boldface and the average bond lengths, and bond angles calculated from the 14 model structures extracted from the CSD are shown in normal italic.

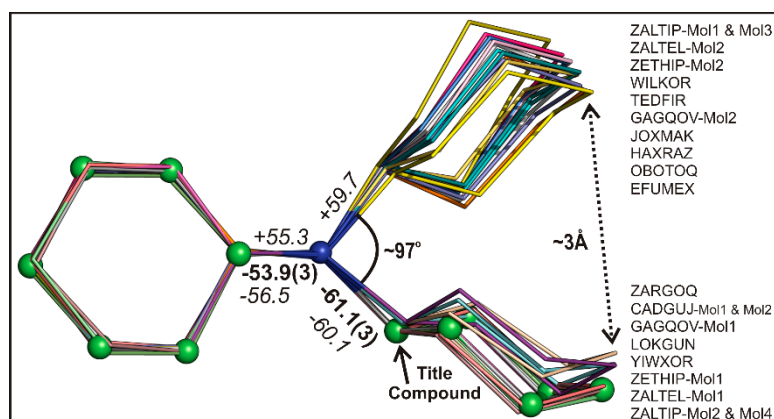


Figure 6. Conformational flexibility of cyclohexyl rings. The cation moiety of the title compound is shown in a ball-and-stick model, and carbon atoms are colored green. The remaining structures are shown in a simple line model. Molecules are marked using CSD REFCODES and molecules with more than one model in the asymmetric unit are marked as Mol1, Mol2, etc. The figure is rendered using PyMOL [22].

The conformational changes of the two cyclohexyl rings are compared with the structures retrieved from the CSD and superimposed with the cation moiety of the title compound. The structures were superimposed with one of the cyclohexyl rings including the nitrogen atom

(N1–C19–C20–C21–C22–C23–C24) as shown in Figure 6. Two significant conformational flexibilities were observed among these structures. The cation moiety of the title compound adopts a $-sc$ (synclinal) conformation with the torsion angles C14–C13–N1–C19 and C24–C19–N1–C13 of $-61.1(3)^\circ$ and $-53.9(3)^\circ$, respectively, which bear a resemblance to the average literature values (Supplementary Table S3, and Figure 6). Ten molecules arising from the eight structures CADGUJ (Molecules 1 and 2), GAGQOV (Molecule 1), LOKGUN, YIWXOR, ZALTEL (Molecule 1), ZARGOQ, ZALTIP (Molecules 2 and 4), and ZETHIP (Molecule 1) adopt similar conformation as the title compound while remaining structures adopt +synclinal conformation. The distance of rings between the two groups is found to be ~ 3.0 Å with an approximate angle of 97° (Figure 6).

The bond lengths excluding the two phenyl rings, selected bond angles, and torsion angles representing Ph–O parts of the anion moiety of the title compound were compared with the reported structures extracted from the CSD. The 12 model structures (CSD REFCODES: CUVSUB [23], DUWWEX [24], ETADIM [25], FAGLEE [26], FAWYOR [27], HUHTEJ [28], OFESID [29], PABMUA [10], PABNAH [10], RUXWOY [30], VOVCYO [31], and ZOXYEN [32]) containing anion “diphenyl phosphate” were retrieved from the CSD. Figure 7 shows the distances of the C–O (C1–O4, C7–O3), P–O_{Ph} (P1–O3, P1–O4), P–O (non-ester; P1–O1, P1–O2) (Supplementary Table S4), and O–P–O bond angles with the reported literature values. The bond lengths and bond angles that correspond to phosphate geometry are favorably comparable with the reported literature.

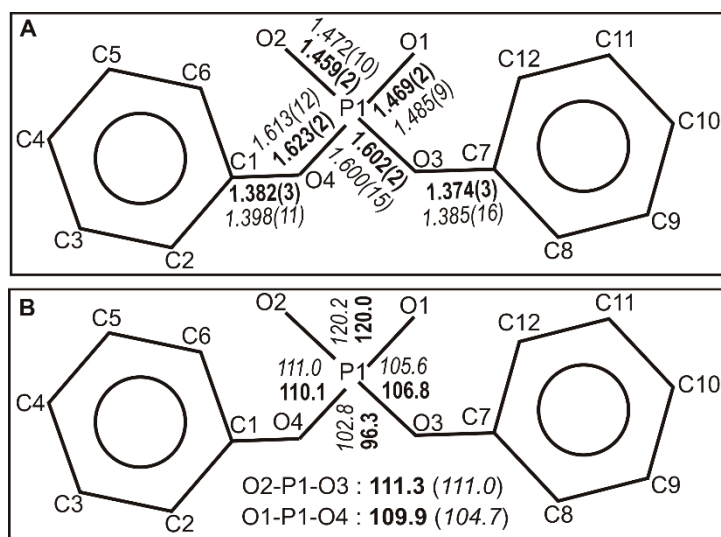


Figure 7. Structural comparison of the anion moiety, diphenyl phosphate, of the title compound. (A) Bond lengths of the diphenyl phosphate moiety, except for two phenyl rings, are shown and compared with the literature values extracted from the CSD. (B) Selected bond angles of the anion moiety of the title compound are marked with the literature values. The bond lengths and angles of the title compound are shown in boldface and the average bond lengths, and bond angles calculated from the 12 model structures extracted from the CSD, are shown in normal italic.

The torsion angles C7–O3–P1–O4 (-72.5°), and C1–O4–P1–O3 (-163.3°) of the diphenyl phosphate moiety of the title compound represent $-synclinal$ and $-antiperiplanar$ conformations, respectively. Superposition of the structures extracted from CSD with the anion moiety of the title compound based on O3–P1–O4 atoms shows two significant conformational flexibilities (Figure 8A). While the torsion angles representing C7–O3–P1–O4 of the entire structures show either $-sc$ or $+sc$ conformation, the torsion angles for C1–O4–P1–O3 show $\pm ap$, $\pm sc$, and $\pm ac$ conformations (Supplementary Table S6). The torsional angles of C7–O3–P1–O4 in the six CSD structures FAGLEE (Molecules 1 and 4), CUVSUB, FAWYOR (Molecule 2), PABMUA, RUXWOY, and ZOXYEN (Molecule 1) including the title compound adopt $-synclinal$ conformation (Figure 8B). Superposition of these molecules with the title compound shows that FAGLEE (Molecule 1) is very close to the

title compound, and the remaining molecules in this group are slightly deviated and clustered together, except ZOXYEN (Molecule 1). While one of the phenyl rings of the ZOXYEN adopts *skew* (−sc) conformation, the other one adopts *trans* (+ap) conformation. Thus, one of the phenyl rings of the ZOXYEN remarkably deviates from the other structures in this group (Figure 8B). The remaining molecules FAGLEE (Molecules 2 and 3), DUWWEX, ETADIM, HUHTJ, OFESID, FAWYOR (Molecule 1), VOVCOY, PABNAH, and ZOXYEN (Molecule 2) are clustered into other groups based on the C7–O3–P1–O4 torsion angle (+sc) conformation (Figure 8C, Supplementary Table S6). In this group, ETADIM, FAGLEE (Molecule 2), HUHTJ, OFESID, FAWYOR (Molecule 1), and VOVCOY molecules adopt similar conformation (+sc), Figure 8B, and the DUWWEX molecule adopts +ac conformation. The FAGLEE (Molecule 3) adopts +ap conformation, PABNAH, and ZOXYEN (Molecule 2) molecules both adopt −ac conformation, and these three structures are slightly deviating from other structures in this cluster (Figure 8C).

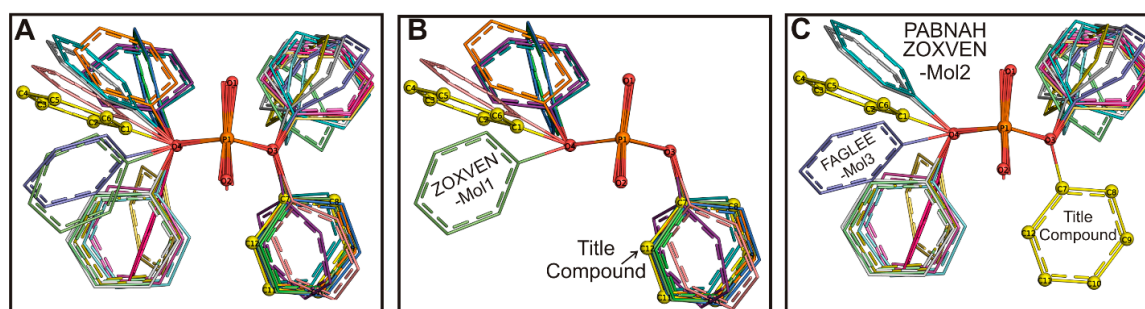


Figure 8. Structural comparison of diphenyl phosphate moiety of the title compound with the literature. (A) Superposition of diphenyl phosphate moieties extracted from the CSD with the title compound. The title compound is shown in yellow (carbon atoms), ball-and-stick model. Based on the torsional angle C7–O3–P1–O4, two major conformational flexibilities −sc and +sc were observed. The models representing −sc group are shown in (B), and the models that adopt +sc are shown in (C). The deviating models in both groups are marked.

Thus, comparison of the cation and anion moieties of the title compound with the similar structures available in the CSD indicates that the title compound is well-matched with the reported literature.

2.3. Hirshfeld Surface Analysis and Fingerprint Plots

The Hirshfeld surface analysis, which uses three-dimensional (3D) surfaces functions, as well as two-dimensional (2D) fingerprint plots [33,34], is a very useful graphical tool for identification and understanding of intermolecular interactions within a crystal structure. The Hirshfeld surfaces mapped with d_{norm} and corresponding shape index associated 2D fingerprint plots of the cation and anion of the title structure were generated using the *Crystal Explorer* software version 3.1 [35], with the structure file in the CIF format as the input.

In the Hirshfeld surfaces of the cation and anion, two large red areas can be seen, which correspond to two intermolecular N–H···O hydrogen bonds, as noted in the crystal structure section. The Hirshfeld surface map is typically represented for the anion and labels 1 and 2 denote to the hydrogen bonds noted (Figure 9); the Hirshfeld surface of the cation represents similar red areas with the hydrogen-bond donor sites, i.e., NH units, within the surface.

Two-dimensional fingerprint plots of the cation and anion are derived from the Hirshfeld surfaces, by plotting the fraction of points on the surface as a function of (d_e , d_i), where d_e and d_i introduce the distances from a point on the Hirshfeld surface to the nearest atoms outside and inside the surface, respectively. The full fingerprint plots of the cation and anion are given in Figure 10. The full plots were also divided into the figures illustrating different contacts observed in the crystal (Figure 11).

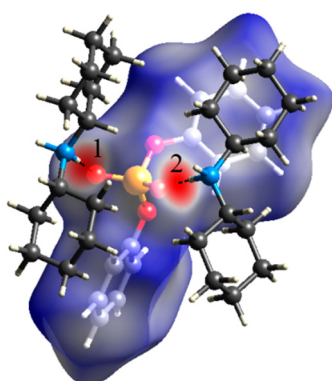


Figure 9. A view of the Hirshfeld surface map of the $[(\text{C}_6\text{H}_5\text{O})_2\text{P}(\text{O})(\text{O})]^-$ anion. The interactions according to the labels are as follows, with the labels in parentheses: N1–HN1B ... O1 (1) and N1–HN1A ... O2 (2). The ball-and-stick models of the anion and two hydrogen-bonded cations are given inside and outside the surface, respectively.

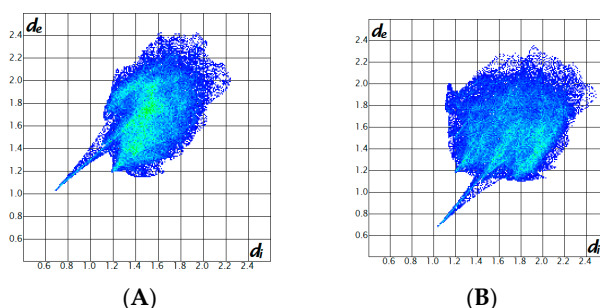


Figure 10. Full fingerprint plot of the cation (A) and anion (B).

According to divided fingerprints, the contribution portions of contacts received by the cation are $\text{H}\cdots\text{H}$ 72.7%, $\text{H}\cdots\text{O}$ 13.7%, and $\text{H}\cdots\text{C}$ 13.5%. Similar contacts in the anion have the contribution portions of 54.2%, 22.9%, and 22.8%, respectively. Furthermore, a minor $\text{P}\cdots\text{H}$ contact is also seen for the anion with the contribution portion of 0.1%. In the fingerprint plots, the $\text{H}\cdots\text{O}$ contacts develop as one sharp spike, indicating the closest interaction in the crystal.

2.4. Spectroscopic Study

In the IR spectrum of the title salt, the intense doublet band with the maxima at 1239 and 1224 cm^{-1} is assigned to phosphorus–oxygen stretches of the $[\text{P}=\text{O}(\text{O})]^-$ moiety. The broad overlapped bands within 2471 to 3016 cm^{-1} are assigned to NH stretching frequencies, aliphatic and aromatic CH stretching frequencies, and the overtone of stretching frequencies of the phosphorus–oxygen bonds in the $[\text{P}=\text{O}(\text{O})]^-$ moiety. The broadening of these overlapped bands is related to strong $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds as were discussed in the X-ray description.

The ^{31}P signal appears at -12.70 ppm, in comparison with the values of -11.7 ppm in the cation–anion compound $[\text{3-Cl-C}_6\text{H}_4\text{NH}_3][(\text{C}_6\text{H}_5\text{O})_2\text{P}(\text{O})(\text{O})]$ [30] and -0.81 ppm in the neutral compound $(\text{C}_6\text{H}_5\text{O})_2((\text{C}_6\text{H}_5)(\text{CH}_3)\text{CHNH})\text{P}(\text{O})$ [36]. The relatively high negative value is attributed to shielding caused by the negative charge on the oxygen atom. In the ^1H NMR, the signal at 8.80 ppm corresponds to the NH_2 protons, and the downfield chemical shift is due to the hydrogen bonding effect, similar to the one that was reported for a compound exhibiting hydrogen bonding in the X-ray structure [37]. The aliphatic and aromatic protons appear within 1.01 to 2.97 ppm and 7.02 to 7.28 ppm, as expected. In the ^{13}C NMR spectrum, the doublet signals at 153.87 ($^2J_{\text{PC}} = 7.0$ Hz) and 120.34 ppm ($^3J_{\text{PC}} = 5.1$ Hz) are related to the *ipso*- and *ortho*- carbon atoms of C_6H_5 ring. The other six signals are singlet.

The mass spectrum indicates the peaks at $m/z = 248$, 247, 182, and 180, respectively attributed to the cations with formulas of $[(C_6H_5O)_2P(O)(O) - H]^+$, $[(C_6H_5O)_2P(O)(O) - 2H]^+$, $[(C_6H_{11})_2NH_2]^+$, and $[(C_6H_{11})_2N]^+$.

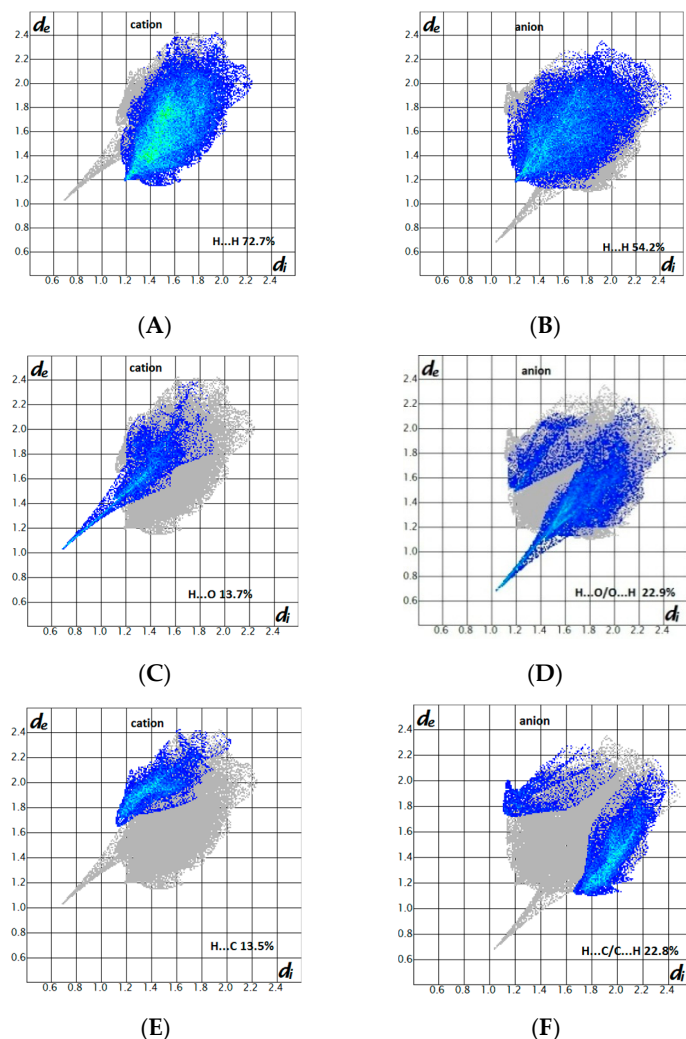


Figure 11. Divided fingerprint plots for the cation and anion components of the title salt: H... H of cation (A), H... H of anion (B), H... O of cation (C), H... O of anion (D), H... C of cation (E) and H... C of anion (F).

3. Materials and Methods

3.1. Synthesis of $[(C_6H_{11})_2NH_2][(C_6H_5O)_2P(O)(O)]$

General procedure for the preparation of some dicyclohexylammonium di(*para*-substituted phenyl) phosphates was reported, together with the melting points and elemental analyses of different derivatives such as the title salt, i.e., with the *para*-substituent H [38]. The synthesis method was based on the reaction of *N*-methylpyridinium di(*para*-substituted phenyl) phosphates) with HCl and dicyclohexylamine. The title salt reported in this article is the product obtained from hydrolysis in the synthesis process in a different reaction condition, as follows. A solution of dicyclohexylamine (1 mmol) and triethylamine (1 mmol) in acetonitrile was added to a solution of diphenylphosphoryl chloride (1 mmol) in the same solvent (at 273 K) under stirring. After 4 h, the mixture was transferred to a beaker in order to evaporate the solvent at room temperature over the course of a few days. The solid which formed was washed with distilled water and dried. Single crystals (yellow needles) were obtained from a solution of the product in a methanol–acetonitrile (1:1 *v/v*) mixture at room

temperature. Yield: 80%. Mp: 188 °C (decomp.) (in literature: 188 to 189.5 °C [38]). Anal. Calc. for $C_{24}H_{34}NO_4P$: C, 66.80; H, 7.94; N, 3.25. Found: C, 66.57; H, 7.90; N, 3.27. 1H NMR (DMSO- d_6 , 300.8 MHz): δ 8.80 (s, 2H, NH), 7.28 (apparent-t, J = 7.7 Hz, 4H), 7.16 (d, J = 7.8 Hz, 4H), 7.02 (t, J = 7.2 Hz, 2H), 2.97 (m, 2H), 1.01–1.97 (m, 20H). $^{13}C\{^1H\}$ NMR (DMSO- d_6 , 75.6 MHz): δ 153.87 (d, J = 7.0 Hz), 129.46, 122.82, 120.34 (d, J = 5.1 Hz), 52.24, 28.84, 25.25, 24.48. $^{31}P\{^1H\}$ NMR (DMSO- d_6 , 121.8 MHz): δ –12.70. IR (cm^{-1}): 3016, 2934, 2859, 2760, 2669, 2564, 2471, 1595, 1495, 1458, 1389, 1239, 1224, 1166, 1096, 1032, 894, 754, 687. MS (70 eV, EI): 248 (4) $[(C_6H_5O)_2P(O)(O) - H]^+$, 247 (5) $[(C_6H_5O)_2P(O)(O) - 2H]^+$, 182 (13) $[(C_6H_{11})_2NH_2]^+$, 180 (76) $[(C_6H_{11})_2N]^+$, 137 (100) $[C_9H_{15}N]^+$, 99 (47) $[C_6H_{13}N]^+$, 82 (76) $[C_6H_{10}]^+$.

3.2. X-ray Data of Crystal Structure

The X-ray data were collected at 293 K with graphite monochromated Mo $K\alpha$ radiation (0.71073 Å) on a Bruker SMART APEXII area-detector diffractometer. The structure was solved with SHELXS97 [39] by the direct methods algorithm and refined using full-matrix least-squares on F^2 with the SHELXL-2016/6 [40]. All carbon-bound H atoms were placed at calculated positions and were refined on their parent atoms with their U_{iso} set to 1.2 U_{eq} . Nitrogen-bound H atoms were located in a difference Fourier map and refined isotropically with their U_{iso} set to 1.2 U_{eq} of the carrier N atom.

The crystallographic data for $C_{12}H_{10}O_4P.C_{12}H_{24}N$ (M = 431.49 g/mol): Orthorhombic, space group $P2_12_12_1$, a = 9.6610(4) Å, b = 10.9649(5) Å, c = 21.8524(11) Å, V = 2314.87(18) Å³, Z = 4, T = 293(2) K, $F(000)$ = 928, $\mu(MoK\alpha)$ = 0.148 mm^{−1}, S = 1.041, D_{calc} = 1.238 g/cm³, 5598 independent reflections, $-12 \leq h \leq 11$, $-14 \leq k \leq 9$, $-28 \leq l \leq 28$, 4466 reflections with $I > 2\sigma(I)$, R_{int} = 0.0289. The final R_1 was 0.0453 ($F^2 > 2\sigma(F^2)$) and wR_2 (F^2) was 0.1122, $\Delta\rho_{max}$ (eÅ^{−3}) = 0.543, $\Delta\rho_{min}$ (eÅ^{−3}) = −0.226. The molecular graphics were generated by Mercury [41] and OLEX2 [42]. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre (CCDC-1887337). These data can be obtained free of charge [43] from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

4. Conclusions

The $[(C_6H_{11})_2NH_2][(C_6H_5O)_2P(O)(O)]$ salt crystallizes in the chiral space group $P2_12_12_1$, and the cation and anion components are assembled through relatively strong charge-assisted N–H ... O hydrogen bonds, together with C–H ... O and C–H ... π weak interactions. The divided fingerprints show the most contribution portions of H ... H contacts and then H ... O and H ... C interactions received by both cation and anion. The negative ^{31}P signal in solution NMR is attributed to shielding caused by the negative charge on the oxygen atom. The cation and anion components of the title salt are well-matched with the structures including similar components from the CSD.

Supplementary Materials: The tables for structural comparisons with CSD, and $^{31}P\{^1H\}$ NMR, 1H NMR, $^{13}C\{^1H\}$ NMR, IR, Mass, and crystallographic data of synthesized compound are available online at <http://www.mdpi.com/1422-8599/2019/1/M1051/s1>.

Author Contributions: A.R.S. and F.S. are supervisors of S.N.M. in her PhD thesis. Designing of the experiment was done by A.R.S. and M.P., the experiment and Hirshfeld surface analysis were performed by F.S., M.P., and S.N.M., the spectroscopic studies were done by M.P., the paper was written by M.P. and A.A.A.S., and the X-ray crystallography experiment and structural comparisons were done by A.A.A.S.; the figures were prepared by M.P., A.A.A.S., and S.N.M.; all authors read and approved the manuscript.

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