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**Abstract:** The crystal structure of tetra-n-butylammonium perchlorate has been successfully elucidated using single-crystal X-ray diffraction. The compound crystallizes in the triclinic space group  $P\overline{1}$  with unit cell of dimensions a = 14.2706(7) Å, b = 20.6904(9) Å, c = 39.970(2) Å,  $\alpha = 89.316(4)^{\circ}$ ,  $\beta = 88.638(4)^{\circ}$ , and  $\gamma = 87.801(4)^{\circ}$ . Although complicated by partial disorder, the structure has remarkable features where columns of some of the perchlorate anions running down [100] lie within what can be regarded as nanotubular entities formed by some of the tetrabutylammonium cations, while the remaining tetrabutylammonium cations lie in parallel columns surrounded by the remaining perchlorate anions, one entity being essentially the inverse of the other. Interactions within the structure have been characterized using Hirshfeld surface analysis and comparisons drawn with other unsolvated salts of the cation.

Keywords: crystal; perchlorate; salt; self-assembly; tetrabutylammonium

# 1. Introduction

Tetra-alkylammonium salts,  $[NR_4]X$ , have a wide variety of applications, perhaps best known being that of phase-transfer catalysis [1,2], although certain derivatives are active catalysts in their own right [3–6]; some, such as those where  $X^- = ClO_4^-$  or  $CF_3SO_3^-$  and R is a simple n-alkyl group, have widespread use as background electrolytes for non-aqueous electrochemistry [7–10], and others which form liquid adducts (deep eutectic solvents [11–14]) have promise as green solvents for industrial use. In the solid state, clathrate hydrates of tetra-alkylammonium halides have been found to show useful absorption of small molecules, including environmentally undesirable carbon dioxide [15,16], with hydrates of the tetra-n-butylammonium halides,  $[N(n-C_4H_9)_4][Cl]$  and  $[N(n-C_4H_9)_4][Br]$ , in particular, displaying high capacity and high selectivity, respectively, explicable in terms of their crystal structures and the fit of the cation to the cavities within the H-bonded water molecule array [17–20].

Of the 430 structures incorporating  $[N(n-C_4H_9)_4]X$  species found in the CSD, nearly all are those of solvates or adducts and only few examples, those where  $X^- = [BF_4]^-$  [21],  $[(C_2F_5)_3PF_3]^-$  [21], Cl<sup>-</sup> [22], Br<sup>-</sup> [23], I<sup>-</sup> [24], I\_3<sup>-</sup> [25], [ClO<sub>3</sub>]<sup>-</sup> [26], [PF<sub>6</sub>]<sup>-</sup> [27], and  $[IO_4]^-$  [28], are known which are not. Interestingly, the structure of tetra-n-butylammonium perchlorate salt shows the closest resemblance of the tetrafluoroborate salt of tetrabutylammonium [21]. Other unsolvated species, such as those where  $X^- = I^-$ , [CF<sub>3</sub>SO<sub>3</sub>]<sup>-</sup> and [ClO<sub>4</sub>]<sup>-</sup>, have been analytically characterized [16] and are commercially available. Recently, [N(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>][ClO<sub>4</sub>] has been subjected to detailed study of its physical properties (phase transition parameters, ionic conductivity, and transport property) and the powder diffraction patterns of two polymorphs, but not to a single crystal structure determination, although this was recognized as important for a more complete understanding of its phase transitions [29]. The inadvertent isolation of crystals of [N(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>][ClO<sub>4</sub>] from a reaction mixture intended to produce a more complicated material has allowed us to determine and report herein the quite remarkable structure of what may be a third polymorph.



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### 2. Materials and Methods

Chemicals, reagents, and solvents were of analytical grade and purchased from commercial suppliers. These were used without further purification.

### 2.1. Synthesis

In attempting to extend earlier work on the formation of inclusion complexes of imidazolium derivatives with lanthanide ion complexes of *p*-sulfonatocalix[4]arene [30], a reaction mixture of  $[N(n-C_4H_9)_4]Br$ , 1-butyl-3-methylimidazolium perchlorate, GdCl<sub>3</sub>, and sodium *p*-sulfonatocalix[4]arene in aqueous THF (1:1) was prepared, Scheme 1. It was gently warmed to provide a clear solution, then left to evaporate slowly over several weeks at room temperature. This led to the deposition of colorless, block-like crystals shown by their X-ray structure determination to be  $[N(n-C_4H_9)_4][ClO_4]$ , probably formed as a result of the loss of THF from the solvent, as it is known to be of low solubility in water. Several crystals were examined in order to establish that the product was homogeneous.



Scheme 1. Synthesis of [N(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>][ClO<sub>4</sub>].

#### 2.2. Single-Crystal X-ray Crystallography

Single-crystal X-ray diffraction data were measured from single crystal using an Oxford Gemini-R Ultra CCD diffractometer at T = 100(2) K operating with monochromatic MoK $\alpha$  ( $\lambda$  = 0.71073 Å) radiation. The data were corrected for Lorentz and polarization effects, and absorption corrections were applied using multiple symmetry equivalent reflections. The structure was solved using direct methods and refined against  $F^2$  with full-matrix least-squares using the SHELX program suite [31]. The structure contains some heavily disordered cations and anions and restraints on the displacement parameters of all disordered atoms were applied and refined as a 2-component twin system. Anisotropic displacement parameters were applied for the non-hydrogen atoms. All hydrogen atoms were added to calculated positions and refined using a riding model with the isotropic displacement parameters based on those of the parent atom. Crystallographic data for the structure reported here have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Copies with CCDC number 2,180,591 can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/ (accessed on 01 July 2023), or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax+ 441223336033; email deposit@ccdc.cam.ac.uk). Crystal and structure refinement data are provided in Table 1. The Hirshfeld surfaces and the corresponding two-dimensional fingerprint plots were generated using CrystalExplorer17 [32].

Formula	$C_{16}H_{36}N^+$ , $ClO_4^-$
Empirical formula	C <sub>16</sub> H <sub>36</sub> NO <sub>4</sub> Cl
Formula weight/g mol <sup>-1</sup>	341.91
Crystal system	Triclinic
Space group	<i>P</i> 1 (No. 2)
a/Å	14.2706(7)
b/Å	20.6904(9)
c/Å	39.970(2)
$\alpha /^{\circ}$	89.316(4)
$\beta/^{\circ}$	88.638(4)
$\gamma/^{\circ}$	87.801(4)
Volume/Å <sup>3</sup>	11789(1)
Z	24
$D_{\rm c}/{\rm g}{\rm cm}^{-3}$	1.156
$\mu/\text{mm}^{-1}$	0.21
$F_{000}$	4512
Crystal size (mm <sup>3</sup> )	0.26 imes 0.14 imes 0.11
Theta range for data collection	2.807-23.256
$2\theta_{\rm max}/^{\circ}$	46.5
	$-15 \le h \le 15$
Miller index ranges	$-22 \leq k \leq 22$
	$-44 \leq l \leq 44$
Reflections total/unique *	49235/17581
Completeness to $\theta_{max}$ (%)	99.8
R <sub>int</sub>	n/a *
Data/restraints/parameters	49235/2498/2519
Reflections ( $I > 2\sigma(I)$ )	5672
Final GooF	0.851
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.1024, $wR2 = 0.2189$
R indices (all data)	R1 = 0.2318, wR2 = 0.2734
Largest diff. peak and hole (e $Å^{-3}$ )	0.684  and  -0.360
CCDC number	2180591

Table 1. Crystal data and structure refinement for [N(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>][ClO<sub>4</sub>].

\* Merge of reflections not implemented in the case of refinement of twinned structures.

# 3. Results

#### 3.1. Description of the Structure of Tetra-n-Butylammonium Perchlorate, $[N(n-C_4H_9)_4][ClO_4]$

 $N(n-C_4H_9)_4$  [ClO<sub>4</sub>] formed as triclinic crystals and its structure has been solved in the P1 space group. In the asymmetric unit, there are twelve crystallographically independent stoichiometric units, with three  $[N(n-C_4H_9)_4]^+$  cations and three  $[ClO_4]^-$  anions disordered. Examination of bond lengths, bond angles, and torsional and dihedral angles within the twelve cations (assessed using the CSD Mogul program [33]) showed that most of these data are in good agreement with those for  $[N(n-C_4H_9)_4]^+$  cations in the CSD. The bond lengths and angles in  $[N(n-C_4H_9)_4]^+$  cations are in the range from 1.453 to 1.557 Å for C-C, from 106.1 to 129.11° for C-C-C, from 1.474 to 1.546 Å for N-C, and from 88.3 to 125.3° for C-N-C. The average bond lengths and angles are 1.512 Å for C-C, 112.7° for the C-C-C angle, 1.511 Å for N-C, and 109.4° for the C-N-C angle (Table S2). The  $[N(n-C_4H_9)_4]^+$  cations in a quasi-tetrahedral geometry adopt different conformations in each of the asymmetric unit components. These relatively subtle differences can be assigned to the facile C-C single bond rotation within the n-butyl chains. A total of six different conformers were identified (determined from the C-C-C torsion angles for each n-butyl chain as defined by the IUPAC Gold Book [34]), as shown in Figure 1. Amongst the six conformers, most of the C-C-C-C units are antiperiplanar (torsion angle 150–180°) but some are synclinal (30–90°) [27]. Three of the  $[N(C_4H_9)_4]^+$  cations have their n-alkyl chains disordered (occupancy = 0.5) and the disordered fragments involve a methyl group (C16L), an ethyl group (C07K, C08K), a propyl group (C10L, C11L, C12L), and three independent butyl groups (C09K, C10K, C11K, C12K, C05F, C06F, C07F, C08F, and C09F, C10F, C11F,



C12F). Conformational isomerism is, of course, to be expected for flexible substituents such as n-alkyl chains [21,35,36].

**Figure 1.** Capped stick models of the 12  $[N(n-C_4H_9)_4]^+$  cations with different conformations in the asymmetric unit. Each n-butyl chain's C-C-C torsion angle was carefully analyzed (ap,  $\pm$ sc,  $\pm$ ac, sp are abbreviations for antiperiplanar,  $\pm$ synclinal,  $\pm$ anticlinal, and synperiplanar, respectively). All hydrogens atoms have been omitted for clarity.

All the  $[ClO_4]^-$  anions have a near-tetrahedral geometry with O-Cl-O angles between 103.1(9) and 115.0(1)° and Cl-O bond lengths between 1.31(1) and 1.435(9) Å (Table S3). Three  $[ClO_4]^-$  anions have some of the O-atoms disordered over two positions (O2B, O3B, O4B, O2C, O3C, O4C, O2H, O3H, and O4H). Disorder of the perchlorate anion in crystal structures is commonly encountered and may be interpreted in different ways, which can have a significant influence on the estimations of both bond lengths and angles [37]. It is probable that the large range of bond lengths seen here is more a consequence of the disorder than any real difference in bonding interactions.

Viewed down [100], the structure of  $[N(n-C_4H_9)_4][ClO_4]$  appears to show in crosssection, consisting of two types of columnar arrays. One, type A, involves a column of perchlorate anions surrounded by a sheath of  $[N(n-C_4H_9)_4]^+$  cations with their Natoms forming a near-rectangular array in projection. The other, type B, has a column of  $[N(n-C_4H_9)_4]^+$  cations with a periphery of anions forming a near-square array in projection (Figure 2). Both the type A and type B columns can be considered to lie in sheets parallel to (012), but there is a complication in that the variations in the cation conformations mean that there are actually two slightly different type A columns, one involving N01A, N01B, N01C, and N01D, the other N01E, N01F, N01G, and N01H, and two slightly different type B columns, one involving N01I and N01J and the other N01K and N01L. While these differences are slight, they are nonetheless obvious by eye in the projection shown in Figure 2.



**Figure 2.** Portion of the structure of  $[N(n-C_4H_9)_4][ClO_4]$ , as viewed down [100], showing, in cross-section, the two types of columnar arrays.

## 3.2. Analysis of the Structure of Tetra-n-Butylammonium Perchlorate, $[N(n-C_4H_9)_4][CIO_4]$

Consideration of  $[N(n-C_4H_9)_4][ClO_4]$  as an ionic compound means that its structure must be determined principally by Coulombic interactions [38–40]. This does not mean that its structure must be an analogue of, say, that of NaCl, since, as shown by Hirshfeld surface analysis [32] of the structure, the orientations of cation. . . anion pairs are determined by CH<sup>...</sup>O interactions (Table S1), in turn influenced by the varied conformations of the cations (Table S4). Full details of these interactions are rendered extremely complicated by the disorder in the structure, but illustration is provided by the interaction of the nondisordered cation involving N01H with the non-disordered anion involving Cl1D, where the contact H01P<sup>...</sup>O30 is 2.24 Å (Figure 3). Hydrogen atom H01P is bound to carbon directly attached to N<sup>+</sup> and such protons are known to be the most acidic of those in tetraalkyl ammonium species [41], thus favoring interaction with the weak base perchlorate-O.



**Figure 3.** ORTEP representation showing one of the CH. . .O interactions (dashed line) of the nondisordered  $[N(n-C_4H_9)_4]^+$  cation centered on N01H with a non-disordered perchlorate anion. (Disordered anions are also close to this cation and are involved in similar contacts.).

Dispersion interactions must always be part of any crystal structure and fingerprint plots from the Hirshfeld surface based on the structure of  $[N(n-C_4H_9)_4][ClO_4]$  show that H...H contacts constitute an average of ~78% of all short intercation contacts. Additionally, minor differences in the conformers manifest in very similar Hirshfeld surface fingerprint plots. In tetra-n-alkylammonium cations with long  $C_{10}$ – $C_{18}$  chains, dispersive interactions between chains  $C_{12}$  or longer of individual cations lead to conformations involving their pairwise association [42]. For short chains as in  $[N(n-C_4H_9)_4][ClO_4]$ , the geometry imposed at N appears to be incompatible with such intramolecular interaction, so that intermolecular contacts impose. In respect to weak hydrogen bonds,  $[N(n-C_4H_9)_4][ClO_4]$  is stabilized by C-H...O intermolecular interactions arising from the interactions between H-atoms of the  $C_4$  chains in  $[N(n-C_4H_9)_4]^+$  cation and oxygen atoms of  $[ClO_4]^-$  anions. The interactions are reasonably within the accepted limits (C...O distances range from 3.10(3) to 3.62(3) Å).

# 3.3. The Structure of $[N(n-C_4H_9)_4][ClO_4]$ within Its Context

Perchlorate and tetrafluoroborate are anions of similar size and weak donor capacity which frequently form salts with similar structures and where disorder arising from the unquenched rotational motion of these small anions is often apparent [37,43]. Thus, an obvious comparison of the present structure is with that of unsolvated  $[N(n-C_4H_9)_4][BF_4]$ (CSD refcode: UYOWEM06) [21]. (Crystals of this material were obtained as part of the present work when 1-butyl-3-methylimidazolium tetrafluoroborate was substituted for the perchlorate in the synthesis described above and its structure was confirmed.) Unsurprisingly, there are marked similarities in the two structures, with the common feature of anion columns within a sheath of cations (type A) but the type B column centered on cations is not present in the tetrafluoroborate, consistent with its adoption of a different crystal system (monoclinic) and space group (P2/c). Instead, [BF<sub>4</sub>]<sup>-</sup> anions occupy the spaces between the columns, appearing as a honeycomb array when viewed down [010], though in fact not one where the central B atoms of any hexagonal unit are coplanar. Disorder is limited to the cations only, with the conformational flexibility of the n-butyl chains being reflected in the presence of six inequivalent cation units, three of which show partial disorder. The greater degree of order in the tetrafluoroborate may be a consequence of the greater basicity of  $[BF_4]^-$  relative to  $[ClO_4]^-$ , as examination of the Hirshfeld surface shows that in some instances, F can be involved in bridging interactions with protons of



the cations, e.g., F61 has contacts to H31A (2.46 Å) and H32A (2.54 Å) of the cation centered by N3, as shown in Figure 4.

**Figure 4.** Interactions beyond dispersion identified from the Hirshfeld surface for one of the ordered cations in the structure of  $[N(n-C_4H_9)_4][BF_4]$  (CSD refcode: UYOWEM06).

Of the structures of other unsolvated salts of  $[N(n-C_4H_9)_4]^+$ , only that of the chlorate (CSD refcode: EJOJEV) [26] shows any similarity to those of the perchlorate and tetrafluoroborate. There are, however, only two inequivalent cations, one fully ordered, the other showing conformational disorder of all four arms, and there is partial inversion disorder of the anions. Viewed down [100], ordered chlorate anions appear to be enclosed within tubes of ellipsoidal cross-section formed by the cations, with disordered anions lying between tube units. The considerably greater basicity of chlorate compared to perchlorate may explain its capacity to act as a bridge through CH $\cdots$ O interactions, either intermolecularly for the ordered species or intramolecularly through the disordered, as shown in Figure 5.

Structures of the unsolvated salts of  $[N(n-C_4H_9)_4]^+$  with tris(pentafluorethyl)trisfluorophosphate (CSD refcode: OLAZAE01) [21], hexafluorophosphate (CSD refcode: NOFKEY05) [27], and chloride (CSD refcode: XUBGIN) [22] are all much simpler to analyze in that a unique and ordered cation is present in all. (The structure of the periodate (CSD refcode BUAMPI) [28] cannot be analyzed in a similar manner because H-atom coordinates are not available.) Their cation arrays, however, are all quite different and in none can tubular entities anything like those just discussed be discerned (Figure 6).

In the structure of  $[N(n-C_4H_9)_4][(C_2F_5)_3PF_3]$ , the anion is split into major and minor components, but taking just the major components, three are involved in F···HC interactions (Figure 7a; 2.39–2.51 Å separations) with each cation, with the bulk of the anion reducing the fraction of H···H contacts about the Hirshfeld surface to 45%. In the structure of  $[N(n-C_4H_9)_4][PF_6]$ , In the structure of F···HC interactions (Figure 7b; 2.34–2.58 Å) but the contribution of H···H contacts about the Hirshfeld surface is now 75%. In the structure of  $[N(n-C_4H_9)_4]Cl$ , four Cl. . .H interactions (Figure 7c; 2.67–2.84 Å) involving three chloride anions occur with each cation and the contribution of H···H contacts about the Hirshfeld surface rises to 91%. In the first two structures, the cation has three arms antiperiplanar and one synclinal, while in the third there are two of each conformation.



**Figure 5.** CH···O interactions of the completely ordered cation found in the crystal structure of  $[N(n-C_4H_9)_4][ClO_3]$  (CSD refcode: EJOJEV). The two interactions for O1 mean that it bridges such cation units.



**Figure 6.** Partial views of the structures of (a)  $[N(n-C_4H_9)_4][(C_2F_5)_3PF_3]$  viewed down [010]; (b)  $[N(n-C_4H_9)_4][PF_6]$  viewed down [100] and (c)  $[N(n-C_4H_9)_4]Cl$  viewed down [010].



**Figure 7.** Interactions (dashed lines) beyond dispersion with the unique cations present in the structure of (a)  $[N(n-C_4H_9)_4][(C_2F_5)_3PF_3]$ , (b)  $[N(n-C_4H_9)_4][PF_6]$ , and (c)  $[N(n-C_4H_9)_4]Cl$ .

What is shown in the crystal structures of these unsolvated salts of the  $[N(n-C_4H_9)_4]^+$ cation is that aside from electrostatic influences, cation ... anion interactions beyond dispersion differ in a manner dependent upon the basicity of the anion but are never numerous, leaving dispersive H...H interactions as important influences upon the cation conformations and forms of aggregation within the crystal. This indicates that the introduction of a third component of the crystal, such as a water molecule capable of relatively strong intermolecular interactions, should have a major influence on the complete structure. No exact comparison of anhydrous and hydrated structures is possible but the structure of the hydrated bromate, [N(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>][BrO<sub>3</sub>]·H<sub>2</sub>O (CSD refcode: EJOJAR) [26], unlike that of the chlorate, has unique and ordered cations, and the bromate anions and water molecules form helical H-bonded chains running down [010] where all four oxygen atoms of every bromate–water pair are involved in O<sup> $\cdots$ </sup>HC interactions with [N(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>]<sup>+</sup> cations. The cations form a sheath about the bromate-water polymer in a pairwise fashion very similar to that in the type A tubes of  $[N(n-C_4H_9)_4][ClO_4]$ , but now all anions (and water) are within the tubes, so that the tubes pack together through  $H^{...}H$  interactions only. Similarly, the structure of the hydrated bromide, [N(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>]Br<sup>-</sup>2.33H<sub>2</sub>O (CSD refcode: AJUQEB) [44], is like that of the anhydrous chloride in that it contains a unique cation, though with partial disorder in one chain, but overall has a closer resemblance to that of the hydrated bromate. Its analysis is complicated by the partial occupancy of bromide sites, but in the original publication, the bromide and water molecules were described as forming  $(Br^{-})_{3}(H_{2}O)_{6}$ clusters enclosed within a cage of six  $[N(n-C_4H_9)_4]^+$  cations. In fact, these clusters lie in columns parallel to [001] so that again there is a resemblance to the type A tubes found in  $[N(n-C_4H_9)_4][ClO_4]$ . Much higher hydrates of  $[N(n-C_4H_9)_4]Br$  (and of other halide salts) are well-known [17] where the extended H-bonded water structure leads to these materials being describable as clathrates and not simple hydrates.

## 4. Conclusions

The characterization of  $[N(n-C_4H_9)_4][ClO_4]$  in the space group  $P\overline{1}$  and not in either of the groups P2/c or  $P\overline{4}3n$  obtained from PXRD measurements [29] indicates that at least three polymorphs may exist. Whether the rather indirect method of crystallization presently exploited may have favored the  $P\overline{1}$  form is unknown, but the variations in structure described above for unsolvated  $[N(n-C_4H_9)_4]^+$  salts and for some simple hydrated species indicate that the balance of various weak interactions can lead to marked structural differences, so that local minima leading to polymorphism could well be achievable. The nanotubular arrays seen in the structures of  $[N(n-C_4H_9)_4][ClO_4]$  and some related species are of interest in that they demonstrate how unidirectional channels may be formed in a crystalline solid, though whether crystal-to-crystal transitions could be observed by heterogeneous exchange of the tube contents is yet to be investigated. Understanding the polymorphism of solids is crucial to a detailed analysis of their properties and is important in scientific disciplines ranging from pharmaceutics to materials chemistry in general. The present work, concerning a seemingly quite simple compound, illustrates just how complicated the full analysis of non-covalent solid-state interactions may be.

**Supplementary Materials:** The following supporting information can be downloaded at: https:// www.mdpi.com/article/10.3390/cryst13081255/s1, Table S1: Hirshfeld surfaces mapped using  $d_{norm}$  and the corresponding delineated fingerprint plots for  $[N(n-C_4H_9)_4]^+$  cations in  $[N(n-C_4H_9)_4][CIO_4]$  crystal structure; Table S2: Table of average, median, standard deviation, minimum and maximum bond lengths and bond angles for different  $[N(n-C_4H_9)_4]^+$  cations, (Å, °); Table S3: Table of average, median, standard deviation, minimum and maximum bond lengths and bond angles for different  $[N(n-C_4H_9)_4]^+$  cations, (Å, °); Table S3: Table of average, median, standard deviation, minimum and maximum bond lengths and bond angles for different  $[CIO_4]^-$  anions, (Å, °); Table S4: Selected hydrogen-bond geometry (Å, °).

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**Data Availability Statement:** Crystal structure of  $[N(n-C_4H_9)_4][ClO_4]$  has been deposited in the CCDC database (2180591).

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