



## ORIGINAL ARTICLE

# Supramolecular structure of bis(*N,N',N''*-triisopropylguanidinium) phthalate



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Phthalate dianion;  
Supramolecular structure

**Abstract** In the structure of the *N,N',N''*-triisopropylguanidinium salt of phthalate (**I**), 2(IPGH)<sup>+</sup>·(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>)<sup>2-</sup>, the asymmetric unit contains two symmetry-independent cations and one anion having different inter-species hydrogen-bonding environments, which includes cyclic *R*<sub>2</sub><sup>2</sup>(8) and *R*<sub>4</sub><sup>4</sup>(16) associations. These interactions give a two dimensional layered structure.

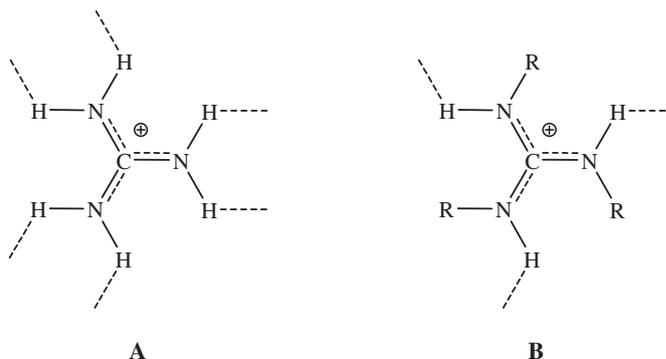
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## 1. Introduction

Non-covalent interactions play an important role in organizing structural units in both natural and artificial systems (Desiraju, 1997). They exercise important effects on the organization and properties of many materials in areas such as biology (Hunter, 1994; Desiraju and Steiner, 1999), crystal engineering (Allen et al., 1997; Dolling et al., 2001) and material science (Panunto et al., 1987; Robinson et al., 2000). The interactions governing the crystal organization are expected to affect the packing and then the specific properties of solids.

Guanidines are of special interest due to their possible application in medicine (Yoshiizumi et al., 1998; Moroni et al., 2001). They are considered super bases as they are easily protonated to generate guanidinium cations (Ishikawa and

Isobe, 2002). The structural features and hydrogen bonding array provided by these cations suggest that they are good building blocks for the formation of supramolecular entities mediated by three pairs of directional hydrogen bonding interactions (A). However, their significance in the generation of multi-dimensional networks has only recently been appreciated (Abrahams et al., 2004; Best et al., 2003; Holman et al., 2001a,b).



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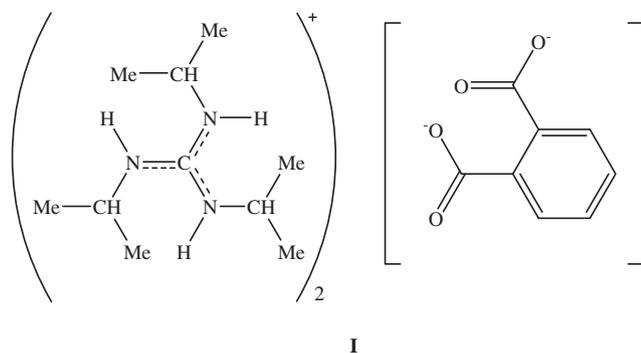
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In contrast to the rich supramolecular chemistry that has been developed around the parent guanidinium cation there are few reports employing  $N,N',N''$ -trisubstituted analogues (Best et al., 2003; Steiner, 2001). Some studies were focused on guanidinium derivatives, in which they are attempting to analyze the influence of the different derivatives of guanidinium and different types of anion on the packing interactions that govern the crystal organization and as consequence, the properties of the resulting salts (Said et al., 2006a; Said et al., 2006b; Said et al., 2005).

Phthalic acid, on the other hand, is also of interest since it is capable of forming supramolecular motifs *via* the versatile hydrogen bonding features of its carboxylate groups. Planar phthalate mono anions, are known to form 1:1 salts with different cations, having most commonly low-dimensional hydrogen-bonded structures which enclose conjoint cyclic associations (Bozkurt et al., 2006; Smith et al., 2008; Smith et al., 2009; Smith and Wermuth, 2010a). While the less common nonplanar dianionic phthalates (having two carboxylate groups that are rotated out of the plane of the benzene ring) form 1:2 salt structures with higher dimensional hydrogen-bonded networks (Büyükgüngör and Odabaşoğlu, 2007; Smith and Wermuth, 2011). With guanidines, the formation of 1:2 salts with dicarboxylic acids is common, e.g., with phthalic acid (Krumbe and Haussuhl, 1986) and terephthalic acids (Smith and Wermuth, 2010b).

In connection with our ongoing studies (Said et al., 2011; Said et al., 2006a; Said et al., 2006b; Said et al., 2005) of the structural aspects of  $N,N',N''$ -trisubstituted guanidinium salts (**B**) containing different anions, we herein report the crystal structure of the compound,  $N,N',N''$ -triisopropylguanidinium with phthalate dianion (**I**), along with the crystal structure supramolecularity.



## 2. Experimental

### 2.1. Synthesis

Synthesis and crystallization of bis( $N,N',N''$ -triisopropylguanidinium) phthalate,  $2(\text{IPGH})^+ \cdot (\text{C}_8\text{H}_4\text{O}_4)^{2-}$ , **I**. In a round bottomed flask, a combination of 0.0690 g (0.373 mmol)  $N,N',N''$ -triisopropylguanidine and 0.124 g (0.746 mmol) phthalic acid were dissolved in 10 mL of THF. White precipitate of **I** was deposited immediately off the solution (0.183 g, 92.4% yield). The product was crystallized from a mixture of methanol and THF to give colorless crystals. Anal. Calcd for  $\text{C}_{28}\text{H}_{52}\text{N}_6\text{O}_4$ : C, 62.65; H, 9.76; N, 15.66. Found: C, 62.88; H, 9.88; N, 15.78.

**Table 1** Crystal data and structure refinement for **I**.

|   |   |
|---|---|
| Empirical formula; formula weight                       | $\text{C}_{28}\text{H}_{46}\text{N}_6\text{O}_4$ ; 530.7          |
| Temperature/K   | 208 (2)   |
| $\lambda/\text{\AA}$                                    | 0.71073   |
| Crystal system; space group                             | Monoclinic, $P2_1/c$  |
| Unit cell dimensions                                    |   |
| $a/\text{\AA}$  | 9.646 (7)   |
| $b/\text{\AA}$  | 27.05 (2)   |
| $c/\text{\AA}$  | 12.410 (9)  |
| $\beta/^\circ$  | 96.213 (13)   |
| Volume/ $\text{\AA}^3$                                  | 3219 (4)  |
| Z   | 4   |
| Density (calculated)/ $\text{Mg/m}^3$                   | 1.095   |
| $\mu/\text{mm}^{-1}$                                    | 0.07  |
| $F(000)$  | 1152  |
| Crystal size/ $\text{mm}^3$                             | $0.30 \times 0.30 \times 0.15$                                    |
| Theta range for data collection                         | 1.5–24.7  |
| Index ranges  | $-11 \leq k \leq 11, -31 \leq l \leq 31,$<br>$-14 \leq m \leq 14$ |
| Reflections collected                                   | 22438   |
| Independent reflections                                 | 41502 [ $R(\text{int}) = 0.045$ ]                                 |
| Completeness to theta = $25.0^\circ$                    | 99.5%   |
| Absorption correction                                   | Semi-empirical from equivalents                                   |
| Max. and min. transmission                              | 0.9780 and 0.9889   |
| Refinement method                                       | Full-matrix least-squares on $F^2$                                |
| Data/restraints/parameters                              | 5482/0/344  |
| Goodness-of-fit on $F^2$                                | 1.049   |
| Final R indices [ $I > 2\sigma(I)$ ]                    | $R1 = 0.066, wR2 = 0.1671$  |
| R indices (all data)                                    | $R1 = 0.0869, wR2 = 0.1671$                                       |
| Largest diff. peak and hole/ $\text{e.}\text{\AA}^{-3}$ | 0.62 and $-0.2$   |

### 2.2. X-ray structure determination

Crystals of compound **I** were grown from a solution of methanol and THF. Unit cell measurements and intensity data collections were performed on a Bruker-AXS SMART 1k CCD diffractometer (Bruker, 2005) at 202 K using graphite monochromatized Mo  $K_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction *SADABS* (Bruker, 2005). The crystal data and refinement parameters for **I** are listed in Table 1. Selected geometrical parameters are listed in Table 2. The reflection data were consistent with a monoclinic system;  $P2_1/c$ .

The crystal structures were solved and refined using the *SHELXTL* program suite (Sheldrick, 2008). Direct methods yielded all non-hydrogen atoms. All hydrogen atom positions were either located from the different Fourier Maps or were calculated geometrically and were riding on their respective carbon atoms.

## 3. Results and discussion

### 3.1. Molecular structure of bis( $N,N',N''$ -triisopropylguanidinium) phthalate

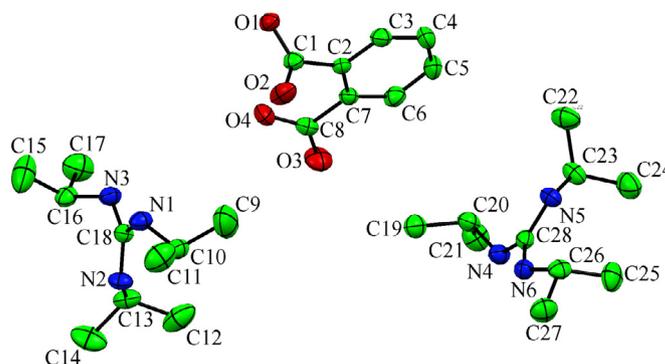
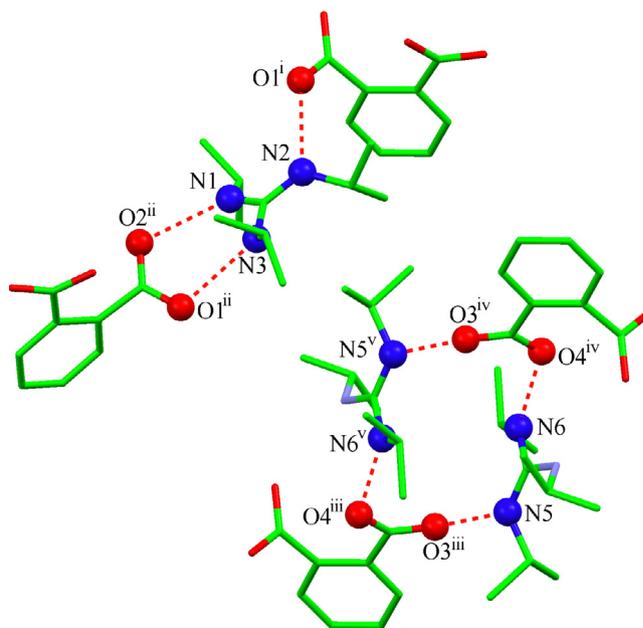
The crystallographic asymmetric unit comprises two independent guanidinium cations [*A* (contains N1, N2 and N3) and *B* (contains N4, N5 and N6)], having almost identical

**Table 2** Selected bond lengths and angles for I.

| Bond distances |           |             |           |
|----------------|-----------|-------------|-----------|
| N1—C18         | 1.342 (3) | N6—C28      | 1.328 (3) |
| N1—C10         | 1.466 (3) | N6—C26      | 1.482 (3) |
| N2—C18         | 1.343 (3) | O1—C1       | 1.262 (3) |
| N2—C13         | 1.474 (3) | O2—C1       | 1.250 (3) |
| N3—C18         | 1.347 (3) | O3—C8       | 1.250 (3) |
| N3—C16         | 1.476 (4) | O4—C8       | 1.251 (3) |
| N4—C28         | 1.361 (3) | C2—C7       | 1.405 (3) |
| N4—C20         | 1.482 (3) | C3—C4       | 1.378 (4) |
| N5—C28         | 1.347 (3) | C6—C7       | 1.395 (4) |
| N5—C23         | 1.474 (3) | C7—C8       | 1.521 (4) |
| Bond angles    |           |             |           |
| C18—N1—C10     | 125.0 (2) | N1—C10—C9   | 108.9 (3) |
| C18—N2—C13     | 124.6 (2) | C11—C10—C9  | 112.1 (3) |
| C18—N3—C16     | 124.7 (2) | N2—C13—C14  | 108.9 (2) |
| C28—N4—C20     | 125.2 (2) | N2—C13—C12  | 109.3 (3) |
| C28—N5—C23     | 125.7 (2) | C14—C13—C12 | 112.5 (3) |
| C28—N6—C26     | 126.0 (2) | N3—C16—C17  | 108.1 (2) |
| O2—C1—O1       | 125.1 (2) | N3—C16—C15  | 108.6 (2) |
| O2—C1—C2       | 118.3 (2) | C17—C16—C15 | 111.8 (3) |
| O1—C1—C2       | 116.3 (2) | N1—C18—N2   | 120.8 (2) |
| C3—C2—C7       | 118.6 (2) | N1—C18—N3   | 116.7 (2) |
| C7—C2—C1       | 124.7 (2) | N2—C18—N3   | 122.5 (2) |
| C4—C3—C2       | 121.8 (2) | N4—C20—C21  | 108.8 (2) |

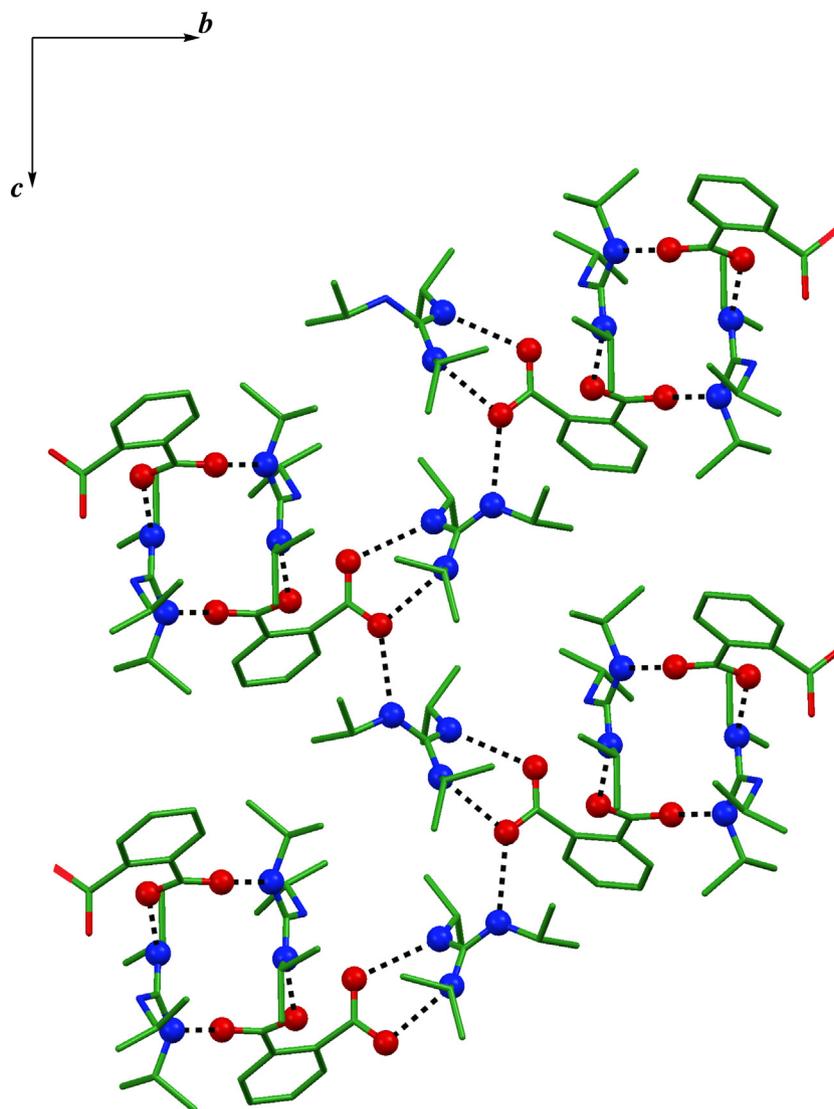
geometrical parameters, as seen from the values of bond distances and angles, Table 2, and one phthalate anion (Fig. 1). The CN<sub>3</sub> fragment of the guanidinium group in (I) is planar [sum of angles 360°], as expected for *sp*<sup>2</sup>-hybridization of the central C atom. The bond lengths (N1, N2, N3)—C18 [A; 1.342 (4), 1.343 (3), 1.347 (4)] and (N4, N5, N6)—C28 [B; 1.361 (4), 1.347 (3), 1.328 (4) Å] are within the range expected for a delocalized C···N bond (Allen et al., 1987).

The benzene ring of the phthalate dianion is planar with the CO<sub>2</sub><sup>-</sup> groups which are slightly twisted (O3—C8—O4) and almost perpendicular (O1—C1—O2) out of the plane of C2—C7 benzene ring as seen in the C2—C7—C8—O4, C6—C7—C8—O3, C3—C2—C1—O1 and C3—C2—C1—O2 torsion angles of 14.9(4), 16.8(4), 74.5(3) and 81.1(3)°, respectively. The interplanar angles between (O3—C8—O4) and (O1—C1—O2) with respect to C2—C7 ring plane are 17.10° and 77.82°, respectively.

**Figure 1** Molecular configuration and atom naming scheme for the two guanidinium cations (*A* and *B*) and the phthalate dianion in the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms omitted for clarity.**Figure 2** Peripheral hydrogen-bonding extension of graph sets  $R_2^2(8)$  and  $R_4^4(16)$  associated guanidinium cations (*A* and *B*) and the phthalate anion in (I). Hydrogen atoms omitted for clarity. Contact atoms presented in balls. Interspecies hydrogen bonds are shown as dashed lines. Symmetry codes: (i)  $x, y, -1 + z$ ; (ii)  $x, \frac{1}{2} - y, -\frac{1}{2} + z$ ; (iii)  $1 + x, y, z$ ; (iv)  $1 - x, 1 - y, 1 - z$ ; (v)  $2 - x, 1 - y, 1 - z$ .

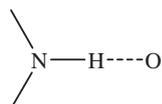
### 3.2. Supramolecular hydrogen-bonding synthons in bis(*N,N',N''*-triisopropylguanidinium) phthalate

A complex strong hydrogen-bonding scheme operates between the cations and the anions (Fig. 2). The guanidinium N atoms act as donors, with the phthalate O atoms as the acceptors. The supramolecular hydrogen-bonding synthon (synthon C) in I is shown in Fig. 2. The pertinent inter-atomic distances for those interactions are [N2···O1<sup>i</sup>, N1···O2<sup>ii</sup>, N3···O1<sup>ii</sup>, N5···O3<sup>iii</sup> and N6···O4<sup>iv</sup>] of 2.867, 2.805, 2.813, 2.791 and 2.704, respectively; symmetry codes: (i)  $x, y, -1 + z$ ; (ii)  $x, 1/2 - y, -1/2 + z$ ; (iii)  $1 + x, y, z$ ; (iv)  $1 - x, 1 - y, 1 - z$ ] which are considered to be viable hydrogen-bonds. A particularly significant feature of the synthon



**Figure 3** The two-dimensional hydrogen-bonded layered structure, viewed down the  $a$  crystallographic axis. All hydrogen atoms omitted for clarity. Contact atoms presented in balls. Interspecies hydrogen bonds are shown as dashed lines.

(A) shown in Fig. 2, is the fact that the multiple N–H hydrogens form significant N–H $\cdots$ O contacts to support the overall connectivity of N–H $\cdots$ O hydrogen-bonds. These interactions ensure planarity of the guanidine CN<sub>3</sub> moiety and the hydrogen-bonded carboxylate oxygen atoms as shown in Fig. 2.



C

### 3.3. The extended structure of bis(*N,N',N''*-triisopropylguanidinium) phthalate. Crystal packing and crystal supramolecularity

Two main motifs dominate the hydrogen bonding in (I). The donor atoms of the two cations form different cyclic hydrogen-bonding interactions with phthalate O acceptors (Fig. 2). Cation *A* has one guanidinium–N1 $\cdots$ O2<sup>ii</sup>-phthalate, guanidinium–N3 $\cdots$ O1<sup>ii</sup>-phthalate association [graph set  $R_2^2(8)$ ; (ii)  $x$ ,

$\frac{1}{2}-y$ ,  $-\frac{1}{2}+z$ ], in addition to one more interaction [N2 $\cdots$ O1<sup>i</sup>; (i)  $x$ ,  $y$ ,  $-1+z$ ], while cation *B* has guanidinium–N5, N6 $\cdots$ O3<sup>iii</sup>, O4<sup>iv</sup>-phthalate association [ $R_4^4(16)$ ; (iii)  $1+x$ ,  $y$ ,  $z$ ; (iv)  $1-x$ ,  $1-y$ ,  $1-z$ ]. These two main ring motifs are linked together leading to a two-dimensional layered structure (Fig. 3).

### 4. Concluding remarks

The crystal and molecular structures of bis(*N,N',N''*-triisopropylguanidinium) phthalate, 2(IPGH)<sup>+</sup>·(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>)<sup>2-</sup>, have been determined and analyzed. The frequent occurring of described interaction motifs demonstrates the inherent stability of these interactions and the possibility of using such supramolecular motifs as a crystal engineering tools. Cation *A* involved in three hydrogen bonds (classical N–H $\cdots$ O) via its three N–H groups with two different anions, while cation *B* uses only two N–H groups to hydrogen bond with two different anions.

The conformation of the hydrogen bonding in the formed rings does not vary significantly.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.arabjc.2012.06.012>.

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