Arabian Journal of Chemistry (2012) **xxx**, xxx–xxx

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Supramolecular structure of bis(*N*,*N*′,*N*″-triisopropylguanidinium) phthalate

Farouq F. Said [a], Basem Fares Ali [a,*], Darrin S. Richeson [b], Ilia Korobkov [b]

[a] *Department of Chemistry, Al al-Bayt University, Mafraq 25113, Jordan*
[b] *Department of Chemistry and Biochemistry, University of Ottawa, Ottawa, Canada ON KIN 6N5*

Received 4 March 2012; accepted 12 June 2012

KEYWORDS

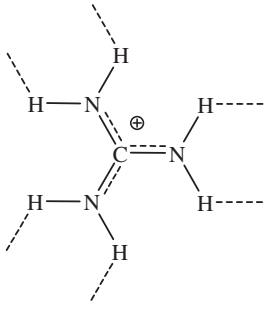
N–H···O Hydrogen bonding;
Trisubstituted guanidinium cation;
Phthalate dianion;
Supramolecular structure

Abstract In the structure of the *N*,*N*′,*N*″-triisopropylguanidinium salt of phthalate (**I**), $2(IPGH)^{+}\cdot(C_8H_4O_4)^{2-}$, the asymmetric unit contains two symmetry-independent cations and one anion having different inter-species hydrogen-bonding environments, which includes cyclic $R_2^2(8)$ and $R_4^4(16)$ associations. These interactions give a two dimensional layered structure.

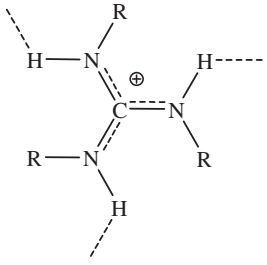
1. Introduction

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 supramoleular 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).



A



B

* Corresponding author.
E-mail address: bfali@aabu.edu.jo (B.F. Ali).

Peer review under responsibility of King Saud University.

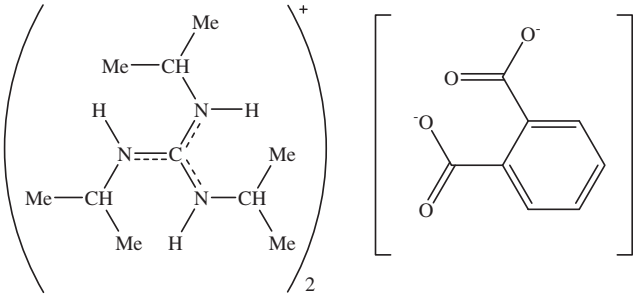
ELSEVIER Production and hosting by Elsevier

1878-5352 © 2012 King Saud University. Production and hosting by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.arabjc.2012.06.012

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.



I

2. Experimental

2.1. Synthesis

Synthesis and crystallization of bis(*N,N′,N″*-triisopropylguanidinium) phthalate, $2(IPGH)^{+}\cdot(C_8H_4O_4)^{2-}$, **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 $C_{28}H_{52}N_6O_4$: 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	$C_{28}H_{46}N_6O_4$; 530.7
Temperature/*K*	208 (2)
λ/Å	0.71073
Crystal system; space group	Monoclinic, $P2_1/c$
Unit cell dimensions	
a/Å	9.646 (7)
b/Å	27.05 (2)
c/Å	12.410 (9)
β/°	96.213 (13)
Volume/Å^3	3219 (4)
Z	4
Density (calculated)/Mg/m^3	1.095
μ/mm^{-1}	0.07
F(000)	1152
Crystal size/mm^3	0.30 × 0.30 × 0.15
Theta range for data collection	1.5–24.7
Index ranges	$-11 \le k \le 11$, $-31 \le k \le 31$, $-14 \le l \le 14$
Reflections collected	22438
Independent reflections	41502 [*R*(int) = 0.045]
Completeness to theta = 25.0°	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)]	*R*1 = 0.066, *wR*2 = 0.1671
R indices (all data)	*R*1 = 0.0869, *wR*2 = 0.1671
Largest diff. peak and hole/e.Å^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_α radiation (λ = 0.71073 Å). 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

Please cite this article in press as: Said, F.F. et al., Supramolecular structure of bis(*N,N′,N″*-triisopropylguanidinium) phthalate. Arabian Journal of Chemistry (2012), http://dx.doi.org/10.1016/j.arabjc.2012.06.012