Journal of Molecular Structure: THEOCHEM 894 (2009) 32–35

Contents lists available at ScienceDirect

Journal of Molecular Structure: THEOCHEM

journal homepage: www.elsevier.com/locate/theochem

On electronic structure of tris(dimethylamino)sulphonium heptafluoro-oxocyclotetraphosphazenate

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ARTICLE INFO

Article history:
Received 28 July 2008
Received in revised form 18 September 2008
Accepted 26 September 2008
Available online 1 October 2008

Keywords:
Electron structure
Quantum Theory of Atoms-in-Molecule
Solid state effects
Geometry optimization

ABSTRACT

The results of 3D periodic B3LYP calculations of tris(dimethylamino)sulphonium heptafluoro-oxocyclotetraphosphazenate in experimental geometry are compared with the analogous results for its isolated anion and cation in experimental and B3LYP optimized geometry. The electronic structure structure is evaluated in the terms of QTAIM topological analysis of electron density. P—N bonds alternation and an increased cyclotetraphosphazene ring puckering is not due to solid state effects but due to O/F substitution. Tris(dimethylamino)sulphonium cation in experimental geometry has two S—N bonds with positive electron density Laplacians at bond critical points (BCP) whereas the third S—N bond has this value negative as expected for covalent bonds. Its B3LYP optimized structure of C_3 symmetry has all S—N bonds with negative BCP electron density Laplacians.

1. Introduction

The halocyclophosphazenes hydrolysis depends on the halogens attached to the phosphorus centers, on the phosphazene ring size and on pH. Fluorophosphazenes react slower than chlorophosphazenes and cyclic tetramers react faster than trimers. This might be the reason why the first compound containing a fluorophosphazenate anion has been isolated in 2004 only. Tris(dimethylamino)sulphonium heptafluoro-oxocyclotetraphosphazenate has been prepared from $[(Me_2N)_3S]^+[N_4P_4F_9]^-$ using $(Me_3Si)_2O$ siloxane (Me = methyl) as F/O exchange agent after heating the reaction mixture at 50 °C for several days [1]. The salt crystallizes in the monoclinic space group $P2_1/n$ with four $[N_4P_4F_7O]^-$ anions and $[(Me_2N)_3S]^+$ cations in the asymmetric unit. Anion and cation seem to form an ion pair, the sulphur of the cation is placed over the phosphazene ring (Fig. 1, Tables 1 and 2 and Tables S1 and S2 in Supplementary data) what can be thought of as a half sandwich, but however, the S–O and S–F distances are appreciably longer (4.387 Å and 4.409 Å) than the sum of their van der Waals radii (3.35 Å and 3.45 Å). An interaction through hydrogen bridges is also very weak, the shortest O–H and F–H distances are in the range of 2.50 Å and 2.90 Å, respectively [1]. Similarly to the structure of the isoelectronic neutral cyclo-$N_4P_4F_8$ [2] verified later by quantum-chemical calculations [3], the $[N_4P_4F_7O]^-$ anion adopts a (significantly more puckered) saddle conformation with the four phosphorus centres forming a plane. P–N bonds lengths alternation (with the longest P_1–N_2 and P_1–N_8 bonds) and significantly longer P_1–F_{1b} bond than the average P–F bond distance may be ascribed to the O atom in the $[N_4P_4F_7O]^-$ anion. In the structure of the $[(Me_2N)_3S]^+$ cation, two dimethylamino branches (denoted by A and B indices in Fig. 1) significantly different from the remaining one may be observed.

The electronic structure of the phosphonitrile skeleton has been an object of many controversies. A phosphazene backbone consists of alternating phosphorus and nitrogen atoms with formally alternating single and double P–N bonds. X-ray crystal structure analysis of cyclic phosphazenes imply that all P–N distances in the cyclophosphazene ring are equal [2,4–6].

The generally accepted “island model” [7,8] describes the bonding between the phosphorus and nitrogen atoms in terms of σ bonding and additional (out-of-plane and in-plane) π bonding arising from the overlap of 3d orbitals of the phosphorus with nitrogen p orbitals being combined into sets of three-centre π molecular orbitals (‘islands’ of electron density over P–N–P units with nodes at the phosphorus centre). Each nitrogen is attached by equally strong π bonds to both neighboring phosphorus atoms. However, the group-theoretical analysis of molecular orbitals in planar cyclophosphazenes of D_{nh} symmetry with odd n [9,10] excludes any d(P)-p(N) bonding and it makes this bonding scheme doubtful in other phosphazenes as well.

More recent bonding models [11–13] are based on prevailingly ionic P–N bonding (involving substantial charge transfer from phosphorus to nitrogen) with negative hyperconjugation contributions resulting from the donor–acceptor interactions of (out-of-plane and in-plane) nitrogen lone pairs into strongly polarized antibonding σ^*_{PN} and σ^*_{PX} orbitals. The extent of this negative hyperconjugation depends significantly on the nature of the X sub-

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doi:10.1016/j.theochem.2008.09.033

stituents on phosphorus atoms. Unequal negative hyperconjugation contributions provide a previously lacking and compelling explanation for the P–N bond length alternation observed in some linear polyphosphazenes.

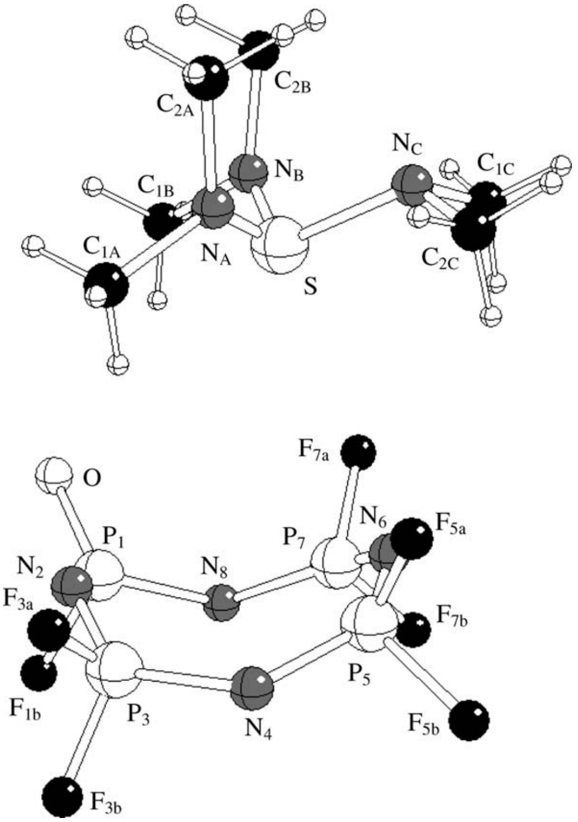

Fig. 1. Experimental structure of tris(dimethylamino)sulphonium heptafluoro-oxocyclotetraphosphazenate [1] with atoms notation.

Table 1
Bond and dihedral angles, [°], in experimental (model I) [1] and optimized (model III) geometries (X,Y = A,B,C).

Model	I	III		I	III
Bond angles			*Dihedral angles*		
$\mathrm{N_8{-}P_1{-}N_2}$	114.1(2)	111.2	$\mathrm{N_8{-}P_1{-}N_2{-}P_3}$	−54.8(6)	−71.5
$\mathrm{P_1{-}N_2{-}P_3}$	135.5(3)	127.9	$\mathrm{P_1{-}N_2{-}P_3{-}N_4}$	50.9(6)	53.5
$\mathrm{N_2{-}P_3{-}N_4}$	124.2(3)	126.0	$\mathrm{N_2{-}P_3{-}N_4{-}P_5}$	28.2(6)	33.9
$\mathrm{P_3{-}N_4{-}P_5}$	133.5(3)	126.1	$\mathrm{P_3{-}N_4{-}P_5{-}N_6}$	−26.4(7)	−17.5
$\mathrm{N_4{-}P_5{-}N_6}$	125.5(3)	127.9	$\mathrm{N_4{-}P_5{-}N_6{-}P_7}$	−32.2(7)	−48.0
$\mathrm{P_5{-}N_6{-}P_7}$	137.8(3)	128.3	$\mathrm{P_5{-}N_6{-}P_7{-}N_8}$	15.7(7)	17.5
$\mathrm{N_6{-}P_7{-}N_8}$	123.7(3)	127.0	$\mathrm{N_6{-}P_7{-}N_8{-}P_1}$	55.9(6)	58.2
$\mathrm{P_7{-}N_8{-}P_1}$	134.8(3)	130.4	$\mathrm{P_7{-}N_8{-}P_1{-}N_2}$	−34.7(6)	−23.0
$\mathrm{O{-}P_1{-}F_{1b}}$	108.4(2)	110.7	$\mathrm{P_1{-}N_2{-}P_3{-}F_{3b}}$	177.3(4)	179.3
$\mathrm{F_{3b}{-}P_3{-}F_{3a}}$	98.3(2)	96.5	$\mathrm{P_5{-}N_4{-}P_3{-}F_{3b}}$	−97.7(5)	−91.9
$\mathrm{F_{5a}{-}P_5{-}F_{5b}}$	97.7(3)	96.5	$\mathrm{P_1{-}N_2{-}P_3{-}F_{3a}}$	−76.1(5)	−75.0
$\mathrm{F_{7a}{-}P_7{-}F_{7b}}$	97.0(3)	96.4	$\mathrm{P_5{-}N_4{-}P_3{-}F_{3a}}$	158.4(4)	167.6
$\mathrm{N_2{-}P_3{-}F_{3b}}$	106.8(2)	106.6	$\mathrm{P_3{-}N_4{-}P_5{-}F_{5a}}$	−156.1(5)	−149.5
$\mathrm{N_4{-}P_3{-}F_{3b}}$	107.9(2)	106.6	$\mathrm{P_7{-}N_6{-}P_5{-}F_{5a}}$	95.7(6)	82.0
$\mathrm{N_2{-}P_3{-}F_{3a}}$	112.0(3)	115.2	$\mathrm{P_3{-}N_4{-}P_5{-}F_{5b}}$	99.7(5)	108.2
$\mathrm{N_4{-}P_3{-}F_{3a}}$	104.6(2)	101.9	$\mathrm{P_7{-}N_6{-}P_5{-}F_{5b}}$	−160.0(5)	−175.4
$\mathrm{N_4{-}P_5{-}F_{5a}}$	105.6(3)	105.0	$\mathrm{P_5{-}N_6{-}P_7{-}F_{7a}}$	−107.7(6)	−107.5
$\mathrm{N_6{-}P_5{-}F_{5a}}$	110.2(3)	110.5	$\mathrm{P_1{-}N_8{-}P_7{-}F_{7a}}$	179.1(4)	−177.4
$\mathrm{N_4{-}P_5{-}F_{5b}}$	109.3(3)	108.4	$\mathrm{P_5{-}N_6{-}P_7{-}F_{7b}}$	150.2(5)	152.3
$\mathrm{N_6{-}P_5{-}F_{5b}}$	105.1(3)	104.0	$\mathrm{P_1{-}N_8{-}P_7{-}F_{7b}}$	−74.7(5)	−71.9
$\mathrm{N_6{-}P_7{-}F_{7a}}$	106.1(3)	105.2	$\mathrm{P_7{-}N_8{-}P_1{-}F_{1b}}$	73.5(5)	80.8
$\mathrm{N_8{-}P_7{-}F_{7a}}$	106.7(2)	106.5	$\mathrm{P_3{-}N_2{-}P_1{-}F_{1b}}$	−165.6(5)	−178.0
$\mathrm{N_6{-}P_7{-}F_{7b}}$	104.9(3)	102.3	$\mathrm{P_7{-}N_8{-}P_1{-}O}$	−169.3(4)	−159.7
$\mathrm{N_8{-}P_7{-}F_{7b}}$	114.9(3)	114.9	$\mathrm{P_3{-}N_2{-}P_1{-}O}$	78.1(5)	63.2
$\mathrm{N_2{-}P_1{-}O}$	116.0(3)	118.2			
$\mathrm{N_8{-}P_1{-}O}$	112.4(3)	114.1			
$\mathrm{N_2{-}P_1{-}F_{1b}}$	100.0(2)	98.1			
$\mathrm{N_8{-}P_1{-}F_{1b}}$	104.4(3)	102.2			
$\mathrm{N_X{-}S{-}N_Y}$	116.6(2)	107.6			
	98.1(2)				
	98.5(2)				

Electronic structure of perfluorinated cyclic tetraphosphazenes has been recently investigated in several quantum-chemical studies [3,9,11]. We have not found any such study on $[(\mathrm{Me_2N})_3\mathrm{S}]^+$ cation. The aim of this article is DFT study of the electronic structure of solid tris(dimethylamino)sulphonium heptafluoro-oxocyclotetraphosphazenate in crystals as well as of its isolated ions. Because basis functions with small exponents desired for precise geometry optimizations are unusable in periodic solid state calculations performed in reciprocal space (poor SCF convergence), two different basis sets must be used in our study.

2. Methods

The electronic structure of tris(dimethylamino)sulphonium heptafluoro-oxocyclotetraphosphazenate (Fig. 1) is investigated at DFT level of theory using B3LYP hybrid functional. The experimental geometry [1] is used in the periodic 3D single-point calculation of this compound (model I) using Crystal03 software [14] and, alternatively, in the calculations of its isolated heptafluoro-oxocyclotetraphosphazenate anion, $[\mathrm{N_4P_4F_7O}]^-$, and tris(dimethylamino)sulphonium cation, $[(\mathrm{Me_2N})_3\mathrm{S}]^+$, using Gaussian03 software [15] (model II). Standard 6-31G* [16,17] or cc-pVDZ [18,19] basis sets are used for all atoms. For comparison, B3LYP/cc-pVDZ geometry optimizations of the above isolated ions (model III) are performed and the stability of the obtained structures is confirmed by vibration analysis (using Gaussian03 software [15]).

The electronic structure of the species under study is investigated using Quantum Theory of Atoms-in-Molecule (QTAIM) topological analysis of electron density [20]. The results are evaluated in terms of atomic volumes V and atomic charges q obtained using the electron density integrated over atomic basins (up to 0.001 e/bohr^3 level). Bond characteristics are evaluated in terms of electron density ρ, its Laplacian $\nabla^2\rho$

$$\nabla^2\rho = \lambda_1 + \lambda_2 + \lambda_3 \tag{1}$$

and bond ellipticity ε

$$\varepsilon = \lambda_1/\lambda_2 - 1 \tag{2}$$

at bond critical points (BCP) where $\lambda_1 < \lambda_2 < 0 < \lambda_3$ are the eigenvalues of the Hessian of the BCP electron density.

TOPOND [21] and AIM2000 [22] software packages are utilized for QTAIM analysis of CRYSTAL03 and Gaussian03 results, respectively. MOLDRAW 2.0 software [23] is used for visualization and geometry manipulation purposes.

3. Results

3.1. Heptafluoro-oxocyclotetraphosphazenate anion

The numbering of atoms in a cyclotetraphosphazene ring begins counterclockwise at the oxygen bonded phosphorus atom. The fluorine atoms are numbered according to the bonded phosphorus atom with an additional a (b) index for the atoms above (under) the $\mathrm{P_1{-}P_3{-}P_5{-}P_7}$ plane (see Fig. 1).

The comparison of experimental and DFT optimized structure data (Tables 1 and 2) confirms the similar P–N bond lengths alternation and significant ring puckering (see dihedral angles in Table 1) in the isolated anion as well. $\mathrm{N_8{-}P_1{-}N_2}$ bond angle is significantly lower than the remaining N–P–N ones due to F/O replacement. Nevertheless, the DFT bonds are significantly longer (by up to 0.09 Å for P–F bonds) and P–N–P bond angles significantly lower