

## Bonding in germatranyl cation and germatranes

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### Abstract

Equilibrium structures of silatranyl and germatranyl cations as well as corresponding fluoroatrane are obtained at the B3LYP/cc-pVDZ level of theory. Changes in the bonding on going from germatranyl cation to a neutral molecule are analyzed by using the NBO method. In contrast to three-coordinate planar germlyium cations, germatranyl cation does not possess a vacant orbital which is involved in the formation of the transannular bond. However, in germatrane upon formation of an “external” bond with a fluorine anion the inversion of this orbital occurs to accept halogen electron pairs. The presence of the GeF bond drastically changes the scheme of bonding in the GeO<sub>3</sub>N moiety compared to that of cation through the formation of interactions of a fluorine atom with equatorial oxygens. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Germatrane; Germatranyl cation; B3LYP; Transannular bond

### 1. Introduction

The synthetic and theoretical aspects of three-coordinated cations of heavier group 14 elements have attracted much attention over many years [1–5]. It was shown that the ability of group 14 elements for the coordination expansion [3,5] allows to stabilize organometallic cations by the introduction of R<sub>2</sub>N or RO groups into hydrocarbyl substituents at the M atom. The stabilization of cations arises from the intramolecular interaction between the lone electron pair(s) of the nitrogen or oxygen atoms with the formally empty p-orbital of the central cation atom M (M = Si, Ge) [6–9]. Recently, it was shown that the germlyium cation [PhGe(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>]<sup>+</sup> can be stabilized by the electronic effects of the β-dimethylaminoethoxy group [10].

Cations of the new type with atrane structure, such as silatranyl and germatranyl cations [M(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]<sup>+</sup>, where M = Si, Ge, are of peculiar interest.

These cations are plausible intermediates in reactions of silatranes and germatranes which possess a specific biological activity [11,12]. Molecular structures of silatranes and hypervalent bonding in their molecules were studied intensively [13].

Germatranes have been rather less studied, although there are experimental data on the crystal structure of fluoro- and chlorogeratranes [14,15] and quantum chemical studies [16–22]. The data indicate that the Ge–N interatomic distance in germatranes is shorter than Si–N bond length in the related silatranes, although the discrepancy between these two estimates is substantial due to the fact that in solid phase, for which the experimental interatomic distances were obtained, the crystal-packing effects shorten the transannular distance [14,15].

In terms of localized orbital interaction theory the attractive interaction N–M(X) in atranes XM(Y–CH<sub>2</sub>–CH<sub>2</sub>)<sub>3</sub>N originates from the donation of the lone pair of

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the nitrogen atom into the antibonding  $\sigma^*M-X$  orbital [16]. As a result the N–M bond strength depends on the electronegativity of the axial substituent X [13].

However, recently it was assumed that the Coulomb interaction of the oppositely charged germanium and nitrogen atoms gives the major contribution to N–Ge bonding in germatranes [19].

To discuss the nature of the transannular bond in atranes it is quite important to address the structure of the corresponding cations. Atranyl cations were not characterized experimentally, although the quantum chemical prediction of the structure of silatranyl and germatranyl cations was recently published [21–23]. Here, we discuss the electronic structure of the germatranyl cation. By comparing its structure with those of halogermatranes we try to analyze the changes in the transannular N–Ge bond on going from cation to a neutral molecule. It should be noted however that our description refers to isolated molecules, in condensed phases, where M–N bond lengths are substantially shorter, the picture of interactions may differ.

## 2. Computational details

Theoretical calculations were performed using GAUSSIAN 03 [24] on the Sun Fire 25 K computers at the Finnish IT centre for science (CSC). Becke's three-parameter exchange functional (B3) [25] was used jointly with the Lee, Yang and Parr's correlation functional (LYP) [26]. The Dunning's-cc-pVDZ correlation-consistent basis set [27,28] was employed. All stationary points were characterized by vibrational frequency calculations in the theoretical method used for optimization. NBO method [29] was used as implemented in Gaussian codes.

## 3. Results and discussion

Since the main goal of this study was to analyze changes in the strength and bond length of transannular X...N interaction on going from cations to F-atranes, the correct reproduction of the experimental X...N interatomic distance (obtained in the gas phase only for F-silatrane [20]) is of the main importance. Practically in all previous theoretical studies of silatranes and germatranes [16–23] Pople's split valence basis sets were employed. Our predicted value (Table 1) of the Si...N interatomic distance in F-silatrane obtained with the correlation-consistent double-zeta gives a better agreement with the experimental value [20] than even that achieved with the largest of the Pople's family basis set used, i.e. the 6-311++G\*\* set [23]. Moreover, our experience evidences that the use of cc-pVnZ sets provides the convergence to experimental values even for DFT methods [30].

The main equilibrium geometry parameters of F-silatrane, silatranyl cation, F-germatrane, and germatranyl cation are presented in Table 1 and Fig. 1. For both atranes with M = Si and M = Ge the loss of fluorine leads to a substantial shortening of M–N and M–O interatomic distances.

Table 1

Geometry parameters of the silatrane and germatrane cage of FM(O–CH<sub>2</sub>–CH<sub>2</sub>)<sub>3</sub>N (M = Si, Ge) and corresponding cations, obtained at the B3LYP/cc-pVDZ level (bond lengths in Å, bond angles in °)

Parameters	M = Si			M = Ge	
	$r_g$ exp [20]	F-atrane	Cation	F-atrane	Cation
M–N	2.318	2.305	1.897	2.329	1.998
N–C	1.479	1.472	1.515	1.474	1.510
O–C	1.390	1.409	1.452	1.412	1.453
M–O	1.651	1.694	1.652	1.813	1.775
C–C	1.512	1.534	1.544	1.535	1.543
N–M–O	81.3	81.7	96.5	81.6	93.5
M–O–C	123.7	121.5	109.5	116.8	107.2
M–N–C	103.2	102.7	102.8	102.8	102.5
C–C–O	117.0	109.6	108.3	110.5	110.0
C–C–N	104.5	107.3	107.6	108.4	108.8
C–N–C	115.3	115.3	115.2	115.2	115.5
O–M–O	117.8	117.9	118.7	117.9	119.6
q M				2.24	2.24
q N				–0.63	–0.69
q O				–0.88	–0.84

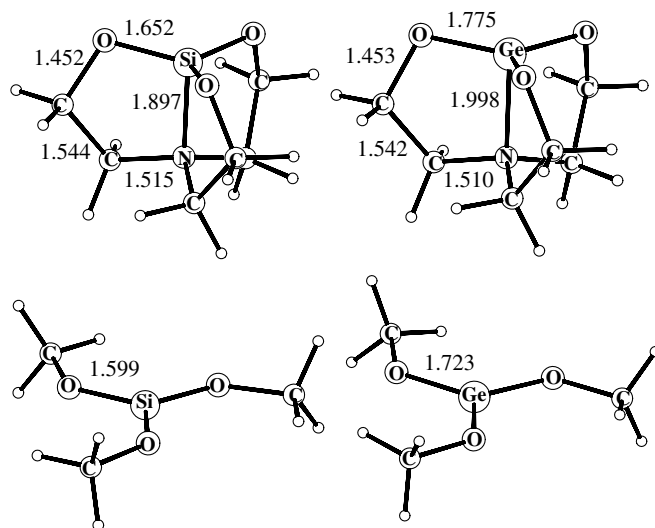


Fig. 1. Equilibrium structures obtained at the B3LYP/cc-pVDZ level of theory of silatranyl and germatranyl cations and corresponding classical cations.

The cation M becomes tetracoordinated and M–N bond formally becomes one of the  $sp^3$  hybrid bonds. This inversion of the configuration at M demonstrates itself in the increase of the N–M–O bond angle which becomes larger than 90°. Note, however, that this effect is less pronounced in germatranyl cation. M–O bonds become stronger due to the disappearance of the fluorine lone pair contribution to the antibonding M–O orbitals.

To understand the differences in the structure of atranyl cations with “classical” cations it is useful to compare them with the structures of  $(CH_3O)_3Si^+$  and  $(CH_3O)_3Ge^+$  cations (Fig. 1). The main difference is the substantially lengthened M–O bonds in atrane cations.

In “classical” cations the shortening of M–O interatomic distances may be explained by the charge transfer

from oxygen lone pairs to the vacant p-orbital of M atom that is confirmed by the natural bond analysis (NBO) [29] of the equilibrium structure of  $(\text{CH}_3\text{O})_3\text{M}^+$  cations. Second-order stabilization energy of the interaction of each oxygen lone pair with a vacant M orbital is  $37.8 \text{ kcal mol}^{-1}$  for  $\text{M} = \text{Si}$  and  $30.8 \text{ kcal mol}^{-1}$  for  $\text{M} = \text{Ge}$ . Note that the smaller interaction energy for Ge is due to longer M–O distances and therefore smaller orbital overlap. In contrast to the “classical” cations, the vacant p-orbital in the atrane cations is involved in N–Si bonding. This significantly decreases the stabilizing interaction.

The comparison of the structure and orbital interactions of  $\text{XM}(\text{Y}-\text{CH}_2-\text{CH}_2)_3\text{N}$  molecules ( $\text{X} = \text{Hal}$ ,  $\text{M} = \text{Si}$ ,  $\text{Ge}$ ) and their cations may give a new insight into the much discussed problem of the nature of N–M bonding. In this approach (to the best of our knowledge this was not discussed before) the atrane molecule is considered as an ion pair between atranyl cation and  $\text{Hal}^-$  anion. For this purpose germatranes have an attractive feature which is missing in silatranes. As it was noticed by Lee et al. [22] the NBO method for silatranes gives completely different results depending on what kind of electron density is used. The SCF density employed in the B3LYP method reveals N–Si transannular bonding in silatranyl cation while NBO analysis (based on SCF densities) shows the absence of this interaction. In contrast to these data, the use of MP2 densities demonstrates the existence of the N–Si bonds in silatranes as well as in corresponding cations. Moreover, NBO analysis reveals the drastic difference in the participation of d-orbitals of the silicon atom in N–Si bonding: in 1-fluorosilatane the silicon atom has an  $s(12\%)p(42\%)d(42\%)$  hybridization with the MP2 density, while only 3% of d-orbitals contribute to this hybridization in B3LYP analysis. Probably, it is an artefact of the NBO analysis as noted by Frenking and Fröhlich [31].

Main equilibrium interatomic bond distances and charge parameters determined by natural population analysis are presented in Table 1. The significant change (with the exception of the charge on germanium) of these parameters is observed on going from the germatranyl cation to 1-fluorogermatrane. The substitution of fluorine by chlorine and bromine does not change these parameters (Table 1).

Let us consider the change of natural bond orbitals and their interactions in going from the germatranyl cation to the 1-fluorogermatrane as revealed by the NBO analysis. Firstly it indicates the distinctive changes in the participation of N and Ge orbitals in the bonding: the contribution of N electrons increases from 88% in the cation to 96% in 1-fluorogermatrane, correspondingly the contribution of Ge decreases from 12% to 4%. This fact evidences that GeN bonding in the cation has a substantially larger covalent character and it may explain the practical identity of NBO (as well as Mulliken) M positive charges on going from cation to F-atrane: the increase of positive charge on M upon the formation of a bond with fluorine is compensated by the increase of electron density in a MN bond

Table 2

Second-order stabilization energy ( $\text{kcal mol}^{-1}$ ) of main interactions between filled and empty antibonding orbitals in germatranyl cation and 1-fluorogermatrane (B3LYP/cc-pVDZ)

Filled	Cation		F-germatrane	
	Empty	$\Delta E$	Empty	$\Delta E$
$\sigma\text{GeO}$	$\sigma^*\text{GeN} (\times 3)$	6.6	$\sigma^*\text{GeN} (\times 3)$	30.5
$\text{LP}(\text{O})1$	$\sigma^*\text{GeO} (\times 3)$	2.0	$\sigma^*\text{GeO} (\times 3)$	5.0
$\text{LP}(\text{O})2$	$\sigma^*\text{GeO} (\times 3)$	13.8	$\sigma^*\text{GeO} (\times 3)$	6.3
$\sigma\text{GeN}$	$\sigma^*\text{GeO} (\times 3)$	2.5	$\sigma^*\text{GeO} (\times 3)$	14.8
$\sigma\text{GeO}$			$\sigma^*\text{GeF} (\times 3)$	22.2
$\sigma\text{GeF}$			$\sigma^*\text{GeO} (\times 3)$	16.0
$\sigma\text{GeF}$			$\sigma^*\text{GeN}$	21.6
$\sigma\text{GeN}$			$\sigma^*\text{GeF}$	12.6

(all methods of calculating atomic charges somehow divide it between atoms).

The main stabilizing two electron-two orbital interactions in germatranyl cation are  $\text{LP}(\text{O})-\sigma^*\text{GeO}$ , and  $\sigma\text{GeO}-\sigma^*\text{GeN}$  interactions (Table 2). As was mentioned above the main interaction ( $31.3 \text{ kcal/mol}$ ) in this “classical” cation exists between  $\text{LP}(\text{O})$ s and a vacant p-orbital at Ge which is replaced by a weaker  $\text{LP}(\text{O})-\sigma^*\text{GeN}$  interaction ( $3.0 \text{ kcal/mol}$ ) in the germatranyl cation. The presence of F–Ge bond does not change the interactions between oxygen lone pairs and antibonding GeO orbitals, however it essentially increases (from 7.6 to  $36.2 \text{ kcal/mol}$ ) the  $\sigma\text{GeO}-\sigma^*\text{N-Ge}$  interactions, which weaken the N–Ge bond. The increase of these orbital interactions may be explained by raising the  $\sigma\text{GeO}$  energy level (from  $-0.8091$  to  $-0.5808$ ) which is pushed up by the appearance of a low-lying  $\sigma\text{GeF}$  orbital. Along with these interactions new strong interactions which involve GeF orbitals appear, i.e.  $\sigma\text{GeO}-\sigma^*\text{GeF}$ ,  $\sigma\text{GeF}-\sigma^*\text{GeO}$ , and  $\sigma\text{GeF}-\sigma^*\text{GeN}$ . The axial N–Ge [or  $\text{LP}(\text{N})$ ]- $\sigma^*\text{GeF}$  interaction which was considered responsible for Ge–N attraction [17] is not the largest interaction (Table 2).

Thus the picture of orbital interactions which takes into account only axial orbitals is not complete. The formation of the M–X bond results in the important change in the scheme of negative hyperconjugation in the  $\text{X}-\text{MO}_3-\text{N}$  moiety. The equatorial oxygen atoms play an important role in the bonding model.

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