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Tetrahydrofuran analogues with silicon and sulphur atoms

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Abstract. Quantum-mechanical calculations at the self-consistent-field–Møller–Plesset level have been performed for various compounds obtained by substituting two or four CH_2 groups of the tetrahydrofuran molecule with SiH_2 groups, as well as the oxygen with a sulphur atom. Cyclic tetrasilane oxide, $(SiH_2)_4O$, and sulphide, $(SiH_2)_4S$, are suggested as possible alternatives to the carbon ring of natural sugars for the design of exobiological molecules because of certain similarities with tetrahydrofuran, $(CH_2)_4O$, especially the relatively small energy differences between different conformers and the subsequent ability to cross the energy barriers between them by puckering on the pseudorotation wheel.

Key words: Five-membered heterocycles – Ab initio – Silicon – Sulphur – Exobiology

1 Introduction

In contrast to science-fiction novelists (e.g., in the first place Rosny at the end of the nineteenth century [1]), scientists interested in molecular exobiology are generally reluctant to consider the possibility of replacing first-row atoms with heavier elements, i.e., carbon with silicon, oxygen with sulphur, etc., in the design of realistic compounds for life outside the present terrestrial environment because of the lack of similarity between their physical properties and those of their homologues of the second row [2]. The situation is rather different for the ones who are concerned with prevision of molecules useful for so-called "artificial chemical life" studies, that is to say those compounds exhibiting the characteristics of a living system (i.e., self-replication and evolution). In this respect, the search for substitutes for the fragments of the RNA–DNA proteins is of paramount importance [3].

The present article gives a first account of a series of quantum-mechanical calculations devoted to the study of silicon and sulphur homologues of the central part of nucleosides, namely the ribofuranose ring, whose flexibility may be connected with the occurrence of a huge variety of conformational structures, as revealed in natural nucleotides by numerous X-ray, NMR and IR/Raman/NIS experiments [4]. In the past, most investigations on the electronic structures of biological sugars have been performed at the semiempirical and simple ab initio levels of the molecular orbital theory, for instance by means of the perturbed configuration interaction with localized orbitals method developed in the Pullman group around 1975 [5]; for computational reasons, studies at a higher theoretical level are quite recent [6–9]. Here, we have focused our attention on the parent saturated heterocycle of pentoses, the tetrahydrofuran (THF) molecule, and we have used the same self-consistent-field–second-order Møller–Plesset (MP2) procedure as in our previous work on THF [10] in order to construct isovalent systems with silicon and sulphur. That picture of the THF system has not been changed very much in new computations at the fourth-order Møller–Plesset and density functional theory levels [11].

We report results only for those molecules retaining a certain degree of symmetry, namely for compounds with identical CH_2 or SiH_2 groups at the α as well as at the β positions with respect to the heteroatom of the ring (oxygen or sulphur). It is well known that the X-ray conformations of the sugar fragments in nucleotides (i.e., C3′-endo C2′-exo, or A forms with equatorial substitution on C3′ and C2′-endo C3′-exo, or B forms with axial substitution) are conveniently described in terms of pseudo-rotation, a concept borrowed from the analysis of the spectroscopic properties of cyclopentane and its homologues in the gas phase [12]. Actually, THF is a nonplanar molecule of C_2 symmetry, whose nuclei make motions of large amplitude leading to nonrigid conformations, characterized by the values of the puckering parameters q and φ of the cycle [13]. Such flexibility is the origin of the distribution of the nucleotides between north A forms and south B forms known in molecular biology by the name "sugar wheel" [14, 15].

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Bearing these considerations in mind, we have tried to see whether and to what extent THF-like molecules containing sulphur and silicon retain flexibility comparable to that of the ribofuranose ring. Such an approach is reminiscent of the successful construction of artificial nucleotides from hexapyranose sugars [3].

2 Computational procedure and results

As in our previous work on the vibrational spectrum of THF [10], complete sets of geometrical parameters were evaluated at the MP2 perturbation level (full MP2) for each possible symmetry group in this family of compounds (Fig. 1): C_2 (twist), C_s (envelope), C_{2v} (planar ring) and, occasionally, C_1 (asymmetrically deformed molecule). The exact nature of the extrema predicted from the calculation of the electronic energies, whether an absolute energy minimum (characterized by all positive force constants) or a maximum or a saddle point (two or one negative force constant, respectively, in the (q, φ) coordinate system), was controlled by harmonic force-field calculations. We selected a 6-31G* basis set where the exponents of the six d Cartesian components for the carbon, oxygen, silicon and sulphur atoms have optimized values [16] (i.e., 0.75, 0.85, 0.45 and 0.65, in that order). The presence of six d functions instead of five generates a symmetrical combination ($x^2 + y^2 + z^2$) whose exponent is not very different from that of the higher uncontracted s orbital in the 311 subset of the 6-311G* basis and, consequently, our basis simulates the effect of the latter on conformational predictions. The Gaussian 94 package [17] was used throughout, except as regards the calculation of the q and φ puckering parameters which were obtained from the optimized geometries by means of the Ring program [18].

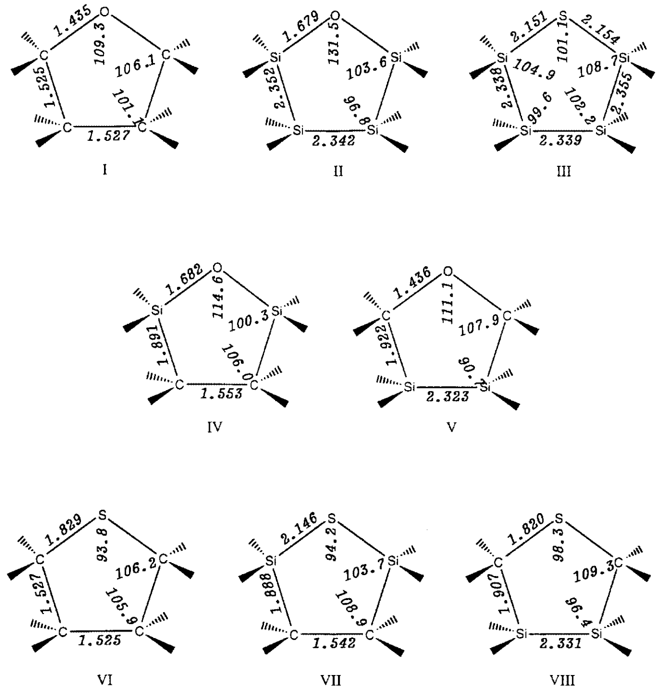

Fig. 1. Second-row analogues of tetrahydrofuran. Bond distances in angstroms and angles in degrees for the most stable forms, as optimized at a full second-order Møller–Plesset 6-31G* level

The calculated total energies of THF and its various analogues for the molecular geometries of lowest energy, as well as their rotational constants and dipole moments, are reported in Table 1. The calculated rotational constants are of valuable support in the assignment of observed microwave spectra; their quality can be estimated with reference to those for THF, where the theoretical values are greater than the observed ones [19] only by 30, 38 and 29 MHz for A, B and C, respectively. In the absence of experimental information, we postpone the inspection of the vibrational frequencies of the THF homologues, as well as the study of possible solvation effects, for the future.

It is seen that molecules with two silicon atoms α to oxygen or sulphur generally prefer C_2 conformations, while two silicons in β positions lead to C_s conformations in well-marked minima. On the other hand, smaller differences among the conformational energies, much more in line with the THF results, are obtained for the compounds $(SiH_2)_4O$ and $(SiH_2)_4S$. The oxygenated species II lies in a C_2 minimum, and at a little higher energy (0.512 kcal mol^{-1}) there is a saddle point, i.e., a point with an imaginary vibrational frequency corresponding to a transition state. In this molecule, as well as in the case of the α disilicon compound IV, a geometry optimization calculation for the saddle point leads to a planar ring, thus to a C_{2v} structure. The sulphured species III has a still more surprising behaviour, namely the loss of any symmetry element during optimization and the presence of C_s and C_2 saddle points (higher in energy by only 0.106 and 0.758 kcal mol^{-1}, respectively) close to the resulting C_1 conformation, whereas a maximum is found for the C_{2v} structure at 1.971 kcal mol^{-1} above the C_1 minimum. The latter has q = 68.2 pm and $\varphi = 152.0°$ and it is intermediate between the forms B5+ and T3+ as defined in Ref. [12]. The forms C_s and C_2 have q = 65.8 and 59.8 pm, respectively.

In brief, it can be said that the analogues of THF with second-row atoms are more or less flexible molecules with their own features; the conformational pattern of THF itself, governed by a potential surface in the (q, φ) coordinates having the form of a very peculiar "Mexican hat", is probably unique. The peculiarities of compound III may be due not to some propensity of sulphur to form a (hypervalent) pyramidalized atom, which should give only a symmetry lowering from C_{2v} to C_s or C_2, but more probably to interactions among the hydrogen atoms, as is the case in simple systems, such as ketones and sulphones.

3 Conclusion

All the molecules considered in this work can be connected in some way to species already detected in the interstellar medium, in the first place to the SiO, SiS and SiH_4 molecules, but also to organic molecules containing sulphur and to silicates of the interstellar dust

Table 1. Ground-state full second-order Møller–Plesset lowest energies and conformational picture of tetrahydrofuran and its analogues. The transition state is indicated by *TS*

Symmetry		Total energy (au)	Rotational constants (GHz)			Dipole moment (D)	Conformational pattern[a]
			A	B	C		
I	C_2	−231.695635	7.127	7.014	4.037	1.90	$C_2 < C_s$ (TS) $\ll C_{2v}$
II	C_2	−1235.798777	2.159	2.003	1.120	0.84	$C_2 < C_{2v}$ (TS)
III	C_1	−1558.374655	1.744	1.574	0.906	1.82	$C_1 < C_s$ (TS) $< C_2$ (TS) $< C_{2v}$
IV	C_2	−733.810170	4.788	3.146	2.082	2.02	$C_2 \ll C_{2v}$ (TS)
V	C_s	−733.681242	3.685	3.447	1.960	1.12	$C_s \ll C_2$ (TS) $< C_{2v}$
VI	C_2	−554.321598	6.063	4.375	2.810	2.21	$C_2 \ll C_s$ (TS) $\ll C_{2v}$
VII	C_2	−1056.383667	3.108	2.659	1.546	2.82	$C_2 \ll C_s$ (TS) $< C_{2v}$
VIII	C_s	−1056.319203	3.039	2.459	1.497	1.34	$C_s \ll C_2$ (TS) $< C_{2v}$

[a] $\ll$ denotes an energy difference of 2 kcal mol^{-1} or more between one conformer and the next

[20]. It is gratifying to note that there are two systems that bear a great resemblance to the THF ring, namely tetrasilane oxide and sulphide and so they may be put forward as plausible candidates for replacing it as a central part of possible exobiological sugars. This is suggested by the small energy differences computed for their various ring conformations. In fact, for tetrasilane oxide, the energy barrier to interconversion between north and south C_2 enantiomers, via the planar C_{2v} form, amounts to about 0.5 kcal mol^{-1}. For tetrasilane sulphide, where the interconversion takes place along the periphery of the wheel, two saddle points are encountered: between C_1 and C_s at 0.11 and between C_1 and C_2 at 0.76 kcal mol^{-1}, respectively. It can be added that the total puckering amplitude q, for the equilibrium conformation of II (42.8 pm) is close to that for THF (39.7 pm) and it drastically changes during the interconversion, taking a zero value at the C_{2v} form. In the case of molecule III q is 68.2 pm, a value definitely higher, which mainly originates from the larger S—Si bond distance with respect to O—Si (215 and 168 pm, respectively); on the other hand, it does not change very much on passing to the forms C_s and C_2. q of the other compounds IV–VIII in their lowest-energy conformations is 39.5, 50.4, 44.6, 47.9 and 62.5 pm, respectively, the phase factor φ being 90° or 180° for their C_2 or C_s forms, respectively.

The present results have to be confirmed by using both larger basis sets and more sophisticated models and by extending the calculations to related unsymmetrical analogues. The next developments would be studies of nucleosides including rings with second-row atoms, as recently made for terrestrial sugars [9].

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