Physical Chemistry

A comparative quantum-chemical analysis of electronic structures and spectroscopic parameters of cycloalkanes and cyclopolysilanes

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A comparative quantum-chemical analysis of the electronic structures and spectroscopic parameters of the cycloalkanes C_3H_6, C_4H_8, C_5H_{10}, and C_6H_{12} and their silicon analogs Si_3H_6, Si_4H_8, Si_5H_{10}, and Si_6H_{12} was performed in the framework of the SCF MO LCAO method in the INDO approximation. Qualitative interpretation of "abnormal" ionization potentials and energies of electronic absorption spectra of cyclopolysilanes has been given.

Key words: cyclopolysilanes, cycloalkanes, ionization potentials, electronic absorption spectra, quantum-chemical analysis, the Huzinaga method with allowance for electronic relaxation, INDO approximation.

In the periodic system of the elements, silicon is the nearest element to carbon, and therefore chemists have long discussed the possibility of the existence of an "organic" chemistry whose basis is silicon rather than carbon. The results of a large number of experimental works carried out in this field have been encouraging and allowed one to conclude that the chemistry of complex chain- and ring-shaped silicon compounds is quite possible.[1] At the same time, a marked distinction between the abilities of silicon and carbon atoms to form relatively inert chemical bonds with hydrogen atoms has been established. Therefore, the synthesis of stable silicon analogs of alkanes and cycloalkanes is associated with the necessity of replacing hydrogen atoms by other atoms or functional groups.

Recently, much success in studies of polysilanes and their derivatives using the methyl group as a substituent has been achieved.[2—6] In this case a number of "anomalies" in the spectroscopic and other physicochemical properties of permethylcyclopolysilanes (PMCPS) was found. In particular, despite the fact that PMCPS are isostructural with their related cycloalkanes, their electronic absorption spectra lie in the range of abnormally low (of ~4—6 eV) energies, which corresponds to the region of wavelengths (λ_{max}) from 200 to 300 nm instead of the vacuum ultraviolet region.[1] The anomaly consists in the fact that PMCPS have no lone electron pairs or multiple chemical bonds, which, as a rule, are characteristic of organic compounds absorbing at $\lambda_{max} >$ 200 nm.

Permethylcyclopolysilanes are also characterized by abnormally low (<8 eV) first ionization potentials, an ability to form colored charge transfer complexes (CTC) with π-electron acceptors, the strong mutual influence of substituents in disubstituted derivatives, and several other peculiarities inherent in aromatic molecules.[4—6] The most reliable evidence for similarity of PMCPS to aromatic hydrocarbons is the comparative ease of the chemical or electrochemical reduction[1] of compounds of both types to the corresponding radical anions that

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can be detected using the ESR technique. As a rule, the ready formation of radical anions is considered to be a peculiar indicator of the fact that the molecule contains a conjugated π-electron system with low-lying vacant π*-molecular orbitals (MOs), as, for instance, in aromatic compounds.

Thus, PMCPS are exceptional among formally saturated structures since some of their electronic properties closely resemble those of aromatic hydrocarbons. Therefore, the character of the chemical bonds in PMCPS must substantially differ from that of those in the related cycloalkanes. This would probably be reflected in the description of the delocalization of the MOs of the σ-bonding electrons in PMCPS. In the framework of the hyperconjugation concept[6,7] (*i.e.*, σ,σ-type conjugation), these cases correspond to a pseudo-π-system delocalized to a certain extent. Such a system can be easily designed by using adequate linear combinations of σ-orbitals initially localized at the chemical σ-bonds.

Methods of Calculation

For simplicity and clarity of the quantum-chemical analysis, we have considered model unsubstituted analogs of PMCPS, cyclic hydropolysilanes $(SiH_2)_n$, n = 3 to 6. It should be emphasized that the ability to consider similar model objects, nonexistent in reality, is an obvious advantage of the theoretical approach, since it allows one to clearly recognize the structural and energetic factors that should most of all be responsible for the characteristic properties of real molecular systems.

The bond lengths and bond angles in $(SiH_2)_n$ were optimized by the MNDO method[8,9] assuming that all silicon atoms in the molecule lie in the same plane. For comparison, an analogous quantum-chemical analysis was performed for related carbon compounds $(CH_2)_n$ whose geometry was chosen in accordance with the experimental data.[10—12] It should be noted that a preliminary analysis of a number of test conformations points to low sensitivity of the parameters under consideration to fairly significant distortions of the molecular geometry. To perform a comparative quantum-chemical analysis, semiempirical calculations of the electronic structure and relative values of the spectroscopic parameters of $(XH_2)_n$ molecules (X = Si and C) were carried out in the framework of the standard INDO approximation[13] according to the one-configuration version of the Huzinaga method taking into account the electronic relaxation[15] using the unified SPECTR program.[14]

Results and Discussion

The calculated energy levels corresponding to the first ionization potentials I_1 (low levels) and to the energies of electronic transitions to the valent-excited singlet state $\Delta E^{S_0 \to S_1}$ (vertical arrows) for molecules $(SiH_2)_n$ and $(CH_2)_n$ are compared in Fig. 1. As can be seen from Fig. 1, the calculated I_1 values for $(SiH_2)_n$ are 10—20% less than the corresponding values for $(CH_2)_n$. This theoretical result is in qualitative agreement with the available experimental data. In particular, according to the photoelectron spectroscopy data, the I_1 values for C_6H_{12} and Si_6Me_{12} are equal to 9.8 and 7.8 eV (see Refs. 16 and 1, respectively). The "stepwise" character of the changes in the I_1 values for $(CH_2)_n$ obtained in the calculations has been qualitatively confirmed by the experimental data.[16]

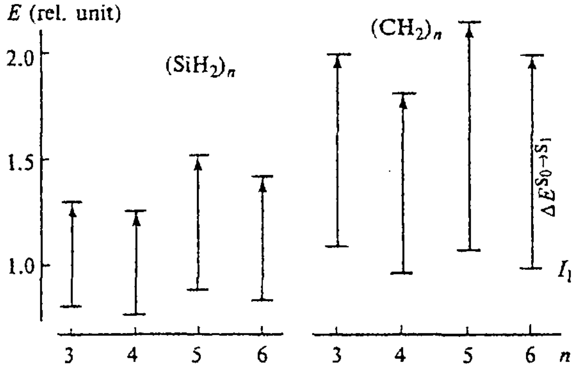

Fig. 1. Relative values of the first ionization potentials (I_1) and energies of the valent singlet-singlet excitation ($\Delta E^{S_0 \to S_1}$) of cyclopolysilanes and cycloalkanes calculated by the INDO method.

It also follows from Fig. 1 that the energies $\Delta E^{S_0 \to S_1}$ for cycloalkanes $(CH_2)_n$ should be about twice as large as for their silicon analogs $(SiH_2)_n$. The $\Delta E^{S_0 \to S_1}$ we calculated for the series $(CH_2)_n$ and $(SiH_2)_n$ change in parallel as n increases from 3 to 6. Note that, according to the calculations, the highest $\Delta E^{S_0 \to S_1}$ value for both series is reached with n = 5.

The excess atomic charges Q^{Si} and Q^{C} and the indices (i_{AB} [15]) of the change in the strength of the Si—Si, C—C, Si—H, and C—H bonds (the strengths of the C—C and C—H bonds in C_6H_{12} were taken as 100%) for $(XH_2)_n$ calculated in the framework of the INDO method are given in Table 1. As can be seen from Table 1, the carbon atoms in $(CH_2)_n$ are nearly electroneutral ($Q^{C} \simeq 0.05$ au), whereas the silicon atoms in $(SiH_2)_n$ have a fairly large positive charge $Q^{Si} \simeq$ 0.25 au. The Si—Si and Si—H bonds in cyclopolysilanes $(SiH_2)_n$ are approximately half as strong as the C—C and C—H bonds in the analogous cycloalkanes.

Using an orthogonalized basis set constructed from the hybrid atomic orbitals (AOs) in the framework of the

Table 1. Atomic charges Q^X (X = Si, C) and indices (i (%)) of the change in the chemical bond strength for the Si—Si, C—C, Si—H, and C—H bonds in cyclopolysilanes and cycloalkanes calculated by the INDO method

n	$(SiH_2)_n$			$(CH_2)_n$		
	Q^X	$-i_{X-X}$	$-i_{X-H}$	Q^X	$-i_{X-X}$	i_{X-H}
3	0.25	59.2	48.3	0.03	7.3	2.4
4	0.28	57.9	49.0	0.05	5.2	0.6
5	0.25	53.1	45.1	0.06	1.1	0.2
6	0.26	52.6	45.2	0.06	≅0	≅0

ZDO scheme,[13] matrix elements of the Hartree—Fock operator $\hat{\mathbf{F}}$ in the first (Hückel) approximation can be written as: $\mathbf{F}_{\sigma\sigma} = \alpha_{\sigma\sigma}$; $\mathbf{F}_{\sigma\sigma'} = \beta_{\sigma\sigma'}$. Since the orbital electronegativities (α) of the H, C, and Si atoms are fairly close (according to Mulliken, $\alpha_s{}^{H} \approx 7$, $\alpha_{te}{}^{C} \approx 8$, and $\alpha_{te}{}^{Si} \approx 7$ eV [17]), the distinctions between compounds $(SiH_2)_n$ and $(CH_2)_n$ both in electronic structure (see Table 1) and in spectral parameters (see Fig. 1) are formally and primarily caused by the differences in the values of the resonance integrals $\beta_{\sigma\sigma'}$.

Taking into account the results of previously published work,[18] the following approximate relation for the two-center resonance integrals β^{AB} of the chemical Si—Si and C—C bonds can be easily obtained:

$$\frac{\beta^{AB}_{SiSi}}{\beta^{AB}_{CC}} \approx \left(\frac{\gamma^{AA}_{SiSi} - \gamma^{AB}_{SiSi}}{\gamma^{AA}_{CC} - \gamma^{AB}_{CC}}\right) \cdot \frac{S^{AB}_{SiSi}}{S^{AB}_{CC}}\ , \qquad (1)$$

where γ^{AA} and γ^{AB} are the one-center and the two-center integrals of electronic interaction, respectively, S^{AB} is the overlap integral of the corresponding σ-AOs at whose expense these chemical bonds are formed. According to the estimates obtained in the INDO approximation,

$$(\gamma^{AA}_{SiSi} - \gamma^{AB}_{SiSi}) \approx 3 \text{ eV},$$
$$(\gamma^{AA}_{CC} - \gamma^{AB}_{CC}) \approx 7 \text{ eV, and } S^{AB}_{SiSi}/S^{AB}_{CC} \approx 1.2.$$

Thus, the above qualitative comparison of quantum-chemical parameters allows one to conclude that the main reason for the "anomalies" in the spectral and other physicochemical properties of cyclopolysilanes is that the energies of the averaged interaction of electrons localized on the AOs of the same Si atom ($\gamma^{AA}{}_{SiSi}$), and those of the average Coulomb repulsion of electrons on the AOs of two adjacent Si atoms ($\gamma^{AB}{}_{SiSi}$) are fairly close. The difference between the corresponding energies of electronic interaction ($\gamma^{AA}{}_{CC}$ and $\gamma^{AB}{}_{CC}$) in the case of the related cycloalkanes is much higher. This difference affects delocalization of the electron density and the reactivity of the structures considered.

In conclusion, the recently published results[19] of theoretical investigations of the ionization potentials of cyclic hydropolysilanes $(SiH_2)_n$ (n = 3 to 6) and corresponding PMCPS performed in the framework of the outervalent Green function approach in combination with approximations of the MNDO type should be noted. These data are in agreement with those that we obtained (see Fig. 1) and point to the same stepwise change in the first ionization potential I_1 with increasing n. For both series, the maximum I_1 value corresponds to $n = 4$. In the Si_4H_8 structure completely optimized by the AM1 method, four silicon atoms are in the same plane and make a square (D_{4h} symmetry), while for Si_6H_{12} and Si_5H_{10} this method resulted in a chair-shaped conformation with D_{3d} symmetry and a distorted nonplanar form with C_s symmetry, respectively.

The problems of the structure and strain of cyclic hydropolysilanes $(SiH_2)_n$ (n = 3 to 5) mostly containing planar silicon rings (with D_{3h}, D_{4h}, and D_{5h} symmetry, respectively) are considered in Ref. 20, in which quantum-chemical calculations were performed by the *ab initio* method using a double-zeta basis set. According to the data obtained, the D_{2h} structure of cyclotetrasilane was found to be more stable than its D_{4h}-conformation, however, the difference between their total energies was found to be only ~0.5 kcal mol^{-1}. Similar small differences in the energies were found for cyclopolysilane structures[21,22] considered in the framework of other variants of the nonempirical approach including the effective core potential approximation.[21]

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