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On the conformation of ethyl groups in diethylsilane molecules

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Conformations of the model dichlorodiethylsilane molecule were systematically studied in order to establish conformations of the alkyl groups relative to the Si—C bond in polydialkylsilanes. The temperature dependence of the Raman and IR spectra was studied. Quantum chemical calculations were performed of the energy characteristics as well as the normal mode frequencies, eigenvectors, and intensities of four possible conformers. In the crystalline state Et_2SiCl_2 exists as the most energetically favorable *aa*-conformer, whereas in the liquid state Et_2SiCl_2 represents a mixture of almost isoenergetic g_+g_+- and *ag*-conformers with the predomination of the latter at room temperature.

Key words: silanes, vibrational spectra, quantum chemical calculations, conformational isomerism, organosilicon compounds.

Although the properties of polydialkylsilanes, *viz.*, industrially promising σ-conjugated polymers, have been under study for more than fifty years (see review[1] and special issue of the journal[2]), some problems of the relationship between the optical and electronic properties of a polymer, on the one hand, and conformations of the main silicon chain and side alkyl substituents, on the other hand, remain yet insufficiently clarified and still evoke interest (see, *e.g.*, Refs 3 and 4). Related oligomeric and model compounds are often studied to solve similar problems.[4—9] In particular, as a model of polymer $[SiEt_2]_n$ (**1**) and its homologs with longer alkyl groups, the authors of Ref. 9 theoretically considered all possible conformations of tetrasilane *n*-Si_4Et_{10} (**2**), experimental data for which are lacking.

Earlier[10,11] we have established by Raman, IR, and UV spectroscopy that at room temperature the insoluble crystalline polymer $[SiEt_2]_n$ has a planar zigzag *trans*- or, according to the new nomenclature,[12,13] *anti*-conformation of the silicon chain (*A*, dihedral angle α(Si—Si—Si—Si) ≈ ≈ 180°). Either *anti*- (*a*) or *gauche*- (*g*) conformation can take place in each ethyl group due to hindered rotation about the Si—C bond. It was concluded[10] that these conformations are the same for each $SiEt_2$ unit; however, their particular type was not ascertained. The authors[14] also suggested the *trans*-skeleton of the $[SiEt_2]_n$ polymer on the basis of the diffraction data. The packing of *trans*-conformers of macromolecules **1** with the *anti*- and *gauche*- (*ag*) conformations of the ethyl substituents in the $SiEt_2$ group was proposed[15] on the basis of coincidence of the theoretically calculated X-ray diffraction pattern with the experimental data.[14] Later we used differential scanning calorimetry (DSC), X-ray diffraction analysis, and vibrational spectroscopy to study this polymer and observed the first-order phase transition (PT) of the disordering type in the range from 20 to 60 °C ($T_c \approx 35$ °C), which occurs without changing the lattice symmetry and conformation of the main chain.[11] The essence of this PT is a slight change in the unit cell volume due to an increase in the distance between the macromolecules. This additional volume allows "defreezing" of isomerism in the ethyl groups about the Si—C bonds to occur on heating. This leads to substantial changes in the regions of 200—300 and 600—800 cm^{-1} of the Raman spectrum, where the conformation-sensitive modes involving internal vibrational coordinates δ(SiCC) and ν(Si—C) are located.[16—18] However, the concrete type of ethyl group conformations that exist above the PT temperature was not established.

An analysis of the vibrational spectra of monoethylsilanes was carried out,[16—18] including the problem of rotational isomerism, particularly, of tetraethylsilane.[19] Only one study[9] is devoted to conformational possibilities of diethylsilanes. The authors of this work studied the potential energy surface and geometry of possible conformers by the *ab initio* quantum chemical calculations and concluded that the Et_2SiH_2 molecule could have three stable conformations of the ethyl groups with close energy values, namely, g_+g_+, *ag*, and *aa*, whereas the presence of the g_+g_--conformation is improbable due to steric interaction of the methyl groups (Fig. 1, conformers are designated according to Ref. 9). When the H atoms are replaced by bulky groups R, the g_+g_+- and *ag*-conformations become

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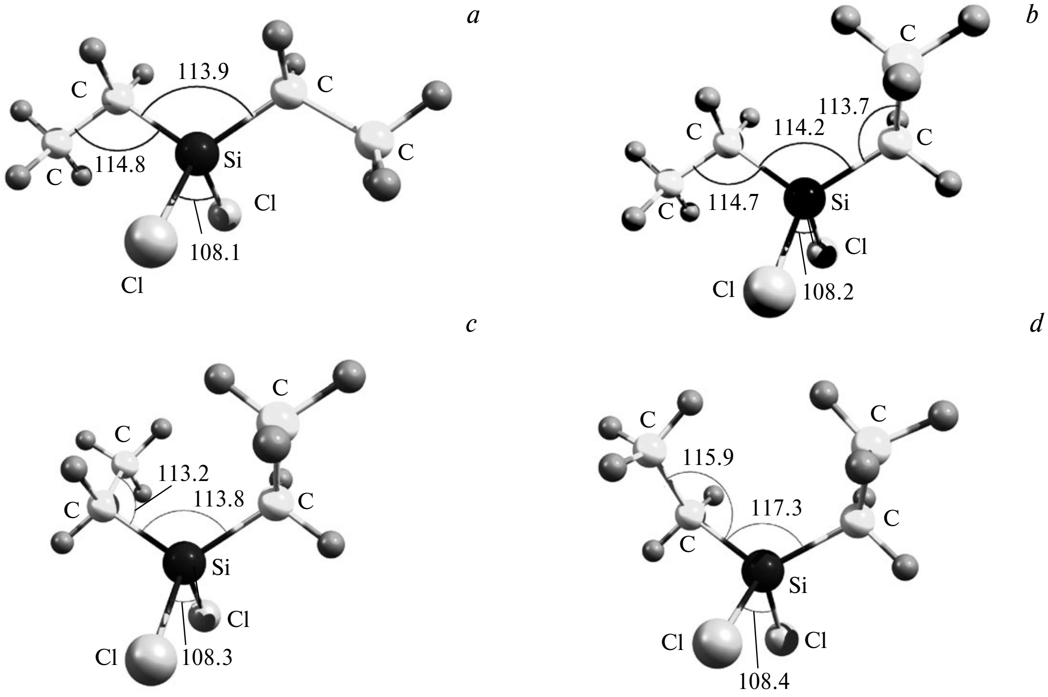

Fig. 1. Structures of possible conformers *aa* (*a*), *ag* (*b*), g_+g_+ (*c*), and g_+g_- (*d*) of the Et_2SiCl_2 molecule calculated by the DFT method.

energetically more favorable, and the *aa*-conformation is less stable but by ~1 kcal mol^{-1} only. As for tetrasilane **2**, the authors[9] suggested that the conformation of the $SiEt_2$ groups depends on the conformation of the silicon skeleton: at the skeleton conformation *deviant* (*D*, $\alpha \approx 145°$) the g_+g_+-conformation of the $SiEt_2$ groups is most favorable, whereas for the *transoid* conformation of the skeleton (*T*, $\alpha \approx 165°$) this is *ag*. This theoretical conclusion obtained by the calculations the authors presumably extend to polydialkylsilanes with ethyl and longer substituents.

In the present work, in order to establish conformations of the ethyl substituents in polymer $[Et_2Si]_n$ (**1**) below and above the PT temperature ($T_g \approx 35$ °C) and in polydiethylsiloxanes, we studied the temperature behavior of the model molecule Et_2SiCl_2 (**3**). The symmetries of the molecular skeleton of **3**, C_2SiCl_2, and of the skeleton of the unit cell of polymer **1**, C_2SiSi_2, are similar, and the masses of the Cl and Si atoms are of the same order of magnitude. Therefore, from the viewpoint of vibrational mechanics, the chosen model seems reasonable. At room temperature substance **3** is a liquid that crystallizes on cooling to −96 °C. Crystallization is hardly achieved, because this substance, as many other *n*-alkyl derivatives of nontransition metals, is rather prone to glassification.[20]

The temperature dependence of the IR and Raman spectra of compound Et_2SiCl_2 was studied in a wide temperature range. The quantum chemical calculations (in terms of MP2 and DFT levels of theory) of the normal mode frequencies and eigenvectors (NCA), as well as intensities of the IR and Raman spectra were performed for four conformers of molecule **3**. The energy characteristics of the conformers were also calculated.

Experimental

Dichlorodiethylsilane (Et_2SiCl_2, purity >99.5% was determined by GLC, an LKhM-80 chromatograph, helium as a carrier gas, phase 5% SE-30 on the support) was used.

The Raman spectra of the samples sealed in capillaries were obtained with a Horiba Jobin Yvon LabRAM 300 laser Raman spectrometer. The 632.8 nm line of a He—Ne laser with a laser power of 5 mW was used as an excitation source. The depolarization ratios of the Raman lines were estimated qualitatively for liquid samples. IR spectra were recorded using an M82 spectrophotometer (Carl Zeiss).

A Linkam THMS 600 cryostat was used in studies of the temperature dependence of the spectra (from 80 to −180 °C). The temperature was maintained with an accuracy of ±1 °C.

The MP2 (see Ref. 21) and DFT (with the PBE functional, see Ref. 22) calculations using the 6-31G(d,p) and 6-311G(d,p) basis sets were performed by the Gaussian-03 program.[23] To determine normal mode eigenvectors and to calculate the potential energy distribution (PED), the results were converted to the internal vibrational coordinates using the NCA-99 program.[24]

Results and Discussion

The results of quantum chemical calculations of an isolated molecule **3** showed that the potential energy sur-

Table 1. Energy characteristics (kcal mol^{-1}) of conformers of the Et_2SiCl_2 molecule according to the data of calculations by the MP2 and DFT PBE methods

Conformer	MP2			DFT PBE		
	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG
aa	0.00	0.00	0.00	0.00	0.00	0.00
ag	0.18	0.20	0.11	0.15	0.16	0.12
g_+g_+	0.17	0.18	0.18	0.21	0.22	0.20
g_+g_-	1.12	1.21	0.59	0.90	0.94	0.72

face contains four minima corresponding to all possible conformers (see Fig. 1). From the geometry optimization it follows that they somewhat differ in the values of the C—Si—C angle, which is minimum for the *aa*-conformer (113.8°) and reaches 117.3° for the g_+g_--conformer due to the mutual repulsion of the methyl groups. Interestingly, the *ag*-conformer having no symmetry elements has the two Si—C—C angles slightly differing in values. At the same time, the calculation data show that the Si—Cl, Si—C, and C—C bond lengths for all conformers are the same, being 2.07, 1.87, and 1.53 Å, respectively. The calculation data show that in the gas phase the *aa*-conformer is most stable, the g_+g_--conformer is least stable (by ~1 kcal mol^{-1}), and the "intermediate" conformers *ag* and g_+g_+ are close in energy (Table 1). However, it should be kept in mind that for dipole molecules the relative stability of conformers depends on the phase state of the substance: in condensed phases the stability order determined for the gas can alter due to intermolecular interactions, especially if the energy differences are small.[25]

The results of the NCA calculation appeared quite unexpected and very useful from the viewpoint of the problem stated, because they revealed substantial distinctions between the spectra of four conformers. It is important that a conformational change results in a dramatic change in the eigenvectors of some normal mode, which, in turn, necessarily induces a noticeable change in their frequencies. The vibrational frequencies of the most salient normal modes and the contributions to PED of the internal coordinates that are mostly involved in the given modes are listed in Table 2.

Table 2. Normal mode frequencies (ν), eigenvectors, and intensities of the conformers *aa*, *ag*, g_+g_-, and g_+g_+ of the Et_2SiCl_2 molecule and the contributions of coordinates to the potential energy distribution (PED) according to the NCA calculations[a]

Assignment[b]	ν/cm^{-1} (PED (%))			
	aa	*ag*	g_+g_-	g_+g_+
δ(ClSiCl)	183 (76) m [vw]	179 (54) m [vw]	183 (49) m [vw]	173 (58) m [vw]
τ(Me)	233 (78) vs[c]	237 (70) w	227 (32) m [w][d]	238 (64) m [w]
	258 (64) w[e]	252 (57) w [vw]	261 (63) w [vw]	239 (50) m [w][e]
δ(SiCC)	295 (32) m [w][c,f]	283 (31) m [vw][c]	274 (42) w [vw][e]	303 (26) s [vw][c,f]
δ^{as}(SiCC)	366 (50) w [vw][g]	358 (40) m [w]	325 (22) s [vw][h]	309 (30) s
ν^{s}(Si—Cl)	430 (82) vs [m]	440 (72) vs [m]	452 (68) vs [m]	457 (62) vs [m]
ν^{as}(Si—Cl)	509 (86) m [vs]	523 (81) m [vs]	554 (77) m [vs]	531 (78) m [vs]
ν(Si—C)	674 (60) m [s][c,i]	628 (48) m [m][c]	613 (66) s [m][c]	624 (70) s [m][c]
ν(Si—C)	—	673 (37) m [m][j]	—	—
		700 (17) w [s][j]		
mix.	664 vw[c]	—	642 w,	669 w [m],
			717 vw [vw][c]	707 vw [m]
ν^{as}(Si—C)	684 (84) sh [m]	724 (48) w [s]	721 (68) m [s]	728 (68) m [s]
ρ^{as}(CH_2)[j]	712 vw [s]	—	—	—

[a] The band intensities in the IR spectra (s is strong, vs is very strong, w is weak, vw is very weak, m is medium, and sh is shoulder) and lines in the Raman spectra (in brackets) are indicated. The contributions of corresponding coordinates to the PED are given in parentheses.

[b] δ, bending vibrations; τ, torsional vibrations; ν, stretching vibrations; mix. are strongly mixed modes; ρ, rocking vibrations; s and as are symmetric and antisymmetric vibrations, respectively.

[c] Symmetric mode.

[d] The contribution of δ[ClSiCl] is 30%.

[e] Antisymmetric mode.

[f] The mode has the contribution of δ[CSiC].

[g] The mode has the contribution of δ^{as}[CSiCl].

[h] The contribution of ν[Si—Cl] is 35%.

[i] The contribution of ν[Si—Cl] is 14%.

[j] Strongly mixed modes.

Of all vibrations of the $(CC)_2SiCl_2$ skeleton, only the deformation of Cl—Si—Cl angle (region 170—185 cm^{-1}) and stretching vibrations of the Si—Cl bonds (region 430—550 cm^{-1}) are more or less localized. However, the contribution of the corresponding coordinates to their PED differs strongly for different conformers, resulting in frequency differency. All the rest normal modes are of heavily mixed origin, therefore, the designation of vibrations given in Table 2 is conditional to some extent. Especially interesting pattern is observed in the range of 600—750 cm^{-1}, where the calculation predicts four bands to occur and where the analytically significant Si—C stretching vibrations should be situated. For the *aa*-, g_+g_--, and g_+g_+-conformers belonging to the point symmetry groups C_{2v}, C_s, and C_2, respectively, these are the symmetric ν^s(Si—C) and antisymmetric ν^{as}(Si—C) vibrations. For the *aa*-conformer these two vibrations manifest themselves as Raman and IR bands at 674 and 684 cm^{-1} with contribution of the ν(Si—C) coordinates to the PED of 60 and 84%, respectively, the difference between their frequencies being only 10 cm^{-1}. For the both *gg*-conformers, the ν^s(Si—C) frequency is much lower (613 and 624 cm^{-1}, contribution to the PED ~70%) and the ν^{as}(Si—C) frequency is much higher (721 and 728 cm^{-1}, contribution to the PED 68%), the difference between the ν^s and ν^{as} frequencies being already ~100 cm^{-1}. The eigenvectors of two other modes in the region 600—750 cm^{-1} for the conformers indicated above are very complicated because of participation of many internal coordinates, with main contributions from the CH_2 group deformations ($\rho(CH_2)$). The nonsymmetric *ag* conformer is of special interest. Its ν(Si—C) coordinate contributes to a greater or lesser extent to all four modes in this region (those with frequencies at 628, 673, 700, and 724 cm^{-1}).

Reminding the results of calculations, let us consider the experimental spectra of compound **3**. The Raman spectra are presented in Fig. 2 (the data on the IR spectra lead to analogous conclusions). It is seen that the Raman spectra of the liquid and crystal differ strongly in the region below 800 cm^{-1}. The spectrum of the crystal is simpler. The data presented in Table 3 seem to be very important: the calculated spectrum of the *aa*-conformer is compared with the experimental spectrum of the crystal. These two spectra are very similar in number and mutual disposition of the bands and in their intensities although all the calculated frequencies are by 10—20 cm^{-1} lower than the experimental ones (the average scaling factor is 1.02). From these data it follows unambiguously that in the crystalline state molecule **3** exists in the *aa*-conformation. On going to the liquid state, new lines appear in

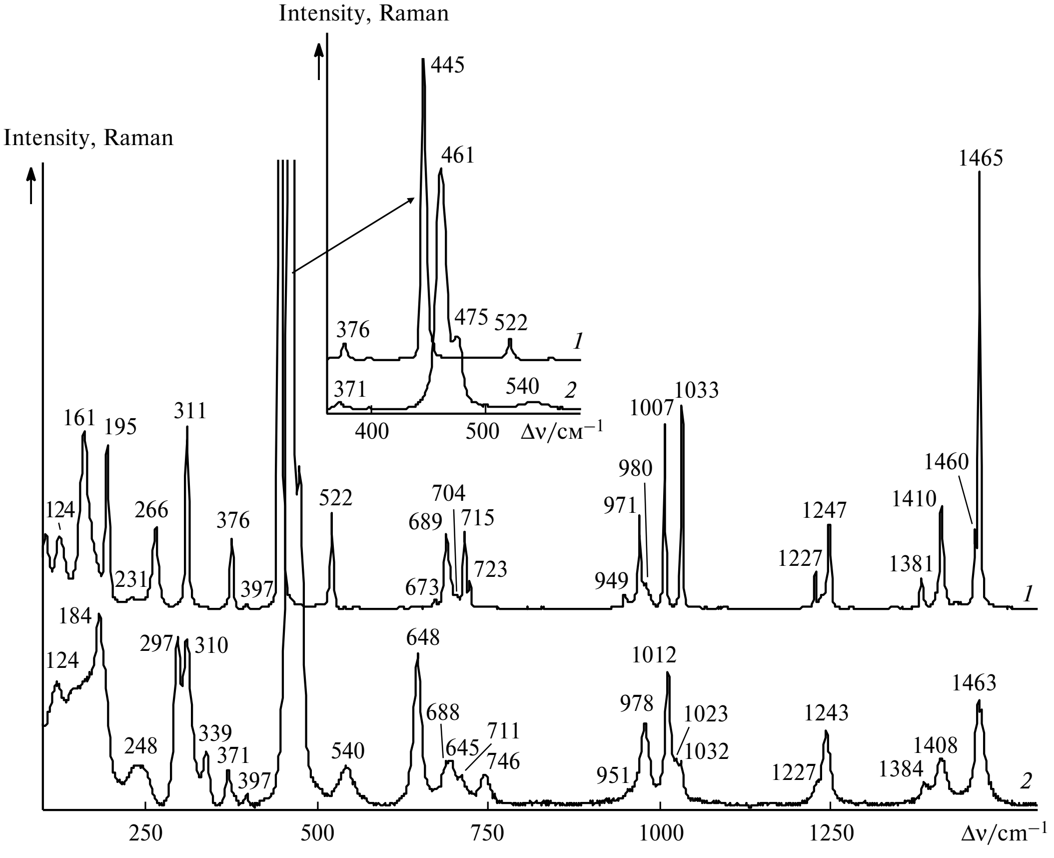

Fig. 2. Raman spectra of compound Et_2SiCl_2 (**3**) in the crystalline (–110 °C) (*1*) and liquid (–80 °C) (*2*) states. Inset: the spectral region from 350 to 600 cm^{-1}.

Table 3. Experimental* and theoretical (DFT PBE) Raman spectra of the *aa*-conformer of the Et_2SiCl_2 molecule

ν/cm^{-1}	
PBE	Experiment
366 m	376 m
430 vs	445 vs
509 m	522 m
664 vw	673 vw
674 m	689 m
684 sh	703 sh
712 w	715/723 m

* Data for the crystalline sample.

the spectra. The Raman lines characteristic of the crystal, ν^{s}(Si—C) 445 cm^{-1} and ν^{as}(Si—C) 522 cm^{-1}, disappear, indicating the absence of the *aa*-conformer in the liquid. A higher-frequency polarized line of a complicated contour with peaks at 461 and 475 cm^{-1} appear in the spectrum of the liquid instead of the Raman line of the crystal at 445 cm^{-1}. Taking into account the data of Table 2 about the positional relationship of the ν^{s}(Si—C) frequencies for four conformers, we may assign the line at 461 cm^{-1} to the *ag*-conformer, while a weaker line at 475 cm^{-1} can be ascribed to one of the *gg*-conformers, and it is seen that the *ag*-conformer prevails in the mixture. Analysis of the broadened contour of the depolarized Raman band at ~540 cm^{-1} corresponding to the ν^{as}(Si—C) vibration in the spectrum of the liquid allows us to refine that the second conformer in the mixture is g_+g_+, because the calculation shows that the ν^{as}(Si—C) frequencies for the *ag*- and g_+g_+-conformers are close in value, unlike the higher frequency for the g_+g_--conformer and the lowered frequency for *aa*-conformer.

The temperature dependence of the Raman spectrum of the liquid shows that the fraction of the g_+g_+-conformer increases on heating, as it is clearly seen from the change in the intensity ratio of the Raman lines at 297 cm^{-1} (conformer *ag*) and 309 cm^{-1} (conformer g_+g_+) corresponding to the conformation-sensitive mode with a considerable participation of the δ(SiCC) coordinate. These experimental data agree well with the results of calculation of the conformer relative stability.

Thus, the combined consideration of the calculation results and experimental data on the temperature behavior of the vibrational spectra allows us to conclude that in the crystalline state the Et_2SiCl_2 molecule exists as the energetically most favorable *aa*-conformer, while a mixture of somewhat less favorable and almost isoenergetic *ag*- and g_+g_+-conformers with predominance of the former at room temperature is observed in the liquid state. It should be emphasized that a change in the conformation of the molecule substantially alters the eigenvectors of the corresponding normal modes.

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