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Fig. 1. Equilibrium configuration of the trimethylbromosilane molecule

Figure 1: Fig. 1. Equilibrium configuration of the trimethylbromosilane molecule

Abstract

Full Text

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POTENTIAL FUNCTIONS OF MOLECULES OF THE HOMOLOGOUS SERIES $(\text{CH}_3)_n\text{SiBr}_{4-n}$ ($n = 1-4$)

(Presented by Academician I. V. Obreimov, October 4, 1961)

The force fields of methylbromosilanes have been investigated only partially (¹); however, in connection with the development of the chemistry of organosilicon compounds, a more detailed study of the physicochemical properties of these monomers is of interest. For the present series of compounds we have calculated the coefficients of the potential energy, the frequencies, and the forms of the vibrational spectra. For CH_3SiBr_3 , the displacements of atoms from their equilibrium positions in normal vibrations were computed. In the present work an analysis of the results obtained is carried out, and a table of influence coefficients is given.

The mechanical vibrational problem for methylbromosilanes was solved by analogy and using the method previously applied to the calculation of the corresponding chloro-substituted compounds (²), and also taking into account the results obtained for them. The following were taken as geometrical data (r in Å):

	$r(\text{C}-\text{H})$	$r(\text{C}-\text{Si})$	$r(\text{Si}-\text{Br})$
CH_3SiBr_3	1.093	1.93	2.17
$(\text{CH}_3)_2\text{SiBr}_2$	1.093	1.92	2.21
$(\text{CH}_3)_3\text{SiBr}$	1.093	1.81	2.24

the angles are tetrahedral. The natural coordinates are denoted in Fig. 1, which represents the equilibrium configuration of the molecule $(\text{CH}_3)_3\text{SiBr}$. The initial data for the calculation were measured combination and infrared spectra published in works (^{1, 3, 4}).

Fig. 1. Equilibrium configuration of the trimethylbromosilane molecule

The frequencies calculated on the basis of the obtained set of potential constants (Table 1) agree well with the experimental ones: the mean absolute deviation lies within 4 cm^{-1} . Analysis of the secular equations and of the computed forms shows that the greatest interaction between the parameters of the molecule occurs for vibrations associated with stretching of the Si—C and Si—Br bonds and deformation of the angles C—Si—C, Br—Si—C, and Br—Si—Br. Thus, for totally symmetric vibrations $\nu(\text{Si—C})$, the relative change in the angles of the groups $\text{C}_i\text{SiBr}_{4-i}$ ($i = 1-3$) is 20–30%, and in the angles H—C—Si and H—C—H, respectively, 35 and 15%. The Si—Br bond length also changes appreciably. For other types of symmetry, the parameters of the methyl groups in the corresponding vibration change to a greater degree. In the symmetric vibration $\nu(\text{Si—Br})$, the change in the angles of the groups $\text{C}_i\text{SiBr}_{4-i}$ reaches 60% relative to

Table 1

Influence coefficients of methylbromosilanes (10^6 cm^{-2})

Molec.	$Q_1, Q_2, Q_3, Q_4, Q_5, Q_6, Q_7, Q_8, Q_9, Q_{10}, Q_{11}, Q_{12}, Q_{13}, Q_{14}, Q_{15}, Q_{16}, Q_{17}, Q_{18}, Q_{19}, Q_{20}, Q_{21}, Q_{22}, Q_{23}, Q_{24}, Q_{25}, Q_{26}, Q_{27}, Q_{28}, Q_{29}, Q_{30}, Q_{31}, Q_{32}, Q_{33}, Q_{34}, Q_{35}, Q_{36}, Q_{37}, Q_{38}, Q_{39}, Q_{40}, Q_{41}, Q_{42}, Q_{43}, Q_{44}, Q_{45}, Q_{46}, Q_{47}, Q_{48}, Q_{49}, Q_{50}, Q_{51}, Q_{52}, Q_{53}, Q_{54}, Q_{55}, Q_{56}, Q_{57}, Q_{58}, Q_{59}, Q_{60}, Q_{61}, Q_{62}, Q_{63}, Q_{64}, Q_{65}, Q_{66}, Q_{67}, Q_{68}, Q_{69}, Q_{70}, Q_{71}, Q_{72}, Q_{73}, Q_{74}, Q_{75}, Q_{76}, Q_{77}, Q_{78}, Q_{79}, Q_{80}, Q_{81}, Q_{82}, Q_{83}, Q_{84}, Q_{85}, Q_{86}, Q_{87}, Q_{88}, Q_{89}, Q_{90}, Q_{91}, Q_{92}, Q_{93}, Q_{94}, Q_{95}, Q_{96}, Q_{97}, Q_{98}, Q_{99}, Q_{100}$
I	0,211 0,285 0,128 1,261 1,352 — 1,075 — 1,048 —0,003 —0,002 —0,030,036
CH ₃ SiBr ₃	
II	0,206 0,296 0,128 1,243 1,297 1,288 0,994 1,196 1,027 —0,003 —0,002 —0,030,035
(CH ₃) ₂ SiBr ₂	
III	0,212 0,319 0,129 1,232 1,264 1,276 — 1,151 1,147 —0,003 —0,002 —0,030,034
(CH ₃) ₃ SiBr	
IV	0,231 — 0,129 1,226 1,256 — — 1,123 — —0,003 —0,002 —0,030,034
(CH ₃) ₄ Si	
	$(q_1, \beta_1, q_2, \beta_2, Q_1, \beta_1, Q_1, \beta_2, Q_1, \alpha_1, \beta_1, \beta_2, \beta_3, \beta_4, \beta_5, \beta_6, \beta_7, \beta_8, \beta_9, \beta_{10}, \beta_{11}, \beta_{12}, \beta_{13}, \beta_{14}, \beta_{15}, \beta_{16}, \beta_{17}, \beta_{18}, \beta_{19}, \beta_{20}, \beta_{21}, \beta_{22}, \beta_{23}, \beta_{24}, \beta_{25}, \beta_{26}, \beta_{27}, \beta_{28}, \beta_{29}, \beta_{30}, \beta_{31}, \beta_{32}, \beta_{33}, \beta_{34}, \beta_{35}, \beta_{36}, \beta_{37}, \beta_{38}, \beta_{39}, \beta_{40}, \beta_{41}, \beta_{42}, \beta_{43}, \beta_{44}, \beta_{45}, \beta_{46}, \beta_{47}, \beta_{48}, \beta_{49}, \beta_{50}, \beta_{51}, \beta_{52}, \beta_{53}, \beta_{54}, \beta_{55}, \beta_{56}, \beta_{57}, \beta_{58}, \beta_{59}, \beta_{60}, \beta_{61}, \beta_{62}, \beta_{63}, \beta_{64}, \beta_{65}, \beta_{66}, \beta_{67}, \beta_{68}, \beta_{69}, \beta_{70}, \beta_{71}, \beta_{72}, \beta_{73}, \beta_{74}, \beta_{75}, \beta_{76}, \beta_{77}, \beta_{78}, \beta_{79}, \beta_{80}, \beta_{81}, \beta_{82}, \beta_{83}, \beta_{84}, \beta_{85}, \beta_{86}, \beta_{87}, \beta_{88}, \beta_{89}, \beta_{90}, \beta_{91}, \beta_{92}, \beta_{93}, \beta_{94}, \beta_{95}, \beta_{96}, \beta_{97}, \beta_{98}, \beta_{99}, \beta_{100})$
I	—0,030,037 —0,060 — 0,060 —0,230 —0,227 —0,275 — —0,348 —0,030 —0,009 —
II	—0,030,035 —0,052 —0,040,049 —0,226 —0,225 —0,252 —0,246 —0,338 —0,038 —0,010,014
III	—0,030,035 —0,047 —0,040,043 —0,224 —0,225 —0,250 —0,241 —0,334 — —0,010,005
IV	—0,030,035 —0,038 — 0,038 —0,221 —0,225 —0,237 — —0,334 — — —0,010
	$a_\delta^{-1} b_\delta^{-1} [q'(\beta_{12})] \cdot b_\gamma^{-1} (Q_1, \gamma_1, Q_1, \gamma_2, \beta_1^{-1} [Q_1, \gamma_1, \gamma_2, \beta_1, \beta_2, \beta_3, \beta_4, \beta_5, \beta_6, \beta_7, \beta_8, \beta_9, \beta_{10}, \beta_{11}, \beta_{12}, \beta_{13}, \beta_{14}, \beta_{15}, \beta_{16}, \beta_{17}, \beta_{18}, \beta_{19}, \beta_{20}, \beta_{21}, \beta_{22}, \beta_{23}, \beta_{24}, \beta_{25}, \beta_{26}, \beta_{27}, \beta_{28}, \beta_{29}, \beta_{30}, \beta_{31}, \beta_{32}, \beta_{33}, \beta_{34}, \beta_{35}, \beta_{36}, \beta_{37}, \beta_{38}, \beta_{39}, \beta_{40}, \beta_{41}, \beta_{42}, \beta_{43}, \beta_{44}, \beta_{45}, \beta_{46}, \beta_{47}, \beta_{48}, \beta_{49}, \beta_{50}, \beta_{51}, \beta_{52}, \beta_{53}, \beta_{54}, \beta_{55}, \beta_{56}, \beta_{57}, \beta_{58}, \beta_{59}, \beta_{60}, \beta_{61}, \beta_{62}, \beta_{63}, \beta_{64}, \beta_{65}, \beta_{66}, \beta_{67}, \beta_{68}, \beta_{69}, \beta_{70}, \beta_{71}, \beta_{72}, \beta_{73}, \beta_{74}, \beta_{75}, \beta_{76}, \beta_{77}, \beta_{78}, \beta_{79}, \beta_{80}, \beta_{81}, \beta_{82}, \beta_{83}, \beta_{84}, \beta_{85}, \beta_{86}, \beta_{87}, \beta_{88}, \beta_{89}, \beta_{90}, \beta_{91}, \beta_{92}, \beta_{93}, \beta_{94}, \beta_{95}, \beta_{96}, \beta_{97}, \beta_{98}, \beta_{99}, \beta_{100})$
I	—0,090,104 —0,100,090 —0,046 — 0,046 — —0,233 —0,209 —0,219 —0,193 —
II	—0,080,097 —0,100,095 —0,030,037 0,047 —0,050 — —0,204 —0,240 —0,180,255
III	— [0,124] —0,124 — —0,030,048 [0,032] —0,047 —0,177] — — [—0,175] —0,310
IV	— — — — — — [0,042] —0,042 —0,249] — — —

Molecule	γ_1	α_{23}^{-1}	$(Q_1, \beta_4 Q_1, \beta_5 Q_1, \beta_6 Q_1, \alpha_{41}, \alpha_{56}, \beta_1) q', \beta_2 \beta_1, \beta_3 \beta_2, \beta_4 \beta_1, \beta_7$	$[\beta_1, \beta_2, \beta_3, \beta_4, \beta_5]$									
I	—	—	—	—	—	—	—	0,001	0,005	—	—	—	0,019
II	—0,139	—0,178	—0,000	—0,002	—	0,002	0,002	0,004	—0,008	0,002	0,013	0,002	0,013
III	[—0,177]	—	0	0,005	—0,006	0	0	0,007	—0,007	0,003	0,012	0	[0,002]—0,004
IV	—	—	0,008	—0,003	—	—0,002	—0,001	—	—	0,003	0,012	0,001	[—0,006]

Molecule	$\beta_1 \gamma_1, \beta_2 \gamma_1, \beta_4 \gamma_1, \beta_5 \gamma_1, \beta_8 \epsilon_{12}, \alpha_{312}, \alpha_{2312}, \alpha_{412}, \beta_{12}, \beta_{13}^{-1} [\epsilon_{12}, \beta_2] q_2, \gamma_1$
I	0,037 0,010 — — — — ? — — — — 0 0,001
II	0,024 0,039 0,017 —0,082—0,021 — 0,008 0,019 0,042 —0,118—0,000—0,001 0,002
III	0,016 0,036 0,017 —0,029—0,000—0,004 0,006 0,017 0,031 —0,118—0,061—0,002 0,001
IV	— — — — — — — —0,000—0,011 0,058 —0,123 — — —

Molecule	$\gamma_1, \epsilon_{12}, \epsilon_{13}, \alpha_{13}, \alpha_{13}, \alpha_{23}, \gamma_{\delta\delta}^{-1} [\epsilon_{12}, \beta_2] q_2, \alpha_{23}$
I	— — — —0,019— — —0,020—0,019— — — — —0,004—0,003
II	0 —0,003—0,005 —0,022—0,009—0,009 —0,021—0,006 —0,023—0,007 — — —0,003—0,001
III	0,001 —0,002—0,005 —0,030—0,004—0,003 —0,028—0,021—0,006—0,006 0,002 —0,001—0,003—0,002
IV	— —0,003—0,006 — — — — — [—0,003]—0,008 — — —0,003—0,001— —

Notes: 1. Order of arrangement of the coefficients: 1 —diagonal, 2 —coefficients referring to interactions of the coordinates of the Si—CH₃ group, 3 —of the C(SiBr_n)C_{3-n} group (n = 0-3), 4 —to interactions of the coordinates of the indicated groups with one another.

2. Brackets denote interactions of representatives of the group of equivalent coordinates as applied to the scheme of the molecule (CH₃)₃SiBr. Coefficients not in brackets describe the mutual influence of the following parameters: k_{δ}^{-1} —(Br_iSiBr_j = S), a_{δ}^{-1} —(SiBr_k, Br_kSiBr_j), b_{δ}^{-1} —(SiBr_k, Br_jSiBr_m), b_{γ}^{-1} —(SiBr_k, Br_jSiC), B_{δ}^{-1} —(SiC, BrSiBr), l_{ij}^{-1} refer to interactions of angles *i* and *j* having a common side, o_{ij} — “opposite angles” (having a common vertex), $n_{\beta\gamma}^{-1}$ —(BrSiC_k, SiC_lH) (the angles do not lie in one plane, analogously to γ_{1a} and β_3 in (CH₃)₂SiH₂⁽⁶⁾), $p_{\delta\delta}^{-1}$ and $r_{\beta\delta}^{-1}$ —(BrSiBr, SiCH) (in the case of $p_{\beta\delta}^{-1}$ the SiCH plane bisects the angle δ).

3. Numbers in square brackets correspond to coefficients written in the same brackets.

to the stretching of the Si—Br bond. Comparison with calculations for methylchlorosilanes⁽⁵⁾ shows that, for the methyl groups, the valence and internal deformation vibrations of type A₁, as well as the corresponding symmetric vibrations of type E, coincide with high accuracy both in frequency and in form; the amplitudes of the external deformation vibrations are equal to

the corresponding ones in methylchlorosilanes with an accuracy of 0.01–0.04 for the coordinates $Q, q', \varepsilon, \delta$, and γ (see Fig. 1), and coincide completely for the remaining coordinates. The forms of the skeletal vibrations of the molecules are different.

Consideration of the influence coefficients, of the displacements of atoms during vibrations, and comparison of them with similar parameters in methylchlorosilanes makes it possible to draw the following conclusions: a) The strength of the C–H bond changes hardly at all and is greater than the strength of Si–C by approximately a factor of 1.6–1.8. The Si–C bond becomes somewhat stronger (of the order of 10%) on going from tetramethylsilane to bromo- and chloro-substituted compounds. b) The Si–Br bond is approximately 20% weaker than the Si–Cl bonds for each pair of analogous halogen-substituted compounds. c) The strength of Si–Br systematically increases with accumulation of Br atoms at silicon. Replacement of methyl groups by Br atoms causes, as in chlorine substitution, strengthening of the covalent character of the neighboring bonds. In bromine compounds this effect is manifested somewhat more weakly, which is explained by the lower electronegativity of the Br atom (2.85) in comparison with chlorine (3.0). The electronization of the C–H bonds changes little. d) The rigidity of the H–C–H angles on going from $(\text{CH}_3)_4\text{Si}$ to CH_3SiBr_3 changes in larger jumps than in chloromethylsilanes. The angles Br–Si–Br and Br–Si–C are more easily deformed than the angles Cl–Si–Cl and Cl–Si–C. e) The SiBr_j groups interact with other parts of the molecule to a greater degree than SiCl_j . f) Calculation of the displacements of atoms in fully symmetric vibrations in the molecules CH_3SiBr_3 and CH_3SiCl_3 gives the following values for the change in the silicon–carbon bond length:

Frequency (cm^{-1})	2898	1249	746	314	153
CH_3SiBr_3 (\AA)	0.0034	0.0139	0.0477	0.0035	0.0022
CH_3SiCl_3 (\AA)	0.0034	0.0137	0.0471	0.0096	0.0009

For type E , Si–C stretching is significant only in rocking vibrations of the halogen groups: in CH_3SiBr_3 , in the vibration with frequency 186 cm^{-1} , it reaches 0.0013 \AA ; in CH_3SiCl_3 (frequency 229 cm^{-1}), 0.0007 \AA .

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REFERENCES

1. H. Murata, S. Hayashi, *J. Chem. Phys.*, **19**, 1217 (1951).
2. I. F. Kovalev, DAN, **136**, 1313 (1961).
3. J. Goubeau, H. Sommer, *Zs. anorg. u. allgem. Chem.*, **289**, 1 (1957).
4. H. Kriegsmann, *Zs. Elektrochem., Ber. Bunsenges. physik. Chem.*, **62**, 1033 (1958).
5. I. F. Kovalev, *Optics and Spectroscopy*, **10**, 707 (1961).
6. I. F. Kovalev, *Optics and Spectroscopy*, **8**, 315 (1960).

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