

ELECTRON DIFFRACTION STUDY ON THE MOLECULAR STRUCTURE OF METHYLTRIMETHOXYSILANE

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Summary

The electron diffraction data for methyltrimethoxysilane are consistent with a C_3 symmetry model, the predominant forms of which have rotational angle(s) between 100 and 155° around the Si—O bond (the *anti* conformation of the C—Si—O—C chain would correspond to 0°). There is probably large amplitude motion around the Si—O bonds. The following bond lengths and bond angles were determined: $r_a(\text{C—H})$ 1.093 ± 0.005, $r_a(\text{Si—C})$ 1.842 ± 0.013, $r_a(\text{Si—O})$ 1.632 ± 0.004, $r_a(\text{O—C})$ 1.425 ± 0.004 Å, $\angle\text{C—Si—O}$ 109.6 ± 0.5°, and $\angle\text{Si—O—C}$ 123.6 ± 0.5°.

Introduction

The primary purpose of the present electron diffraction investigation of methyltrimethoxysilane, $\text{CH}_3\text{Si}(\text{OCH}_3)_3$, was to determine the Si—O bond length, the Si—O—C bond angle and to form some picture of its conformational characteristics. This work is part of our structural study of the series of compounds $(\text{CH}_3)_{4-n}\text{Si}(\text{OCH}_3)_n$ ($n = 1, 2, 3, 4$)*.

Experimental

The electron diffraction patterns of the methyltrimethoxysilane sample were recorded with a modified EG-100A apparatus [3,4] at a nozzle temperature of about 40°C. The ranges of intensity data corresponding to the 50 cm and 19

* For $n = 1$ see ref. 1, for $n = 4$ see ref. 2. The study of the compound with $n = 2$ is in progress.

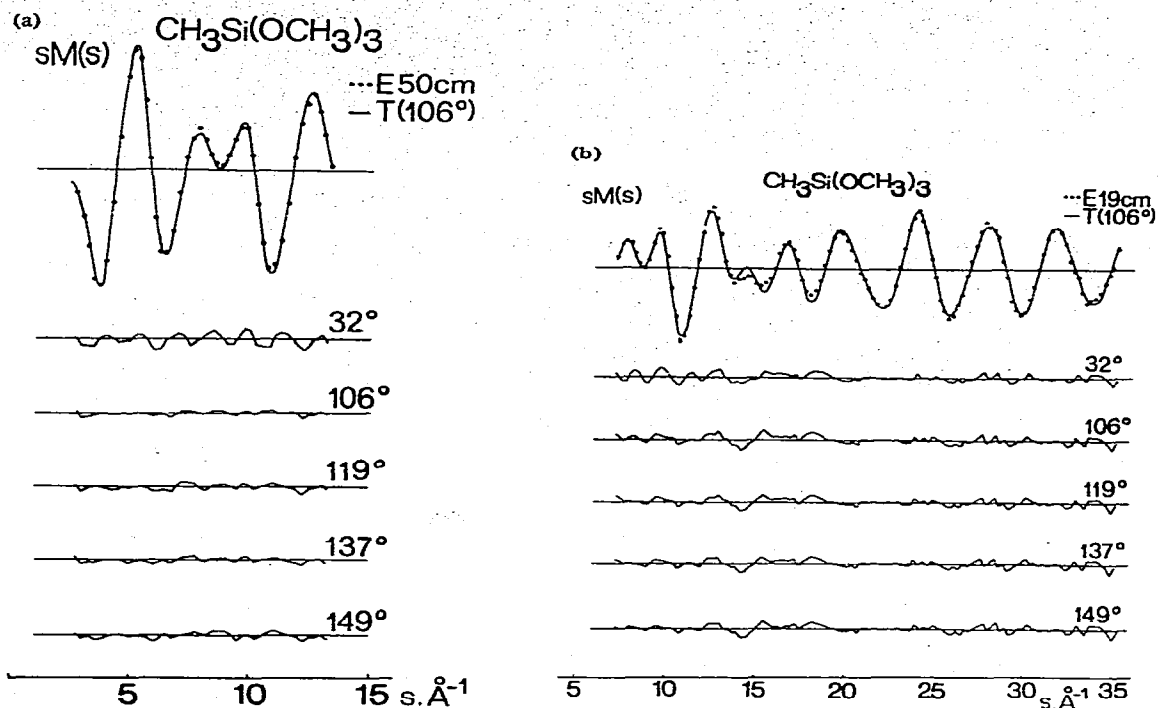


Fig. 1. Experimental (E) and theoretical (T) molecular intensities. The experimental data refer to the 50 and 19 cm camera ranges in Fig. 1a and 1b, respectively. The theoretical curves were calculated for a model with τ 106°. The difference curves refer to models with rotational angles indicated.

cm nozzle-to-plate distances were $2.50 \leq s \leq 13.25 \text{ \AA}^{-1}$ and $7.25 \leq s \leq 35.25 \text{ \AA}^{-1}$, respectively. The procedure of data reduction, including the determination and subsequent modifications of the experimental background, was similar to that described elsewhere [5]. The two sets of data corresponding to the two nozzle-to-plate distances were used simultaneously in the analysis [6] and are shown in Fig. 1a and 1b.

Structure analysis

Only models with C_3 symmetry were considered, as in the electron diffraction analyses of trimethyl phosphate [7] and triethylsilane [8]. The following bond distances and bond angles were chosen to be independent parameters*: $r(\text{C-H})$, $r(\text{Si-C})$, $r(\text{Si-O})$, $r(\text{C-O})$, $\angle \text{Si-C-H}$, $\angle \text{C-Si-O}$, $\angle \text{Si-O-C}$ and $\angle \text{O-C-H}$, in addition to the angle of rotation around the Si-O bond (τ) which was equal to zero when the C-Si and O-C bonds were in an *anti* conformation (Fig. 2).

The experimental radial distribution shown in Fig. 3 revealed considerable direct information on the bond distances [$r(\text{C-H}) \approx 1.09$, $r(\text{C-O}) \approx 1.42$, and $r(\text{Si-O}) \approx 1.63 \text{ \AA}$], except that for Si-C which is buried under the maximum

* All C-H bonds were assumed to be of equal length and all H-C-H angles to be the same. The methyl groups had C_{3v} symmetry and were in a staggered form with respect to the corresponding bonds to silicon.

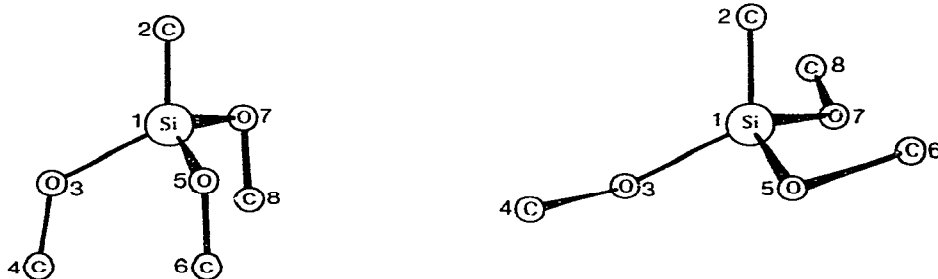
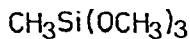


Fig. 2. Models of the $\text{CSi}(\text{OC})_3$ skeleton and the numbering of atoms.

originating mainly from the Si—O bonds. A rough estimate could also be made for the angle Si—O—C by tentatively assigning the maximum at 2.71 Å to the non-bonding distance Si···C, resulting in a value of 124° . These values were utilized in the trial structures of the least-squares refinements. However, for the angle Si—O—C, as well as for the other bond angles, several starting values were tested.

The least-squares refinement technique based on the molecular intensities was applied as described elsewhere [5,6], where references for the scattering factors used can also be found.

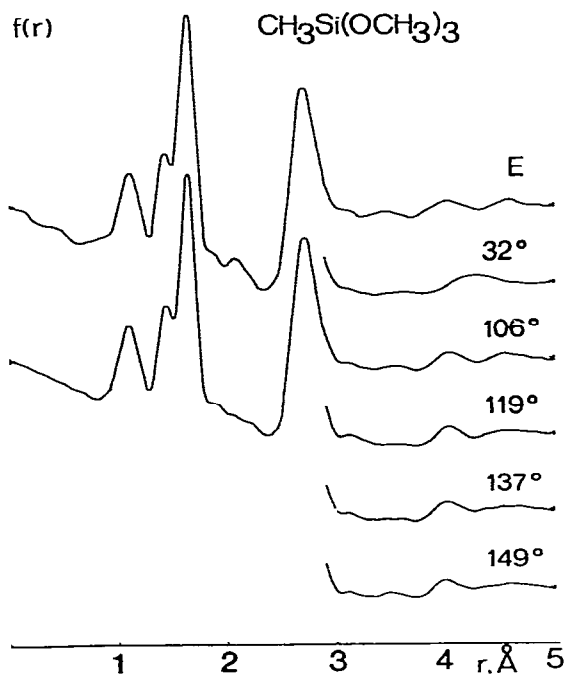


Fig. 3. Radial distributions, E - experimental and theoretical curves referring to the models with rotational angles indicated.

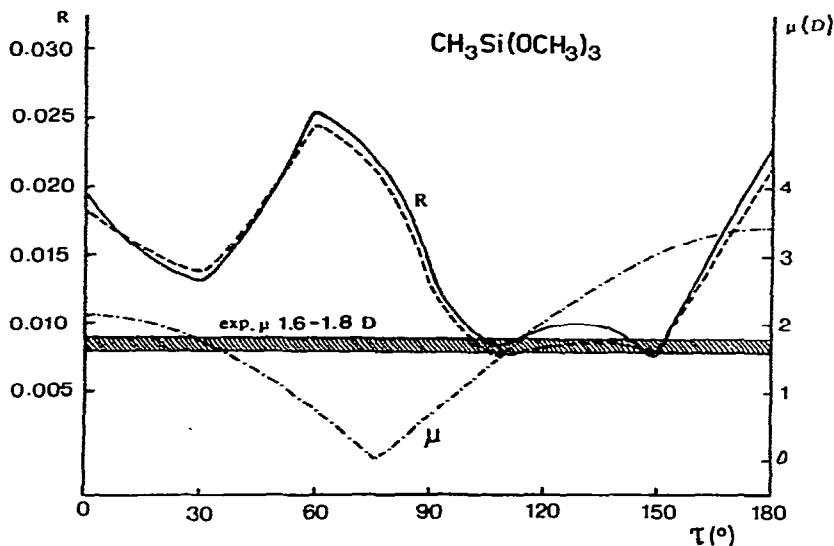


Fig. 4. The R-factor vs. rotational angle and the dipole moment (μ) vs. rotational angle plots. The two R-factor curves refer to slightly different conditions of refinement. The shadowed area indicates the measured values of the dipole moment (see references in text).

The bond lengths, bond angles and some mean amplitudes of vibration (l values) were refined first at fixed values of the rotational angle (τ) in the interval $0-180^\circ$ with $\Delta\tau$ steps of 15° . Later, the constraint on τ was removed in selected

TABLE I

THE RESULTS OF THE LEAST-SQUARES REFINEMENT (r AND l VALUES IN Å, ANGLES IN DEGREES) FOR METHYLTRIMETHOXSILANE

	i	ii	iii	iv	σ_t^a
$r(\text{C-H})$	1.093	1.094	1.095	1.094	0.005
$l(\text{C-H})$	0.071	0.071	0.071	0.071	0.004
$r(\text{Si-C})$	1.845	1.840	1.839	1.845	0.013
$l(\text{Si-C})$	0.079	0.078	0.078	0.079	0.007
$r(\text{Si-O})$	1.632	1.632	1.632	1.632	0.004
$l(\text{Si-O})$	0.034	0.034	0.034	0.034	0.002
$r(\text{O-C})$	1.425	1.425	1.426	1.426	0.004
$l(\text{O-C})$	0.044	0.044	0.044	0.044	0.002
$\angle\text{C-Si-O}$	109.5	109.7	109.9	109.4	0.5
$\angle\text{Si-O-C}$	123.7	123.5	123.7	123.4	0.5
τ	106.2	119.1	136.9	149.2	
$r(\text{C2}\cdots\text{C4})$	3.539	3.413	3.271	3.174	
$l(\text{C2}\cdots\text{C4})$	0.159	0.232	0.272	0.173	
$r(\text{C4}\cdots\text{O5})$	3.170	3.267	3.425	3.536	
$l(\text{C4}\cdots\text{O5})$	0.201	0.215	0.256	0.157	
$r(\text{C4}\cdots\text{O7})$	4.014	4.025	4.004	3.969	
$l(\text{C4}\cdots\text{O7})$	0.129	0.112	0.120	0.123	
$r(\text{C4}\cdots\text{C6})$	4.593	4.646	4.674	4.666	
$l(\text{C4}\cdots\text{C6})$	0.194	0.215	0.235	0.238	
R	0.078	0.079	0.076	0.077	

^a The values of the total errors (σ_t) were estimated in the usual way [5]. Thus, they include a 0.2 and 2% experimental error for distances and amplitudes, respectively and are increased to cover the variations of the parameters in the sets i-iv.

refinements. The angle Si—C—H was assumed to be 109.5° in most of the refinements and an estimate of value of 110.3° was used for the angle O—C—H, based on the values of $r(\text{O—C})$, $r(\text{C—H})$, and $r(\text{O}\cdots\text{H})$ from the experimental radial distribution.

The refinements converged to four different values of τ , viz. 106, 119, 137, and 149° , and a local minimum of the R -factor * appeared at $\tau 32^\circ$ (Fig. 4). It was concluded from these results that the predominant form was a rotational angle somewhere between, say, 100 and 155° . Large amplitude torsional motion around the Si—O bond seems to be probable and a smaller amount of a form with τ in the vicinity of 30° cannot be excluded. The bond lengths, bond angles and also the l values associated with the bonds proved to be hardly dependent on the rotational angle, as shown by the data in Table 1.

Discussion

The bond distances, bond angles, and l values determined ** (Table 1) seem reasonable except for $l(\text{Si—C})$, which is too large. The length of the Si—O bond was found to be nearly the same as that in disiloxane ($1.634 \pm 0.002 \text{ \AA}$ [9]) and hexamethyldisiloxane ($1.631 \pm 0.003 \text{ \AA}$ [10]), and somewhat, though not significantly, shorter than that in trimethylmethoxysilane ($1.639 \pm 0.004 \text{ \AA}$ [1]). The shortest Si—O bond in the $(\text{CH}_3)_{4-n}\text{Si}(\text{OCH}_3)_n$ series (so far $n = 1, 3, 4$) is in $\text{Si}(\text{OCH}_3)_4$, viz. $1.612 \pm 0.003 \text{ \AA}$ [2].

When the bond angle Si—O—C in $\text{CH}_3\text{Si}(\text{OCH}_3)_3$ is compared to that in other molecules (Table 2) it seems to be relatively constant, except for the angle in F_3SiOCH_3 . Especially noteworthy are the similarities in the bond angles in the following analogous boron and silicon molecules: $\text{B}(\text{OCH}_3)_3$, $\angle \text{B—O—C}$ $121.4 \pm 0.5^\circ$ [14]; $\text{CH}_3\text{Si}(\text{OCH}_3)_3$, $\angle \text{Si—O—C}$ $123.6 \pm 0.5^\circ$ [present work]; and $(\text{CH}_3)_2\text{BOB}(\text{CH}_3)_2$, $\angle \text{B—O—B}$ $144.4 \pm 2.7^\circ$ [15]; $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$, $\angle \text{Si—O—Si}$ $148 \pm 3^\circ$ [10]; and the large differences when compared with the C—O—C bond angle of $111.5 \pm 1.5^\circ$ in dimethyl ether.

The electron diffraction study of the methyltrimethoxysilane vapour provides only a limited amount of conformational information. The two most severe restrictions applied in our analysis were the following: (i) all three angles of rotation around the Si—O bonds were assumed to be the same (C_3 symmetry); (ii)

TABLE 2

Compound	$\angle \text{Si—O—C}$ ($^\circ$)	Ref.
H_3SiOCH_3	120.6 ± 1.0	11
$(\text{CH}_3)_3\text{SiOCH}_3$	122.5 ± 0.6	1
F_3SiOCH_3	131.4 ± 3.2	12
$\text{H}_3\text{SiOC}_6\text{H}_5$	121 ± 1	13
$\text{Si}(\text{OCH}_3)_4$	120 ± 2	2

* $R = \{ \sum [sM^E(s) - sM^T(s)]^2 / \sum [sM^E(s)]^2 \}^{1/2}$, $sM^E(s)$ and $sM^T(s)$ are the experimental and theoretical molecular intensities, respectively.

** The parameters that are considered to be the results were calculated by averaging the values of the sets i–iv of Table 1; see also footnote to Table 1.

only the predominant conformer was sought. As values of the rotational angles between 0 and 180° were tested, the changes in the R -factor showed a local minimum at $\tau 32^\circ$ and a deeper and more shallow minimum in the interval of about $\tau 100$ – 155° . The model with $\tau 32^\circ$ could be ruled out as the dominant one on the basis of the radial distributions (Fig. 3). On the other hand, as the rotation-dependent portions of the radial distributions (Fig. 3) were considered, together with the calculated variations of the most important rotation-dependent distances (Fig. 5), models with rotational angles in the interval indicated seemed to be very probable. The results for the predominating conformer may be interpreted in terms of a mixture of conformers or of the molecules performing large amplitude torsional motion around the Si–O bonds.

It is noteworthy that the total energy vs. rotational angle calculations [16] by the CNDO/2 method reproduced the general features of the R -factor vs. rotational angle variations. Also, the measured values of the dipole moment [17] are consistent with those calculated for the models with τ approximately 30° and 110 – 115° (Fig. 4) [18].

The molecules of triethylsilane, $\text{HSi}(\text{CH}_2\text{CH}_3)_3$, were found to have conformational characteristics [8] similar to those of methyltrimethoxysilane in an analysis involving similar assumptions. On the other hand, the electron diffraction data on trimethyl phosphate, $\text{O}=\text{P}(\text{OCH}_3)_3$, were interpreted in terms of two rotational isomers with C_3 symmetry occurring in a ratio of 3 : 1, with the predominant form having a rotational angle of about 30° [7]. In the light of the results of

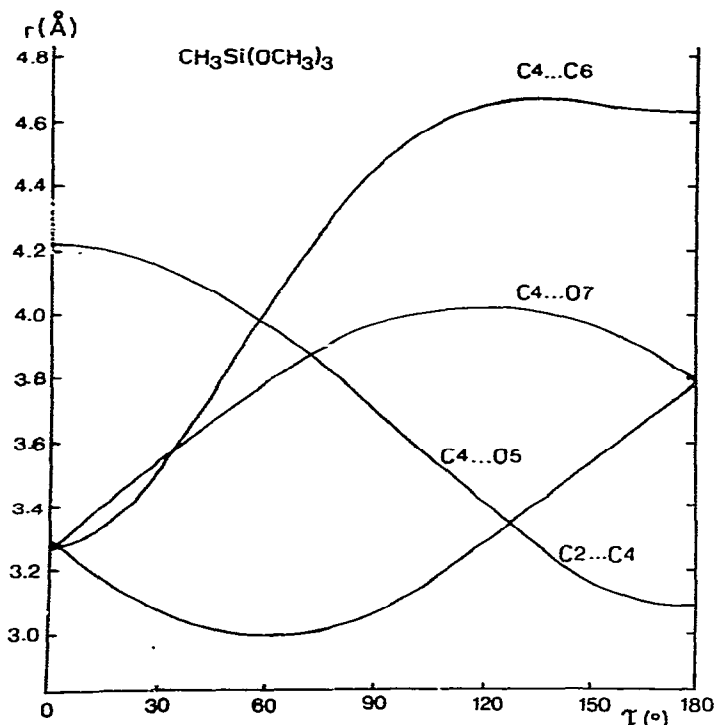


Fig. 5. The variations of the most important rotation-dependent distances vs. the rotational angle around the Si–O bond. The numbering of atoms is given in Fig. 2.

CNDO/2 calculations performed for $\text{O}=\text{P}(\text{OCH}_3)_3$, and of the published experimental radial distribution [7], it has been suggested [19] that the electron diffraction results can be reinterpreted with a model in which the predominant form is analogous to those in triethylsilane and methyltrimethoxysilane.

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References

- 1 B. Csákvári, Zs. Wagner, P. Gömöry, I. Hargittai, B. Rozsondai and F.C. Mijlhoff, *Acta Chim. Acad. Sci. Hung.*, submitted.
- 2 L.H. Boonstra, F.C. Mijlhoff, G. Renes, A. Spelbos and I. Hargittai, *J. Mol. Struct.*, 28 (1975) 129.
- 3 I. Hargittai, J. Hernádi, M. Kolonits and Gy. Schultz, *Rev. Sci. Inst.*, 42 (1971) 546.
- 4 I. Hargittai, J. Hernádi and M. Kolonits, *Prib. Tekh. Eksp.*, (1972) 239.
- 5 M. Hargittai and I. Hargittai, *J. Chem. Phys.*, 59 (1973) 2513.
- 6 I. Hargittai and M. Hargittai, *J. Mol. Struct.*, 15 (1973) 399.
- 7 H. Oberhammer, *Z. Naturforsch.*, A, 28 (1973) 1140.
- 8 B. Csákvári, Zs. Wagner and I. Hargittai, *Acta Chim. Acad. Sci. Hung.*, submitted.
- 9 A. Almenningen, O. Bastiansen, V. Ewing, K. Hedberg and M. Traetteberg, *Acta Chem. Scand.*, 17 (1963) 2455.
- 10 B. Csákvári, Zs. Wagner, P. Gömöry, F.C. Mijlhoff, B. Rozsondai and I. Hargittai, *J. Organometal. Chem.*, 107 (1976) 287.
- 11 C. Glidewell, D.W.H. Rankin, A.G. Robiette, G.M. Sheldrick, B. Beagley and J.M. Freeman, *J. Mol. Struct.*, 5 (1970) 417.
- 12 W. Airey, C. Glidewell, A.G. Robiette and G.M. Sheldrick, *J. Mol. Struct.*, 8 (1971) 413.
- 13 C. Glidewell, D.W.H. Rankin, A.G. Robiette, G.M. Sheldrick, B. Beagley and J.M. Freeman, *Trans. Faraday Soc.*, 65 (1969) 2621.
- 14 G. Gundersen, *J. Mol. Struct.*, to be published.
- 15 G. Gundersen and H. Vahrenkamp, *J. Mol. Struct.*, to be published.
- 16 T. Veszprémi, personal communication, Budapest, 1975.
- 17 (a) J. Nagy, S. Ferenczi-Gresz, R. Farkas, I. Barta and A. Borbély-Kuszmán, *Acta Chim. Acad. Sci. Hung.*, 69 (1970) 397; (b) L. Matsumura, *Bull. Chem. Soc. Japan*, 35 (1962) 801; (c) S.W.N. Cumper, A. Melnikoff and A. Vogel, *J. Chem. Soc. A*, (1966) 242; (d) E. Larsson, *Trans. Chalmers Univ. Technol. Göteborg*, No. 115 (1951) 15.
- 18 J. Nagy, S. Ferenczi-Gresz, E. Hengge and S. Waldhör, *J. Organometal. Chem.*, 96 (1975) 199.
- 19 J.-M. Savariault, J.-F. Labarre and I. Hargittai, *Z. Naturforsch.*, submitted.