STRUCTURE OF THE 3,3-DIMETHYL-3-SILATHIETANE MOLECULE ACCORDING TO DATA FROM GAS-PHASE ELECTRON DIFFRACTION ANALYSIS WITH CONSIDERATION OF VIBRATIONAL EFFECTS

V. S. Mastryukov, S. A. Strelkov,
A. V. Golubinskii, L. V. Vilkov,
L. V. Khristenko, S. V. Krasnoshchekov,
Yu. A. Pentin, S. V. Kirpichenko,
E. N. Suslova, and M. G. Voronkov

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The 3,3-dimethyl-3-silathietane molecule has been investigated by gas-phase electron diffraction analysis with consideration of the vibrational effects. The following geometric parameters were obtained (the distances r_a, the angles $\angle_\alpha$, the errors in the form of 3σ in parentheses, for $\varphi - 5\sigma$): S–C 1.853(4), Si–C_m 1.870(5) (m stands for methyl), Si–C_r 1.916(3) (r stands for ring), C–H 1.086(3) Å, $\angle$(C–Si–C)$_m$ = 106.9(7), $\angle$(C–Si–C)$_r$ = 86.1(3), $\angle$Si–C–S = 90.5(5), and $\angle$C–S–C = 89.5(4)°. The four-membered ring is nonplanar; the angle φ between the CSiC and CSC planes equals 20.3(20)°.

Numerous four-membered molecules with one or two heteroatoms in positions 1 and 3 were previously studied by gas-phase electron diffraction analysis [1, 2]. There is far less information on similar systems containing two different heteroatoms, although their chemistry has undergone considerable development. In order to fill in this gap, we obtained preliminary data on the geometric structure of 3,3-dimethyl-3-silathietane (MDST) [3], which were used for the analysis of its x-ray photoelectron spectrum and some quantum-chemical calculations [4]. The purpose of this communication is to present the final data on the structure of

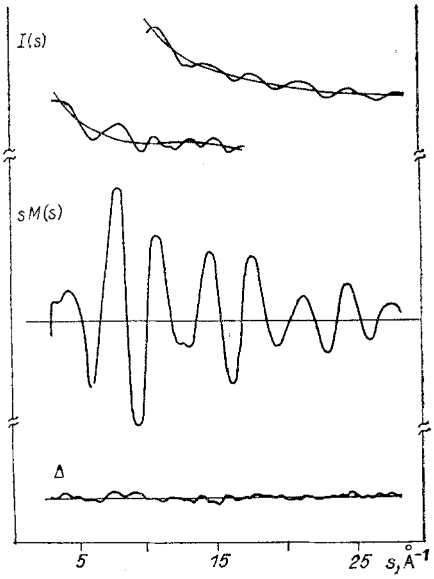

Fig. 1. Experimental plots of the total intensity I(s), the molecular component of the intensity sM(s), and its difference for the final theoretical model.

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TABLE 1. Force Constants Used in the Calculation of the Vibrational Spectrum of the DMST Molecule (10^6 cm^{-2})

No.	Diagonal	Value	No.	Off-diagonal	Value
				Interactions:	
	Stretching			Bond–bond	
1	$(SiC)_m$	4,77	19	$(SiC)_r$, $(SiC)_r$	0,05
2	(CS)	4,07	20	$(SiC)_r$, (CS)	—0,22
3	$(SiC)_r$	4,62	21	$(SiC)_r$, $(SiC)_m$	—0,08
4	$(CH)_r$	7,94	22	$(SiC)_m$, $(SiC)_m$	0,19
5	$(CH)_m$	8,05	23	(CS), (CS)	—0,16
			24	$(CH)_r$, $(CH)_r$	0,08
	Deformation		25	$(CH)_m$, $(CH)_m$	0,07
6	$(CSiC)_r$	1,23		Bond–angle	
7	$(SiCS)$	1,30	26	$(SiC)_r$, $(CSiC)_r$	0,25
8	(CSC)	1,04	27	$(SiC)_r$, $(SiCS)$	—0,35
9	$(CSiC)_m$	0,83	28	$(SiC)_r$, (C_rSiC_m)	0,28
10	(C_mSiC_r)	0,91	29	(CS), (CSC)	0,01
11	$(SiCH)_m$	0,58	30	$(SiC)_m$, $(CSiC)_m$	0,25
12	$(SiCH)_r$	0,90	31	$(SiC)_m$, (C_rSiC_m)	0,28
13	(HCS)	1,05	32	(CH), (HCH)	0,35
14	$(HCH)_r$	0,50		Angle–angle	
15	$(HCH)_m$	0,69	33	$(SiCS)$, $(CSiC)_r$	—0,15
	Twisting		34	(CSC), $(CSiC)_r$	0,20
16	τ (C—S)	0,07	35	(C_rSiC_m), $(CSiC)_r$	0,08
17	τ (Si—C_r)	0,06	36	$(SiCS)$, $(SiCS)$	0,20
18	τ (S—C_m)	0,09	37	(CSC), $(SiCS)$	—0,15
			38	$(HCSi)_r$, $(HCSi)_r$	0,01
			39	(HCS), $(HCSi)_r$	0,04
			40	(HCS), (HCS)	—0,02
			41	$(SiCH)_m$, (C_rSiC_m)	—0,01
			42	$(SiCH)_m$, $(SiCH)_m$	—0,08
			43	$(HCH)_m$, $(HCH)_m$	—0,05
			44	$(HCH)_m$, $(SiCH)_m$	—0,05

DMST, which were obtained by the parallel use of vibrational spectroscopy and gas-phase electron diffraction analysis.

EXPERIMENTAL

DMST was synthesized according to the method previously described in [5] and purified by preparative gas chromatography. The purity of the sample was confirmed by its IR and NMR spectra. The electron diffraction patterns were obtained on an EG-100A electron-diffraction camera [6] at an accelerating voltage of 60 kV with the use of benzene [7] as an internal gaseous standard. Four and five plates, respectively, were selected for analysis from photographs with two nozzle-plate distances (L), and the intensity curves [I(s)] were measured in the following ranges: 3.0-18.8 Å^{-1} (L = 495 mm, λ = 0.04925 Å) and 10.0-27.8 Å^{-1} (L = 187 mm, λ = 0.04933 Å). The densities were assumed to be proportional to the intensities and varied in the following ranges for the different values of L: 0.52-0.77 and 0.31-0.68. The molecular component of the intensity sM(s) was isolated by carrying out a cubic approximate spline analysis. The plots of I(s) and sM(s) are presented in Fig. 1.

The vibrational effects were taken into account with the aid of the experimental data on the IR and Raman spectra of DMST presented in [8]. The calculations of the frequencies, the normal modes of vibration, the mean-square amplitudes of the vibrations, and the corrections for the perpendicular vibrations of DMST were performed with the force field presented in Table 1 and the preliminarily data on the geometry of the molecule in a model with overall

TABLE 2. Experimental and Calculated Frequencies, cm^{-1}

No.	Symmetry type	Experiment	Calc.	PED, percent	Provisional assignment
1	A'	2970	2969	$93(CH_3)$	$\nu_{as}(CH_3)$
2	A''	2970	2969	$94(CH_3)$	$\nu_{as}(CH_3)$
3	A''	2964	2969	$92(CH_3)$	$\nu_{as}(CH_3)$
4	A'	2964	2969	$92(CH_3)$	$\nu_{as}(CH_3)$
5	A'	2955	2967	$89(CH_2)$	$\nu_{as}(CH_2)$
6	A''	2955	2967	$92(CH_2)$	$\nu_{as}(CH_2)$
7	A'	2932	2913	$100(CH_2)$	$\nu_s(CH_2)$
8	A''	2920	2911	$100(CH_2)$	$\nu_s(CH_2)$
9	A'	2898	2898	$86(CH_3)$	$\nu_s(CH_3)$
10	A'	2898	2898	$84(CH_3)$	$\nu_s(CH_3)$
11	A''	1445	1464	$91(HCH)$	$\delta_{as}(CH_3)$
12	A'	1445	1464	$91(HCH)$	$\delta_{as}(CH_3)$
13	A'	1445	1442	$93(HCH)$	$\delta_{as}(CH_3)$
14	A'	1413	1422	$54(HCH)_r + 21(HCS) + 18(HCSi)_r$	$\delta(CH_2)$
15	A''	1413	1416	$54(HCH)_r + 24(HCS) + 16(HCSi)_r$	$\delta(CH_2)$
16	A'	1413	1405	$93(HCH)_m$	$\delta_{as}(CH_3)$
17	A'	1265	1265	$46(HCH)_m + 23(SiCH)_m$	$\delta_s(CH_3)$
18	A'	1260	1249	$19(HCH)_m + 22(SiCH)_r + 20(SCH)$	$\rho(CH_2)_w$
19	A''	1253	1240	$29(HCH)_m + 16(SiCH)_m$	$\delta_s(CH_3)$
20	A''	1240	1228	$52(SiCH)_r + 40(SCH)$	$\rho(CH_2)_w$
21	A'	1085	1117	$72(HCS)$	$\rho(CH_2)_t$
22	A''	1070	1100	$72(HCS)$	$\rho(CH_2)_t$
23	A'	1008	1023	$98(HCSi)_r$	$\rho(CH_2)_r$
24	A''	1002	995	$95(HCSi)_r$	$\rho(CH_2)_r$
25	A''	844	858	$78(HCSi)_m$	$\rho(CH_3)_r$
26	A'	844	844	$86(HCSi)_m$	$\rho(CH_3)_r$
27	A'	833	823	$92(HCSi)_m$	$\rho(CH_3)_r$
28	A''	810	818	$84(HCSi)_m$	$\rho(CH_3)_r$
29	A'	752	760	$46(CSi)_r + 18(SiC)_m + 18(SiCH)_m$	ν(ring)
30	A''	743	737	$44(CSi)_r + 24(CS) + 16(SiCS)$	ν(ring)
31	A'	709	680	$31(SiC)_m + 37(CS) + 10(CSiC)_r + 10(SiCS)$	ν + δ(ring)
32	A'	685	668	$70(SiC)_m + 13(CS)$	$\nu_{as}(SiC_2)$
33	A''	671	657	$62(CS) + 28(SiC)_r$	ν(ring)
34	A'	608	607	$37(SiC)_m + 26(CS)$	$\nu_s(SiC_2)$
35	A'	378	380	$14(CSiC)_r + 26(SiCS) + 11(CSC)$	δ(ring)
36	A'	261	291	$83(C_r SiC_m)$	$\rho(SiC_2)_{\parallel}$
37	A''	240	237	$86(C_r SiC_m)$	$\rho(SiC_2)_{\perp}$
38	A'	216	234	$59(CSiC)_m + 33(C_r SiC_m)$	$\delta(CSiC)_m$
39	A''	205	217	$96(CSiC_r)$	$\rho(SiC_2)_{\perp}$
40	A''	188	178	$97\tau(CH_3)$	$\tau(CH_3)$
41	A''	188	178	$97\tau(CH_3)$	$\tau(CH_3)$
42	A'	85	83	$83\chi_r$	χ(ring)

C_s symmetry [3]. Table 2 presents the experimental and calculated frequencies and their provisional assignment, which were made on the basis of the potential energy distribution (PED) along the coordinates, and Table 3 presents the mean-square amplitudes of the vibrations and the corrections for the perpendicular vibrations.

STRUCTURAL ANALYSIS

The model of the DMST molecule with C_s symmetry is shown in Fig. 2. It was analyzed under the following assumptions: 1) the lengths of the C–H bonds in the methyl groups (m) and the ring (r) are equal; 2) the $-CH_2-$ and $>Si(CH_3)_2$ groups have local C_{2v} symmetry; 3) the $-CH_3$ groups have local C_{3v} symmetry and a staggered conformation. As a result, the

TABLE 3. Geometric Parameters of the 3,3-Dimethyl-3-silathietane Molecule (distances in Å, angles in deg, values of the error 3σ in parentheses, for φ – 5σ)

No.	Parameters	r_a, $\angle_\alpha$	l_{ij}	K_{ij}
1	S—C	1,853(4)	0,054	0,013
2	Si—C_m	1,870(5)	0,053	0,007
3	Si—C_r	1,916(3)	0,052	0,004
4	C—H	1,086(3)	0,078	0,022
5	$\angle$(H—C—H)$_m$	109 (assumed)	—	—
6	$\angle$(H—C—H)$_r$	112 (assumed)	—	—
7	$\angle$(C—Si—C)$_m$	106,9(7)	—	—
8	$\angle$(C—Si—C)$_r$	86,1(3)	—	—
9	φ	20,3(20)	—	—
10	Si ... S	2,674	0,060	0,005
11	Si ... H_m	2,471	0,120	0,029
12	Si ... H_r	2,520	0,114	0,013
13	S ... C_2	3,982	0,156	0.001
14	S ... C_6	4,201	0,113	0,001
15	S ... H_{13}	2,493	0,111	0,024
16	S ... H_3	3,843	0,263	0,013
17	S ... H_4	4,668	0,212	0,010
18	S ... H_7	4,203	0,224	0,012
19	S ... H_8	4,855	0,179	0,011
20	C_{10} ... C_{11}	2,607	0,065	0,003
21	C_2 ... C_6	2,983	0,100	0,007
22	C_2 ... C_{10}	3,203	0,094	0,005

Notes. 1. The dependent angles are: ∠Si—C—S = 90.5(5), ∠C—S—C = 89.5(4). 2. The R factor equals 6.93%.

geometry of the DMST molecule is described by nine independent parameters, which are enumerated in Table 3.

During the structural analysis, the (H—C—H)$_m$ and (H—C—H)$_r$ bond angles were determined with large errors and converged at unreasonable values; therefore, in the final stage they were fixed at typical values for these parameters.

A certain difficulty was caused by the refinement of the similar Si—C_m and Si—C_r distances, which are found in a single peak on the radial distribution curve (Fig. 3) and are characterized by a correlation coefficient equal to 0.65. In order to separate these distances, the following geometric relation was imposed in the calculation of the theoretical models: $r(\text{Si—C}_r) = r(\text{Si—C}_m) + \Delta$, and the cases of $-0.1 \leq \Delta \leq 0.1$ Å were analyzed with a spacing equal to 0.02 Å. On the plot of the dependence of the R factor on Δ obtained there was one minimum at $\Delta = 0.02$ Å. The further refinement was initiated with this result, but both Si—C distances were varied independently.

A second difficulty was associated with the determination of the dihedral angle φ and the (CSiC)$_m$ angle, which determine the position and form of the peaks on the radial distribution curve in the 3.9-4.2-Å region. The main contribution to this peak is made by the S—C_m distances, which are equal, if the ring is planar, and differ, if it is not. As a consequence of the correlations between the parameters studied, we analyzed numerous models, in which the values of the parameters were varied in the following possible ranges: $0° \leq \varphi \leq 30°$ and $105° \leq \angle(\text{CSiC})_m \leq 112°$. In both cases, the uniqueness of the solution was demonstrated, but the specific result was dependent on the refinement conditions.

In the last stage of the structural analysis after completion of the spectroscopic part of the present work, the vibrational effects were quantitatively taken into account. Blocks for the group variation of the amplitudes were formed on the basis of the calculated amplitudes, and numerous refinements were conducted. At this point it became clear that the group

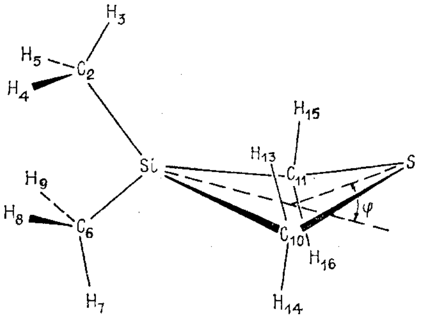


Fig. 2

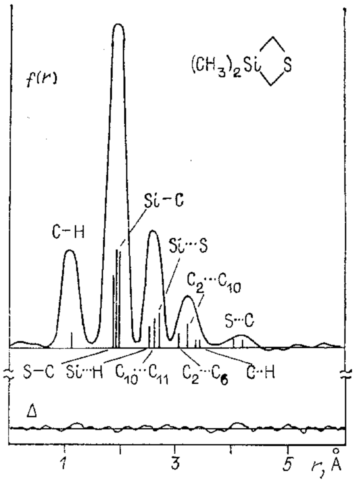


Fig. 3

Fig. 2. Model of the DMST molecule.

Fig. 3. Experimental radial distribution curve. The assignment of the peaks and the difference curve correspond to the final theoretical model in Table 3.

amplitude for the S–C, Si–C_r, and Si–C_m bonds has a high correlation coefficient (up to 0.9) with the corresponding internuclear distances, as well as with both CSiC angles (0.6-0.7). The variation of the vibrational amplitudes was accompanied by a 1.5% improvement in the R factor and did not result in significant changes in the values of the geometric parameters, with the exception of the $(CSiC)_m$ angle, which became equal to 104(1)°. Such a value seemed underestimated to us, since a value of 109(3)° was found for this angle in the parallel investigation of $Si_4(CH_3)_8$ [9]. On the basis of the foregoing arguments, we decided to give preference to the results of the refinement with the fixed amplitudes of the vibrations which were presented in Table 3.

RESULTS AND DISCUSSION

The main geometric parameters of DMST are compared with the characteristics of some closely related compounds in Table 4. An examination of these data reveals the following facts.

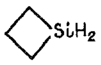
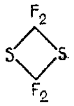
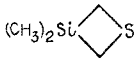
In DMST the Si–C distances is slightly increased in comparison to silacyclobutane, but the S–C distance remained unchanged in the range of the experimental errors (in comparison to thietane). The shortening of the distance in tetrafluorothietane may be a consequence of the entry of the electronegative fluorine atoms.

The bond angles at the heteroatoms have a different type of variations, if the comparison is conducted in the "one heteroatom" → "two identical heteroatoms" → "two different heteroatoms" direction, i.e., with DMST last. The corresponding changes in the bond angles are as follows: +8 and –3° (for Si) and +6 and +6° (for S).

The dihedral angles in the systems studied are distinguished by great diversity, varying from 0 to 34°. The four-membered ring DMST has a clearly nonplanar structure, since consideration of the vibrational effects also resulted in an increase in the dihedral angle from 13.2 to 20.3° in comparison to the preliminary results in [3]. A similar procedure applied to azetidine, which has been studied in the theoretical and experimental respect in greater detail than DMST, led [14, 15] to agreement between the theoretical equilibrium estimate ($\varphi_e = 28°$) and the electron-diffraction estimate ($\varphi_e = 29.7 \pm 1.4°$) of the dihedral angle in the four-membered ring.

Our conclusion regarding the conformation of the ring in DMST is at variance with the result of the semiempirical quantum-chemical calculation in [4], which indicated a planar structure for the ring. We believe that the reasons for this disparity should be sought in the theory in analogy to cyclobutane, azetidine (see [14] and the literature cited therein) and cyclotetrasilane [16]. It was convincingly demonstrated in these examples that all the various simplifications introduced into the calculations invariably resulted in underestimation of the dihedral angles in the four-membered rings.

TABLE 4. Geometric Parameters of Four-Membered Rings Containing Silicon and Sulfur

Molecule	Si–C$_r$, Å	S–C, Å	(CSiC)$_r$ deg	CSC, deg	φ, deg	Lit. cited
	1,895(2)	—	80,8(5)	—	34(2)	[10]
	1,89(1)	—	89(1)	—	14(3)	[11]
	—	1,847(3)	—	76,8(3)	26(2)	[12]
	—	1,820(2)	—	82,7(2)	0	[13]
	1,916(3)	1,853(4)	86,1(3)	89,5(4)	20,3(20)	Present work

Among the bond angles, the exocyclic (C–Si–C)$_m$ angle is of greatest interest. The unusualness of its value (106.9°) stems from the fact that both this angle and the cyclic angle at the silicon atom are smaller than the tetrahedral angle. Such cases are unknown for molecules of organic compounds, and the expected value for this angle (according to the empirical equation in [17]) is 111°.

One of the interesting questions in the stereochemistry of cyclic compounds with sulfur and silicon atoms is the appearance of an Si...S interaction as a function of the size of the ring. In this respect DMST is a standard with the smallest possible Si...S distance (2.67 Å) on the basis of purely geometric arguments. Therefore, the interaction sought is possible, if the Si...S distance falls in the 2.67-3.90-Å range, whose upper limit is determined by the sum of the van de Waals radii. Such an interaction is apparently realized in a nine-membered ring with Si and S atoms, which approach one another to a distance of 3.438(3) Å [18].

LITERATURE CITED

1. L. V. Vilkov, V. S. Mastryukov, and N. I. Sadova, Determination of the Geometric Structure of Free Molecules [in Russian], Khimiya, Leningrad (1978).
2. A. C. Legon, Chem. Rev., 80, 3231 (1980).
3. V. S. Mastryukov, S. A. Strelkov, A. V. Golubinskii, et al., Dokl. Akad. Nauk SSSR, 271, 384 (1983).
4. V. F. Traven', V. I. Rokitskaya, O. G. Rodin, et al., Dokl. Akad. Nauk SSSR, 282, 1160 (1986).
5. M. G. Voronkov, S. V. Kirpichenko, E. N. Suslova, and V. V. Keiko, J. Organomet. Chem., 204, 13 (1981).
6. V. S. Mastryukov, O. V. Dorofeeva, A. V. Golubinskii, et al., Zh. Strukt. Khim., 16, 171 (1975).
7. A. V. Golubinskii, L. V. Vilkov, V. S. Mastryukov, and V. P. Novikov, Vestn. Mosk. Univ., Ser. Khim., 20, 99 (1979).
8. L. V. Khristenko, O. I. Kolobova, V. K. Matveev, and Yu. A. Pentin, Zh. Prikl. Spektrosk., 47, No. 1, 58 (1987).
9. S. A. Strelkov, V. S. Mastryukov, L. V. Vilkov, et al., in: Tenth Austin Symposium on Molecular Structure, Austin, U.S.A. (1984), p. 112.
10. V. S. Mastryukov, O. V. Dorofeeva, L. V. Vilkov, et al., Zh. Strukt. Khim., 16, 473 (1975).
11. L. V. Vilkov, V. S. Mastryukov, V. D. Oppengeim, and N. A. Tarasenko, in: S. J. Cyvin, Molecular Structures and Vibrations, Amsterdam, Elsevier (1972), p. 310.
12. K. Karakida and K. Kuchitsu, Bull. Chem. Soc. Jpn., 48, 1691 (1975).
13. Z. Smith and R. Seip, Acta Chem. Scand., A30, 759 (1976).
14. D. Cremer, O. V. Dorofeeva, and V. S. Mastryukov, J. Mol. Struct., 75, 225 (1981).
15. H. Günther, G. Schrem, and H. Oberhammer, J. Mol. Spectrosc., 104, 152 (1984).
16. A. F. Sax, Chem. Phys. Lett., 127, 163 (1986).
17. V. S. Mastryukov and E. L. Osina, J. Mol. Struct., 36, 127 (1977).
18. V. E. Shklover, Yu. T. Struchkov, O. G. Rodin, et al., J. Organomet. Chem., 266, 117 (1984).