Molecular Structure and Pseudorotation in 3,3-Dimethyl-3-silatetrahydrothiophene from a Joint Gas-Phase Electron Diffraction and *Ab Initio* Molecular Orbital Study

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The molecular structure of 3,3-dimethyl-3-silatetrahydrothiophene has been reinvestigated utilizing a joint electron diffraction/*ab initio* approach. Two local minima with $_1T^5$ and $_4T^5$ conformations of the ring could not be distinguished on the basis of electron-diffraction data alone. However, the model with the five-membered ring having a distorted $_1T^5$ form was in agreement with the *ab initio* calculations and had a slightly lower *R*-factor than the $_4T^5$ form. Molecular mechanics calculations suggest that the conformation is determined mainly by angular and torsional strains in the molecule, with the angular strain predominating. The barrier to pseudorotation was estimated to be 9.6 kJ mol^{-1} from the HF/6-311 + +G** *ab initio* calculations including correction for the zero-point vibrational energy. Differences between C–S, Si–C bond lengths and between exocyclic C–Si–C angles obtained from the MP2(FC)/6-311 + +G** *ab initio* calculations were used as constraints in the electron diffraction structure analysis. Two different methods were used to calculate the shrinkage corrections from the force field scaled to fit the experimental frequencies. The following values (r_g bond lengths and $\angle_\alpha$ angles with total errors) were found for the main parameters in the molecule: $r(S–C)_{mean}$ 1.829 ± 0.005 Å; $r(Si–C)_{mean}$ 1.883 ± 0.006 Å; $r(C–C)$ 1.541 ± 0.007 Å; $r(C–H)_{mean}$ 1.112 ± 0.003 Å; $\angle(C–S–C)_{ring}$ 98.6 ± 0.8°; $\angle(C–Si–C)_{ring}$ 97.7 ± 0.6°; ring puckering amplitude, q_0, 10.7 ± 0.6°; pseudorotation phase angle, *f*, 168.1 ± 4.4° (corresponds to a distorted $_1T^5$ form of the ring).

A principal structural problem concerning 3,3-dimethyl-3-silatetrahydrothiophene (Fig. 1) is the conformation of its five-membered ring. In general, the five-membered ring in this molecule, or in any other compound with a five-membered ring, may have different conformations. Among these conformations envelope and twist forms, denominated as E^x or $_xT^y$, respectively,[1,2] may be discerned. The x and y indices represent the atoms deviating from the plane of the remaining atoms in the ring. These different conformations may be described in terms of two parameters: a pseudorotation puckering amplitude and a pseudorotation phase angle.[3,4] There can be 10 different envelope and twist forms of 3,3-dimethyl-3-silatetrahydrothiophene as presented in Fig. 2. Usually, the interchange over all the possible conformations is
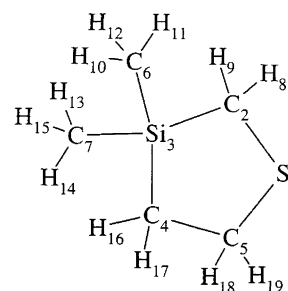

Fig. 1. 3,3-Dimethyl-3-silatetrahydrothiophene with the numbering of atoms.

governed by a low-barrier intramolecular motion known as pseudorotation,[3] which complicates determination of the molecular structure.

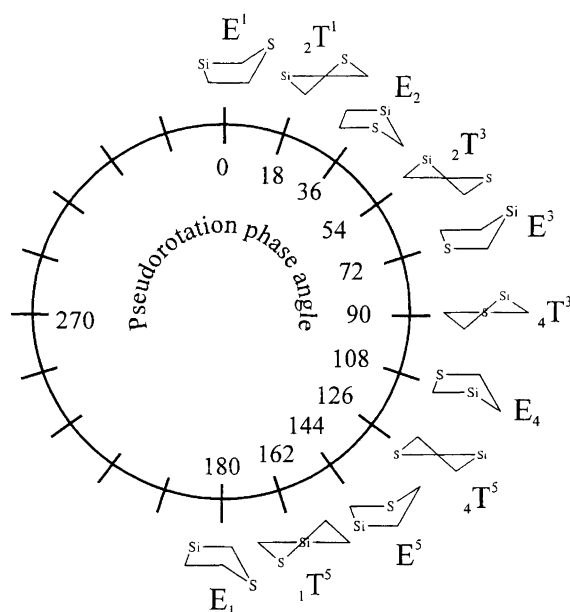*To whom correspondence should be addressed.

Fig. 2. Conformations of 3,3-dimethyl-3-silatetrahydrothio-phene occurring along the pseudorotation pathway. The methyl groups and hydrogen atoms are not shown for simplicity. The E^1 conformation at zero pseudorotation phase angle and the E_1 at 180 are enantiomeric forms.

The factors determining the conformations of the five-membered rings in different molecules are still not understood completely. The uncertainty of these factors may be due to a paucity of available experimental data on the five-membered ring compounds, which in turn is caused by the inherent difficulty of structure investigation of such systems. If the main factors determining the conformations were the relative torsional moments about single bonds in the ring, 3,3-dimethyl-3-silatetrahydro-thiophene would be expected to have a $_4T^5$ equilibrium conformation. This conformation allows the largest torsional angle about the C–C bond, which is supposed to have the largest barrier to torsion. Indeed, a previous investigation of the title compound by electron diffraction has found a $_4T^5$ conformation of the ring.[5] However, the main parameters of the molecule were poorly determined because of large standard deviations. Recent *ab initio* and electron diffraction studies of the analogue 3,3-dimethyl-3-silatetrahydrofuran[6] have shown that the O-envelope (E^1) conformation of the ring is preferred. This finding disagrees with the expectations based on the relative torsional moments as principal components determining the conformation of the five-membered ring. Among the molecules which appear to violate this principle is also pyrrolidine. Pyrrolidine was found to have an *N*-envelope form by electron diffraction,[7] microwave spectroscopy[8] and by quantum chemical calculations.[7] More recent *ab initio* calculations seem to confirm this result.[2] The conformation of *N*-nitropyrrolidine was found to be an E^3 envelope, which can not be explained simply on the basis of torsional moments about single bonds from model compounds.[9,10] To gain further insight

into the conformational problems of five-membered rings, we decided to reinvestigate the molecular structure of 3,3-dimethyl-3-silatetrahydrothiophene with newly recorded data utilizing constraints from *ab initio* calculations in the electron diffraction analysis. This approach would give more precise and reliable results suitable for comparison with other related molecular systems. More reliable determination of the structure of 3,3-dimethyl-3-silatetrahydrothiophene would also help to explain the driving forces behind the conformation of five-membered rings in different systems.

Experimental

3,3-Dimethyl-3-silatetrahydrothiophene was prepared from (chloromethyl)vinyldimethylsilane with 66% yield according to a previously described procedure.[11] The crude product was purified by column chromatography on Silicagel L 100/400 (Chemapol) with a hexane/methyl-ene chloride 9:1 mixture as an eluent. Parameters of the ^{1}H NMR spectra of the product agreed with the literature data for 3,3-dimethyl-3-silatetrahydrothiophene.[12]

Electron diffraction experiment. Electron diffraction total intensities were recorded on a Balzers Eldigraph KDG-2 apparatus[13] with a brass inlet system at a nozzle temperature of 21 °C. Kodak electron image plates were used to record the data. Six plates from the long (498.76 mm) and six plates from the middle (248.77 mm) nozzle-to-plate distances were obtained and utilized in the structure analysis. The photographic plates were traced applying a commercial scanner, and the data were processed as described in Ref. 14. The wavelength of the electrons was 0.058 59 Å with an estimated uncertainty of 0.1%. The *s*-ranges used in the least-squares structure refinements were 2.0–15.0 Å^{-1} with a step of 0.125 Å^{-1} and 4.0–30.0 with a step of 0.25 Å^{-1} for the long and middle camera distances, respectively. Atomic scattering factors from Ref. 15 were applied. The backgrounds for the total intensity data from the left and right sides of the plates were drawn separately. After background subtraction, the molecular intensities from the six left and six right sides of the photographic plates were averaged. This gave two average molecular intensity curves, left and right, for each camera distance. These four average curves were used in the structure refinements. The reason for this treatment is that there may be, and often are, small systematic differences in the optical density at comparable regions on the left and right sides of a photographic plate. Therefore it is an advantage to draw backgrounds separately on the left and right side and average these two curves, rather than average the left and right sides first and then draw the background on the average curve.

The degrees of the polynomials used in the background subtraction were 9 and 8 for the middle and long camera distances, respectively. The experimental and theoretical molecular intensities and radial distributions obtained in

the present study are shown in Figs. 3 and 4. The numbering of atoms is presented in Fig. 1.

Ab initio *calculations.* The *ab initio* molecular orbital calculations were carried out using the GAUSSIAN 94 program package.[16] The standard 6-311++G** basis set[17] augmented by diffuse and polarization functions was used throughout.

Initially the pseudorotation potential was calculated at the Hartree–Fock level of theory. Since the potential to pseudorotation in 3,3-dimethyl-3-silatetrahydrothiophene is expected to be symmetric with respect to the E^1 conformer, five different envelope forms of the molecule were optimized assuming one of the angles of torsion in the ring to be zero. The five half-chair forms, which occur between the envelope forms, were omitted from the calculations, because they were believed to have no substantial influence on the form of the potential energy curve. The pseudorotation potential energy curve was interpolated by a spline through the calculated envelope forms. The structures in the vicinity of the maximum and minimum on the calculated potential energy curve (Fig. 5) were further fully optimized. Frequency calculations were performed for these structures to identify the nature of the obtained points as real minimum (all positive frequencies) or transition state (one negative frequency), and to provide an estimation of the zero point vibrational energy. The structures corresponding to the maximum and minimum of the potential energy curve were also fully optimized at the second-order level of Møller–Plesset perturbation theory,[18] with only val-

ence orbitals active, i.e. MP2(FC)/6-311++G**, to include the effect of electron correlation into the calculations. The results of the computations are presented in Tables 1 and 2.

Structure analysis

The electron diffraction structure analysis of 3,3-dimethyl-3-silatetrahydrothiophene was carried out by the least-squares fitting of calculated molecular scattering intensities to the experimental data.

The geometry of the five-membered ring was described by five bond lengths, two bond angles, and two pseudorotation parameters, the puckering amplitude, q_0, and the pseudorotation phase angle, f. We have used the pseudorotation model as suggested in Refs. 2 and 4, and applied with some modifications in our recent investigation of the molecular structure of N-nitropyrrolidine.[10]

The electron diffraction least-squares refinements were carried out with the following constraints: All C–H bonds were assumed to have the same length. Each CH_2 group in the ring was assumed to have local C_{2v} symmetry with one of the symmetry planes passing through the H–C–H atoms, and the other being formed by the carbon of the CH_2 group and the two adjacent atoms. The geometry of methylene groups was thus described by the C–H bond length and the H–C–H bond angle.

The methyl groups were assumed to have local C_{3v} symmetry, with the symmetry axis passing through the C–Si bonds. The Si–C–H angle, equal for all hydrogen atoms in both methyl groups, was refined as an indepen-
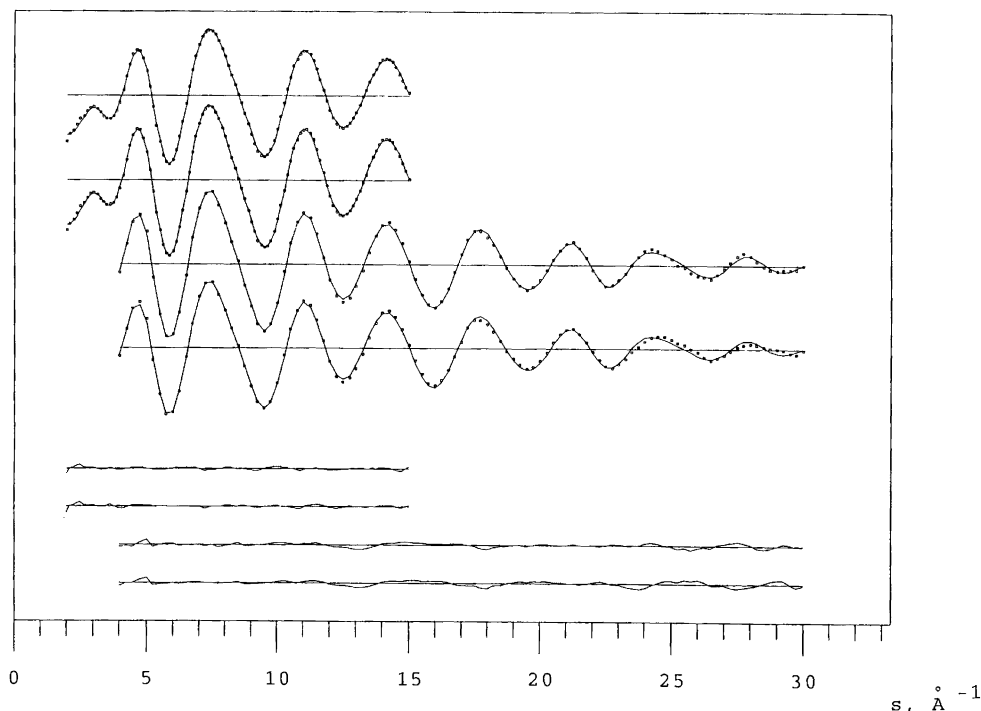

Fig. 3. Experimental (dots) and theoretical (lines) molecular intensities and their differences for 3,3-dimethyl-3-silatetra-hydrothiophene.
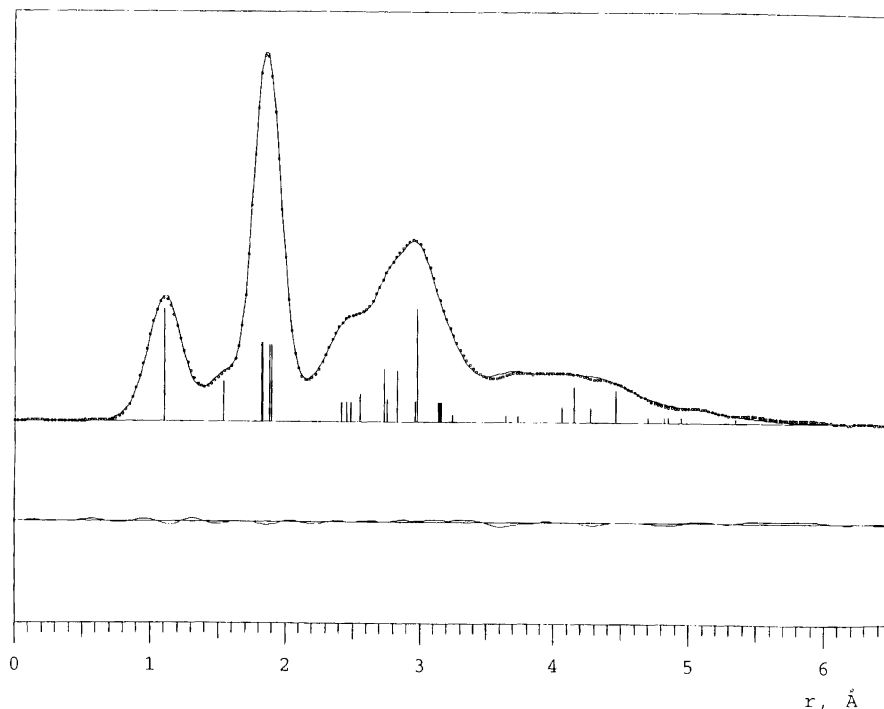
Fig. 4. Experimental (dots) and theoretical (lines) radial distributions and their difference for 3,3-dimethyl-3-silatetra-hydrothiophene.
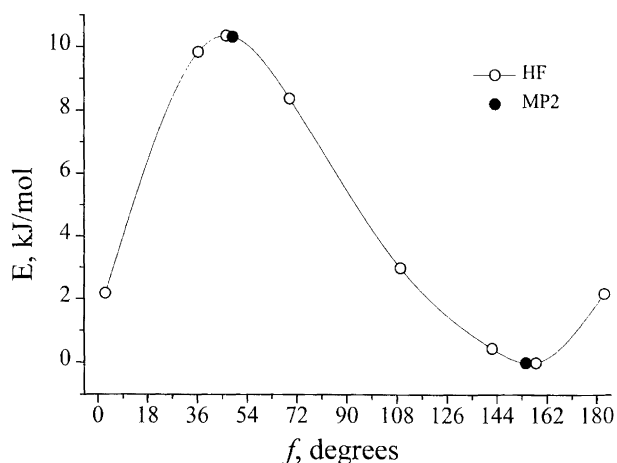

Fig. 5. Potential energy curve for pseudorotation of the ring in 3,3-dimethyl-3-silatetrahydrothiophene computed at the HF/6-311++G** level. Structures optimized at the MP2(FC)/6-311++G** level are indicated by filled dots.

dent parameter. The angle of methyl torsion, $\varphi = 0$, corresponds to the conformation in which one of the hydrogens of the methyl group eclipses the Si–C bond of the other group. These torsion angles were assumed to move in opposite directions and to be equal for both methyl groups. Its value was refined in the final stages of the structure analysis.

The positions of the C_6 and C_7 atoms were determined by corresponding Si–C bond lengths and two pairs of the exocyclic C–Si–C angles.

It was not possible to refine the Si–C and C–S bond

lengths together with the exocyclic C–Si–C angles independently. The C_2–S_1 and C_5–S_1 distances, Si_3–C_2, Si_3–C_4, Si_3–C_6 and Si_3–C_7 distances, and C_2–Si_3–C_6, C_4–Si_3–C_6, C_2–Si_3–C_7 and C_4–Si_3–C_7 angles were grouped together in three groups. The differences between the parameters within a group, i.e. between the C–S bonds, Si–C bonds and the C–Si–C exocyclic angles, were introduced from the MP2/6-311++G** *ab initio* calculations in the final stage of the analysis. This improved the agreement between the calculated and experimental intensities, but did not influence the other parameters and conformation of the molecule.

The initial amplitudes were calculated utilizing the force field from the *ab initio* HF/6-311++G** computations and the ASYM40 program.[19] In the final stages of the analysis the amplitudes were calculated from a force field scaled to fit experimental frequencies. The experimental infrared spectra were recorded in Moscow, and detailed spectroscopic results will be published in a separate paper. The r_α structure corrections D ($r_\alpha = r_a + D$) have also been calculated from the scaled force field utilizing a conventional method[19] and the method suggested in Ref. 20. Introduction of such corrections is necessary to eliminate the distortions in the observed average structure caused by vibrational effects. The amplitudes of vibrations for the C–C, C–S and Si–C bonds were further included in the refinements. They were refined in a group, assuming the calculated differences between the amplitudes.

The main results of the refinements with different conditions are summarized in Table 3. Introduction of

Table 1. Computed geometries[a] for the stable form and transition state to pseudorotation for 3,3-dimethyl-3-silatetrahydrothiophene.

Parameter	A[b]		B[c]	
	HF	MP2	HF	MP2
S_1-C_2	1.826	1.822	1.824	1.818
C_2-Si_3	1.908	1.904	1.893	1.887
Si_3-C_4	1.900	1.892	1.895	1.888
C_4-C_5	1.535	1.535	1.546	1.545
C_5-S_1	1.826	1.822	1.847	1.848
Si_3-C_6	1.885	1.879	1.882	1.875
Si_3-C_7	1.883	1.876	1.884	1.878
C_2-H_8	1.085	1.095	1.084	1.094
C_6-H_{10}	1.088	1.095	1.088	1.095
$S_1-C_2-Si_3$	106.7	107.2	104.8	104.0
$C_2-Si_3-C_4$	99.1	98.7	97.7	96.9
$Si_3-C_4-C_5$	107.3	106.2	110.1	109.1
$C_4-C_5-S_1$	110.1	109.5	113.6	113.6
$C_5-S_1-C_2$	97.2	96.1	100.3	99.4
$C_2-Si_3-C_6$	111.0	110.7	110.8	110.1
$C_2-Si_3-C_7$	111.7	111.6	113.1	113.6
$C_4-Si_3-C_6$	112.4	111.7	112.3	112.2
$C_4-Si_3-C_7$	112.2	112.5	112.5	112.8
$H_8-C_2-H_9$	107.7	107.7	108.1	108.3
$Si_3-C_6-H_{10}$	111.1	111.3	111.0	111.1
$S_1-C_2-Si_3-C_4$	11.0	9.1	324.3	319.9
$C_2-Si_3-C_4-C_5$	17.7	21.2	26.8	31.1
$Si_3-C_4-C_5-S_1$	318.8	314.6	352.4	349.6
$C_4-C_5-S_1-C_2$	46.2	48.7	343.9	343.9
$C_5-S_1-C_2-Si_3$	329.3	329.5	32.3	35.1
q_0[d]	11.985	12.800	10.606	11.947
f[e]	158.126	154.422	46.369	48.709
Energy (a.u.)	−882.885 209	−883.880 159	−882.881 2691	−883.876 2335
Relative energy[f]/kJ mol^{-1}	0.0	0.0	10.3 (9.6)	10.3

[a] 'r_e' equilibrium bond lengths (in Å), bond angles, and angles of torsion (in °) computed using 6-311++G** basis set at HF or MP2 level. [b] Stable structure at the minimum of the potential energy. [c] Transition state to pseudorotation of the ring. [d] Pseudorotation puckering amplitude calculated from the optimized geometry. [e] Pseudorotation phase angle calculated from the optimized geometry. [f] Relative energy corrected for ZPVE is presented in parenthesis.

Table 2. Vibrational frequencies (in cm^{-1}) computed at the HF/6-311++G** level for the stable conformer (A) of 3,3-dimethyl-3-silatetrahydrothiophene.

42.2	459.7	847.6	1264.4	1578.2	3210.4
158.0	627.6	882.3	1383.4	1582.1	3213.4
171.0	691.3	928.8	1410.2	1611.5	3214.4
182.1	709.2	930.2	1416.4	3145.3	3220.1
203.2	730.4	990.0	1421.3	3147.3	3239.5
231.7	732.1	1037.8	1566.0	3161.6	3240.5
235.6	742.4	1163.7	1568.4	3183.6	
271.9	768.2	1200.1	1569.0	3187.5	
375.5	797.5	1249.0	1572.4	3204.1	

the vibrational amplitudes into the refinements (column 2, Table 3) caused a decrease in the R-factor from 5.6 to 5.1%. This also had a considerable influence on the C_2-S_1 and Si_3-C_2 bond lengths. Without refining the amplitudes these bonds refined to (r_a) 1.804(2) and 1.908(1) Å (column 1, Table 3), while simultaneous refinement of the amplitudes and these bond lengths gave 1.824(2) and 1.898(2) Å for C_2-S_1 and Si_3-C_2, respectively. The C–S bond length found in tetrahydrothiophene, 1.839(2) Å,[21] and the calculated *ab initio*

(MP2(FC)/6-311++G**) value in 3,3-dimethyl-3-sila-tetrahydrothiophene, 1.826 Å, both seem to support the assumption that the length of the C–S bonds in the molecule is about 1.83 Å. The C–S–C angle also became closer to the one observed in tetrahydrothiophene and calculated by *ab initio* methods for 3,3-dimethyl-3-sila-tetrahydrothiophene.

Starting the refinements from the conformation of the molecule with a pseudorotation phase angle equal to 126° ($_4T^5$), we obtained a local minimum with a higher R-factor and a conformation of the ring close to the $_4T^5$ form (column 3, Table 3). The lowest minimum was obtained with the $_1T^5$ starting conformation of the ring (pseudorotation phase angle equal to 162°). Although the difference between the R-factors for these two models did not exceed 0.3 %, there were considerable differences between the structural parameters for these two models which exceed the experimental errors. The most pronounced differences were observed between the C–S–C angles in these models. The model with the $_4T^5$ conformation of the ring had a value of 101.1(2)° for the C–S–C angle versus 96.5(4)° for the model with the $_1T^5$ con-

Table 3. The main structural parameters of 3,3-dimethyl-3-silatetrahydrothiophene from refinements with different conditions.

Parameter	1[a]	2[b]	3[c]	4[d]	5[e]	6[f]	7[g]
S_1–C_2	1.804(2)	1.824(2)	1.831(3)	1.836(2)	1.824(3)	1.826(2)	1.827(2)
C_2–Si_3	1.908(1)	1.898(2)	1.895(2)	1.893(2)	1.898(2)	1.896(2)	1.897(2)
C_4–C_5	1.539(3)	1.535(3)	1.540(3)	1.540(3)	1.540(3)	1.538(3)	1.538(3)
$(C–H)_{mean}$	1.107(1)	1.106(1)	1.106(1)	1.106(1)	1.106(1)	1.106(1)	1.106(1)
C_5–S_1–C_2	99.4(3)	96.5(4)	101.1(2)	97.8(4)	97.2(4)	98.6(4)	98.6(4)
S_1–C_2–Si_3	106.5(2)	106.6(1)	106.6(1)	107.4(2)	107.8(2)	107.3(2)	107.2(2)
C_2–Si_3–C_6	112.0(2)	112.8(1)	113.1(1)	112.5(2)	112.7(2)	112.7(2)	112.8(2)
H–C–H	112(1)	112(1)	114(1)	107(1)	109(1)	112(1)	112(1)
Si–C–H	116.0(5)	115.5(4)	115.5(4)	114.5(5)	115.3(5)	116.4(5)	116.4(5)
φ[h]	27(2)	42(4)	29(3)	37(3)	38(3)	36(3)	36(3)
q_0[i]	10.7(2)	11.1(3)	10.5(2)	9.9(3)	10.5(3)	10.7(3)	10.7(3)
f[j]	168(2)	167(1)	116(1)	166(2)	165(2)	168(2)	168(2)
Conformation	Between E_1 and $_1T^5$	Between E_1 and $_1T^5$	Between E_4 and $_4T^5$	Between E_1 and $_1T^5$	Between E_1 and $_1T^5$	Between E_1 and $_1T^5$	Between E_1 and $_1T^5$
R-factor (%)	5.6	5.1	5.4	5.4	5.3	5.1	5.1

[a] Amplitudes were not included into the refinement. r_a bond lengths (in Å) and angles (in °) with standard deviations in parenthesis. [b] Amplitudes for C–C, C–S and Si–C bonds were refined. [c] The starting conformation in the refinement was $_4T^5$. [d] Conventional D-values $(r_\alpha = r_a + D)$ were used. *Ab initio* differences are introduced into the r_α structure. r_a bond lengths (in Å) and $\angle_\alpha$ angles (in °) with standard deviations in parenthesis. [e] Conventional D-values were used. *Ab initio* differences are introduced into the r_a structure. [f] D-values calculated using the procedure from Ref. 20 were used. *Ab initio* differences are introduced into the r_α structure. [g] D-values calculated using the procedure from Ref. 20 were used. *Ab initio* differences are introduced into the r_a structure. [h] Angle of the methyl groups torsion, see text. [i] Pseudorotation puckering amplitude. [j] Pseudorotation phase angle.

formation. The latter is in better agreement with that observed in tetrahydrothiophene[21] at 93.4(5)°, and with the present *ab initio* MP2(FC)/6-311++G** value of 96.1°.

If the conformation of the five-membered ring was assumed at different points of the pseudorotation pathway, the *R*-factor of the electron diffraction refinements resembled the pattern of the *ab initio* calculated pseudorotation potential. Going from zero pseudorotation phase angle to 72°, i.e. from the E^1 conformation to the E^3 conformation, the *R*-factor increased from 6.2 to 7.3%, and thereafter decreased to 5.2% at the pseudorotation phase angle of 162°. When the pseudorotation angle was refined using a starting value of 162°, it converged to 167(1)° with an *R*-factor of 5.1%.

Introduction of shrinkage corrections, computed using the conventional approach into the refinements, did not improve the agreement between the calculated and experimental data. Table 3 shows the results from these calculations assuming *ab initio* differences between r_α (column 4) and r_a (column 5) structures. Although the refinement with the implied differences in r_a structure has given a better agreement with the experimental data, the application of the *ab initio* differences in r_α structure seems to be more consistent with the physical meaning of this kind of parameter. This observation may be due to the fact that D-values for bonds computed with the conventional approach are rather large.

The D-values computed using the procedure suggested in Ref. 20 did not influence the agreement with experimental data as compared to the refinement from column 2 in the Table 3. It made no difference if *ab initio* bond

length differences were introduced into r_α (column 6, Table 3) or r_a (column 7, Table 3) structures.

The final results of the least-squares refinements, utilizing the computed differences in the r_α structure and the D-values calculated by the procedure from Ref. 20, are presented in Table 4. For comparison, the D-values calculated by the conventional method are also shown in Table 4. Bond lengths and bond angles from the joint electron diffraction/*ab initio* investigation of the molecular structure of 3,3-dimethyl-3-silatetrahydrothiophene, with estimated total errors, are presented in Table 5.

Results and discussion

The *ab initio* calculations indicated a conformation of the five-membered ring in the molecule between the E^5 envelope and the $_1T^5$ twist forms.

When the geometries computed at the HF and MP2 levels of theory are compared, the introduction of electron correlation into the calculations decreases the bond lengths and bond angles, except for the C–H bonds and S_1–C_2–Si_3 angle, which increase slightly. The conformation is also slightly altered. The introduction of the electron correlation shifts the conformation towards the E^5 envelope form in the E^5–$_1T^5$ interval, while the Hartree–Fock method gives a conformation closer to the $_1T^5$ twist form.

The barrier to pseudorotation is computed to be 10.3 kJ mol^{-1} at both HF and MP2 theoretical levels. It decreases to 9.6 kJ mol^{-1} when correction for the zero point vibrational energy is included at the HF level.

Structural parameters of the molecule undergo consid-

Table 4. The final results of electron diffraction least-squares refinements[a] of 3,3-dimethyl-3-silatetrahydrothiophene corresponding to column 6 in Table 3.

Parameter	$r_a, \angle_\alpha$	l	Group[b]	D_1[c]	D_2[d]
Independent parameters[e]					
$S_1–C_2$	1.826(2)	0.066(1)	i	0.002	−0.038
ΔCS[f]	0.000[m]				
$Si_3–C_2$	1.896(2)	0.068(1)	i	0.004	−0.006
$\Delta SiC1$[g]	0.012[m]				
$\Delta SiC2$[h]	0.025[m]				
$\Delta SiC3$[i]	0.028[m]				
$C_4–C_5$	1.538(3)	0.066(1)	i	0.000	−0.023
$(C–H)_{mean}$	1.106(1)	0.079		0.006	−0.047
$C_5–S_1–C_2$	98.6(4)				
$S_1–C_2–Si_3$	107.3(2)				
$C_2–Si_3–C_6$	112.7(2)				
$\Delta CSiC1$[j]	−1.0[m]				
$\Delta CSiC2$[k]	−0.9[m]				
$\Delta CSiC3$[l]	−1.8[m]				
$(Si–C–H)_{mean}$	116.4(5)				
$(H–C–H)_{ring}$	112.3(10)				
q_0[n]	10.7(3)				
f^o	168.1(22)				
φ^p	36(3)				
Dependent parameters[q]					
$Si_3–C_4$	1.885(2)	0.068(1)	i	0.002	−0.003
$S_1–C_5$	1.828(2)	0.065(1)	i	−0.001	−0.009
$Si_3–C_6$	1.873(2)	0.064(1)	i	0.001	−0.018
$Si_3–C_7$	1.870(2)	0.064(1)	i	0.001	−0.018
$Si_3\cdots S_1$	2.980(3)	0.075		0.023	−0.009
$S_1\cdots C_4$	2.736(4)	0.068		0.009	−0.018
$S_1\cdots C_6$	4.460(13)	0.177		0.054	0.006
$S_1\cdots C_7$	4.151(17)	0.291		0.065	0.019
$Si_3\cdots C_5$	2.831(7)	0.073		0.016	−0.005
$C_2\cdots C_4$	2.830(8)	0.072		0.023	−0.001
$C_2\cdots C_5$	2.757(7)	0.089		0.014	−0.015
$C_2\cdots C_6$	3.136(3)	0.099		0.006	−0.017
$C_2\cdots C_7$	3.150(3)	0.102		0.007	−0.016
$C_4\cdots C_6$	3.145(3)	0.101		0.005	−0.012
$C_4\cdots C_7$	3.157(3)	0.098		0.005	−0.014
$C_5\cdots C_6$	4.066(22)	0.257		0.046	0.014
$C_5\cdots C_7$	4.271(9)	0.148		0.041	0.003
$C_6\cdots C_7$	2.965(15)	0.097		0.004	−0.025
$S_1\cdots H_8$	2.422(4)	0.115		0.011	−0.068
$S_1\cdots H_{10}$	5.351(15)	0.204		0.097	−0.009
$S_1\cdots H_{11}$	4.700(34)	0.361		0.046	0.011
$S_1\cdots H_{12}$	4.851(24)	0.273		0.086	−0.001
$S_1\cdots H_{13}$	4.944(30)	0.349		0.099	0.010
$S_1\cdots H_{14}$	4.067(29)	0.469		0.056	0.034
$S_1\cdots H_{15}$	4.818(28)	0.329		0.112	0.003
$S_1\cdots H_{16}$	3.643(7)	0.101		0.026	−0.036
$S_1\cdots H_{17}$	3.141(18)	0.193		0.025	−0.019
$S_1\cdots H_{18}$	2.418(4)	0.115		0.009	−0.028
$Si_3\cdots H_8$	2.485(4)	0.121		0.013	−0.028
$Si_3\cdots H_{10}$	2.555(6)	0.126		0.015	−0.054
$Si_3\cdots H_{13}$	2.552(6)	0.125		0.015	−0.047
$Si_3\cdots H_{16}$	2.459(5)	0.120		0.012	−0.017
$Si_3\cdots H_{18}$	3.239(22)	0.191		0.031	−0.008
$Si_3\cdots H_{19}$	3.734(4)	0.101		0.032	−0.016
$C_2–Si_3–C_7$	113.6(2)				
$C_4–Si_3–C_6$	113.7(2)				
$C_4–Si_3–C_7$	114.5(2)				
$C_6–Si_3–C_7$	104.8(6)				
$C_2–Si_3–C_4$	97.7(3)				
$Si_3–C_4–C_5$	112.0(5)				
$C_4–C_5–S_1$	109.0(3)				
$S_1–C_2–Si_3–C_4$	15.7(13)				

Table 4. (Continued.)

Parameter	r_a, $\angle_\alpha$	l	Group[b]	D_1[c]	D_2[d]
$C_2-Si_3-C_4-C_5$	10.1(14)				
$Si_3-C_4-C_5-S_1$	327.4(13)				
$C_4-C_5-S_1-C_2$	40.2(10)				
$C_5-S_1-C_2-Si_3$	328.1(11)				
R-factor (%)	5.1				

[a] r_a distances (in Å) and $\angle_\alpha$ angles (in °) with least-squares standard deviations parenthesized in units of the last digit. [b] The group of the amplitudes included in the refinement. [c] Shrinkage corrections calculated by the method from Ref. 20 and used in the refinement. [d] Shrinkage corrections calculated by the conventional procedure, Ref. 19, are shown for comparison. [e] Correlation matrix elements larger than 0.7 in absolute value: S_1-C_2/C_2-Si_3 -0.75; $C_5-S_1-C_2/q_0$ -0.81; $S_1-C_2-Si_3/C_2-Si_3-C_6$ 0.83. [f] $\Delta CS = r_\alpha(C_2-S_1) - r_\alpha(C_5-S_1)$. [g] $\Delta SiC1 = r_\alpha(Si_3-C_2) - r_\alpha(Si_3-C_4)$. [h] $\Delta SiC2 = r_\alpha(Si_3-C_2) - r_\alpha(Si_3-C_6)$. [i] $\Delta SiC3 = r_\alpha(Si_3-C_2) - r_\alpha(Si_3-C_7)$. [j] $\Delta CSiC1 = \angle_\alpha(C_2-Si_3-C_6) - \angle_\alpha(C_4-Si_3-C_6)$. [k] $\Delta CSiC2 = \angle_\alpha(C_2-Si_3-C_6) - \angle_\alpha(C_2-Si_3-C_7)$. [l] $\Delta SiC3 = \angle_\alpha(C_2-Si_3-C_6) - \angle_\alpha(C_4-Si_3-C_7)$. [m] Assumed from the results of the *ab initio* MP2(FC)/6-311++G** calculations. [n] Pseudorotation puckering amplitude. [o] Pseudorotation phase angle. [p] Angle of the methyl groups torsion, see text. [q] The $C\cdots H$ and $H\cdots H$ distances are not shown.

Table 5. Bond lengths (r_g, in Å), bond angles, pseudorotation parameters, and angles of torsion ($\angle_\alpha$, in °) of 3,3-dimethyl-3-silatetrahydrothiophene with estimated total errors[a] from the electron diffraction analysis incorporating constraints[b] from *ab initio* MP2(FC)/6-311++G** calculations.

S_1-C_2	1.828 ± 0.005[c]	$C_2-Si_3-C_7$	113.6[d]
C_2-Si_3	1.898 ± 0.006[c]	$C_4-Si_3-C_6$	113.7[d]
Si_3-C_4	1.887[d]	$C_4-Si_3-C_7$	114.5[d]
C_4-C_5	1.541 ± 0.007	$C_6-Si_3-C_7$	104.8 ± 1.2
C_5-S_1	1.830[d]	$(H-C-H)_{mean}$	112.3 ± 2.0
Si_3-C_6	1.875[d]	$(Si-C-H)_{mean}$	116.4 ± 1.0
Si_3-C_7	1.872[d]	$S_1-C_2-Si_3-C_4$	15.7 ± 2.6
$(C-H)_{mean}$	1.112 ± 0.003	$C_2-Si_3-C_4-C_5$	10.1 ± 2.8
$C_5-S_1-C_2$	98.6 ± 0.8	$Si_3-C_4-C_5-S_1$	327.4 ± 2.6
$S_1-C_2-Si_3$	107.3 ± 0.4	$C_4-C_5-S_1-C_2$	40.2 ± 2.0
$C_2-Si_3-C_4$	97.7 ± 0.6	$C_5-S_1-C_2-Si_3$	328.1 ± 2.2
$Si_3-C_4-C_5$	112.0 ± 1.0	q_0[e]	10.7 ± 0.6
$C_4-C_5-S_1$	109.0 ± 0.6	f[f]	168.1 ± 4.4
$C_2-Si_3-C_6$	112.7 ± 0.4[c]	φ[g]	36 ± 6

[a] Total errors were calculated as $\sigma_{total} = 2[\sigma_{LS}^2 + (0.001 r)^2]^{1/2}$ for the bond lengths, where r is the bond length and 0.001 reflects the 0.1% uncertainty in the wavelength of electrons, and $\sigma_{total} = 2\sigma_{LS}$ for the angles. [b] The constraints included the differences between the S_1-C_2 and C_5-S_1 r_α bond lengths, between the C_2-Si_3, Si_3-C_4, Si_3-C_6, and Si_3-C_7 r_α bond lengths, as well as between the $C_2-Si_3-C_6$, $C_2-Si_3-C_7$, $C_4-Si_3-C_6$, and $C_4-Si_3-C_7$ bond angles. [c] The total errors were obtained assuming the *ab initio* calculated differences between the parameters and do not reflect correlations between them. The total errors for these parameters refined independently would be larger. Calculated $(S-C)_{mean}$ and $(Si-C)_{mean}$ bond lengths are 1.829 ± 0.005 Å and 1.883 ± 0.006 Å, respectively. [d] Parameters constrained by the *ab initio* differences. [e] Pseudorotation puckering amplitude. [f] Pseudorotation phase angle. [g] Angle of the methyl group torsion, see text.
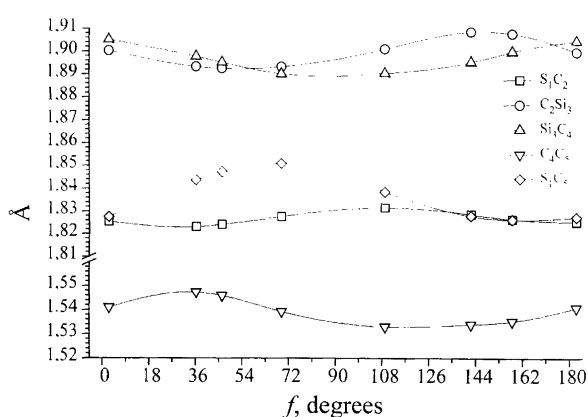

Fig. 6. Variation of the bond lengths and in the ring in 3,3-dimethyl-3-silatetrahydrothiophene with the change of the conformation as computed at the HF/6-311++G** level.

erable changes along the pseudorotation cycle, as indicated in Figs. 6 and 7, based on the results of the HF/6-311++G** calculations. Apart from the expected variation in the endocyclic bond angles, some of the ring bond lengths also change considerably. The most pronounced alteration is observed for the S_1-C_5 bond length, which amounts to 0.025 Å. This suggests a considerable electron density redistribution accompanying the pseudo-

rotation in the five-membered ring. Bond angle variation can be as large as 5°, as for the $C_5-S_1-C_2$ angle. Similar relatively large variations were computed for *N*-nitropyrrolidine.[10]

A comparison of the main parameters obtained in the present electron diffraction study with those from the previous investigation of 3,3-dimethyl-3-silatetrahydrothiophene and similar molecules is presented in Table 6. Bond lengths and bond angles of the ring are in general agreement with those obtained in the previous electron diffraction study of the molecule, taking into account the relatively large experimental errors of the previous study. However, a difference is observed for the C–Si–C angle in the ring. A value smaller than 100° in the present model seems to be in better agreement with the angles found in 3,3-dimethyl-3-silatetrahydrofuran[6] and silacyclopentane[22] than the value found in the previous study.[5]

The amplitudes for the bonds in 3,3-dimethyl-3-silatetrahydrothiophene refined to somewhat larger values than calculated and usually obtained for similar bonds in other molecules. Beyond the possible correlations with other parameters and uncertainties in the blackness cor-

Table 6. Comparison of the parameters of 3,3-dimethyl-3-silatetrahydrothiophene with those from the similar molecules.

	3-Dimethyl-3-silatetrahydrothiophene (present work)[a]	3,3-Dimethyl-3-silatetrahydrothiophene[b]	3,3-Dimethyl-3-silatetrahydrofurane[c]	Tetrahydro-thiophene[d]	Silacyclo-pentane[e]
$(C-S)_{mean}$	1.829(5)	1.86(3)	—	1.841(2)	—
$(Si-C)_{mean}$	1.883(6)	1.88(2)	1.889(3)	—	1.892(2)
$C-C$	1.541(7)	1.53(3)	1.558(7)	1.538(2)	—
$(C-H)_{mean}$	1.112(3)	1.09(1)	1.11(2)	1.126(5)	—
$C-S-C$	98.6(8)	102(3)	—	93.4(5)	—
$S-C-Si$	107.3(4)	103(3)	—	—	—
$(C-Si-C)_{ring}$	97.7(6)	103(3)	92.2(5)	—	96.3(3)
$CH_3-Si-CH_3$	104.8(12)	110(3)	107.2(8)	—	—
$(Si-C-H)_{mean}$	116.4(10)	–	111.6(14)	—	—
$(H-C-H)_{mean}$	112(2)	112 assumed	111(5)	108(3)	—
Conformation	Between $_1T^5$ and E_1	$_4T^5$	E^1	$_4T^3$	$_1T^5$

[a] Electron diffraction r_g distances and $\angle_\alpha$ angles with total errors in units of the last digit in parenthesis. [b] Ref. 5. r_a distances and $\angle_a$ angles. [c] Ref. 6. r_g distances and $\angle_a$ angles. The r_g distances were calculated from the data presented in the reference. [d] Ref. 7. r_g distances and $\angle_a$ angles. The r_g distances were calculated from the data presented in the reference. [e] Ref. 22. r_a distances and $\angle_a$ angles. The conformation was denominated using the numbering of the ring atoms as that for 3,3-dimethyl-3-silatetrahydrothiophene.

rection associated with the experimental data, the reason for this observation may also be due to bond-length variation during the large-amplitude motion (pseudo-rotation) in the molecule. Variation in a bond length will always lead to a larger effective amplitude being observed. On the other hand, refinement of the amplitudes has not only reduced the R-factor, but has led to the parameters of the molecule showing better agreement with previously studied species and with the results of the present *ab initio* calculations.

Results of molecular mechanics calculations of the total energy and different energy components for 3,3-dimethyl-3-silatetrahydrothiophene are presented in Fig. 8. The universal force field[23] implemented in the MSI Cerius[2] 3.0 program package[24] was applied. In these

calculations the *ab initio* geometry optimized at the HF/6-311++G** level was used to calculate the total energy and the energy components by molecular mechanics. The results indicate quite good agreement in the overall shape of the potential, while the barrier to pseudorotation is considerably higher from molecular mechanics, 18.3 versus 9.6 kJ mol^{-1} from the *ab initio* calculations. According to these calculations the torsional and the angular strain in the molecule play the key roles in determining the overall shape of the conformational potential energy. While the torsional strain suggests a minimum between the E^3 and E_4 forms, the predominating angular strain leads to the $_1T^5$ form. Consideration of both of them gives a shape of the total potential
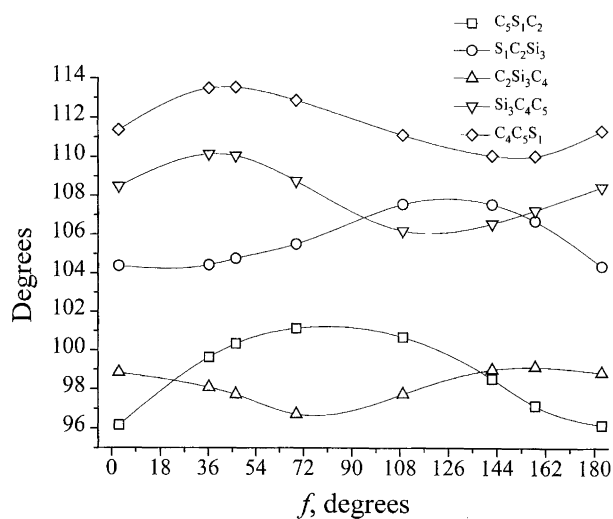

Fig. 7. Variation of the bond angles in the ring in 3,3-dimethyl-3-silatetrahydrothiophene with the change of the conformation as computed at the HF/6-311++G** level.
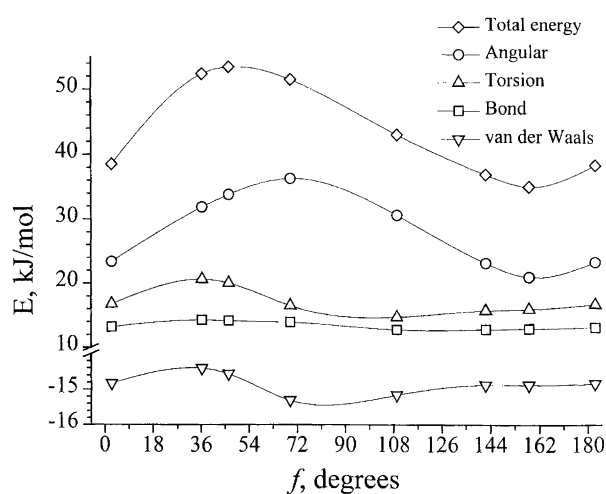

Fig. 8. Potential energy curve for pseudorotation of the ring in 3,3-dimethyl-3-silatetrahydrothiophene and contributions of different energy components computed by molecular mechanics.

energy with maximum and minimum in agreement with the *ab initio* calculations.

References

1. Altona, C. and Sundaralingam, M. *J. Am. Chem. Soc. 94* (1972) 8205.
2. Han, S. J. and Kang, Y. K. *J. Mol. Struct. (Theochem) 369* (1996) 157.
3. Kilpatrick, J. E., Pitzer, K. S. and Spitzer, R. *J. Am. Chem. Soc. 69* (1947) 2483.
4. Han, S. J. and Kang, Y. K. *J. Mol. Struct. (Theochem) 362* (1996) 243.
5. Mastryukov, V. S., Golubinskii, A. V., Vilkov, L. V., Kirpichenko, S. V., Suslova, E. N. and Voronkov, M. G. *Zh. Strukt. Khim. 32* (1991) 148.
6. Gromov, A. Yu., Shishkov, I. F., Skancke, A., Vilkov, L. V., Yesipenko, A. V. and Kirpichenko, S. V. *J. Mol. Struct. 352/353* (1995) 115.
7. Plafferott, G., Oberhammer, H., Boggs, J. E. and Caminati, W. *J. Am. Chem. Soc. 107* (1985) 2305.
8. Caminati, W., Oberhammer, H., Plafferott, G., Filgueira, R. R. and Gomez, C. H. *J. Mol. Spectrosc. 106* (1984) 217.
9. Shustov, G. V., Parvez, M. and Rauk, A. *J. Chem. Soc., Perkin Trans. 2* (1996) 1907.
10. Borisenko, K. B., Samdal, S., Shishkov, I. F. and Vilkov, L. V. *Acta Chem. Scand. 52* (1998) 312.
11. Kirpichenko, S. V., Suslova, E. N., Tolstikova, L. L.,
    Albanov, A. I. and Shainyan, B. A. *Zh. Obshch. Khim. 67* (1997) 1542.
12. Voronkov, M. G., Kirpichenko, S. V., Suslova, E. N., Keiko, V. V. and Albanov, A. I. *J. Organomet. Chem. 243* (1983) 271.
13. Bastiansen, O., Graber, R. and Wegmann, L. *Balzers High Vacuum Report 25* (1969) 1.
14. Gundersen, S. and Strand T. G. *J. Appl. Crystallogr. 29* (1996) 638.
15. Ross, A. W., Fink, M. and Hilderbrandt, R. In Wilson, A. J. C., Ed. *International Tables for X-Ray Crystallography*, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C.
16. Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T., Petersson, G. A., Montgomery, J. A., Raghavachari, K., Al-Laham, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Cioslowski, J., Stefanov, B. B., Nanayakkara, A., Challacombe, M., Peng, C. Y., Ayala, P. Y., Chen, W., Wong, M. W., Andres, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. J., Binkley, J. S., Defrees, D. J., Baker, J., Stewart, J. P., Head-Gordon, M., Gonzalez, C. and Pople, J. A. *Gaussian 94*, Revision D.2, Gaussian Inc., Pittsburgh, PA 1995.
17. McLean, A. D. and Chandler, G. S. *J. Chem. Phys. 72* (1980) 5639. Krishnan, R., Binkley, J. S., Seeger, R. and Pople, J. A. *J. Chem. Phys. 72* (1980) 650.
18. Møller, C. and Plesset, M. S. *Phys. Rev. 46* (1934) 618.
19. Hedberg, L. and Mills, I. M. *J. Mol. Spectrosc. 160* (1993) 117.
20. Sipachev, V. A. *J. Mol. Struct. (Theochem) 121* (1985) 143.
21. Náhlovská, Z., Náhlovský, B. and Seip, H. M. *Acta Chem. Scand. 23* (1969) 3534.
22. Mastryukov, V. S., Golubinskii, A. V., Atavin, E. G., Vilkov, L. V., Cyvin, B. N. and Cyvin, S. J. *J. Struct. Chem. 20* (1979) 615.
23. Rappé, A. K., Casewit, C. J., Colwell, K. S., Goddard, W. A. and Skiff, W. M. *J. Am. Chem. Soc. 114* (1992) 10024.
24. *Cerius² 3.0*, April 1997. San Diego: Molecular Simulations Inc., 1997.