Mendeleev Commun., 1999, 9(6), 217–218

The molecular structure and the puckering potential function of octamethylcyclotetrasilane, Si_4Me_8, determined by gas electron diffraction and *ab initio* calculations

Vladimir P. Novikov,*[a] Svetlana A. Tarasenko,[a] Svein Samdal[b] and Lev V. Vilkov[a]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation. Fax: +7 095 932 8846; e-mail: VPNovikov@phys.chem.msu.ru*
[b] *Department of Chemistry, University of Oslo, N-0315 Oslo, Norway*

The structural parameters, the barrier of inversion and the equilibrium puckering angle of Si_4Me_8 were determined using a dynamic model (V_0 = 1.0±0.5 kcal mol^{-1}, φ_e = 28.3±1.9°).

The reactivity of silacyclobutane derivatives is closely related to the ring strain energy. Since the balance of angular and torsional strains in the ring determines the degree of its planarity,[1] it can be expected that the structure of this class of compounds is responsible for their reactivity. However, the data on the molecular structure of cyclotetrasilane derivatives are inconsistent in many respects. Thus, for crystals of Si_4Cl_8 and Si_4Br_8, a planar ring structure was found,[2] whereas a vibrational spectroscopy study revealed a nonplanar ring structure.[3] The molecule of octamethylcyclotetrasilane shows no exception. The results of X-ray analysis give evidence of a planar ring, while it is nonplanar according to vibrational spectroscopy data.[5]

Earlier, the Si_4Me_8 molecule was studied by gas electron diffraction within the static model approximation,[6] and the average dihedral angle φ (Figure 1) was found to be 29.4±4.0°. Note that this angle can differ from zero even if the ring has a planar equilibrium configuration. This follows from the fact that the static model produces the mean value of φ averaged over vibrational levels of the puckering motion. As a rule, the puckering of four-membered rings is a large-amplitude motion of high anharmonicity. Therefore, to solve the problem whether the ring is planar or not, we should introduce a potential function to describe this motion and use a dynamic model which takes into account contributions to the scattering from all local conformations arising along the puckering pathway in accordance to their population.

To describe the ring puckering, it is convenient to use the puckering coordinate z (Figure 1), which is defined as a half-height between the diagonals Si···Si in the ring and characterises the displacement of atoms from a planar configuration. This description corresponds to the normal mode of ring puckering. The Si_4Me_8 molecule has D_{2d} symmetry for the nonplanar ring and D_{4h} for the planar one. With these types of symmetry, the relation between the dihedral angle and the coordinate z can be expressed as follows:

$$z = 0.5r(\text{Si–Si})\cos(\alpha/2)\sin(\varphi/2),$$

where α is the Si–Si–Si angle: $\alpha = 2\arctan[\cos(\varphi/2)]$, which is valid if the Si–Si bond length does not change during the ring puckering. However, an electron diffraction study[7] of 1,1-dichlorosilacyclobutane showed that changes in the bond lengths and valence angles of the ring are sufficiently large, and that these changes should be included in the structure analysis.

Therefore, in this work, for more accurate determination of the structure of Si_4Me_8, we applied a dynamic model which takes into account the relaxation of geometric parameters estimated from *ab initio* calculations. These calculations were also used to obtain the mean-square amplitudes and vibration corrections.

We used the total scattering intensity $I_t(s)$ and the background line $I_b(s)$ data obtained in the Budapest laboratory of electron diffraction[6] and deposited at the British Library.[8] The range of experimental $sM(s)$ values was 2–36 Å^{-1}. The numbering of atoms of the Si_4Me_8 molecule is shown in Figure 1. The deviations of the bisectors of the C–Si–C angles from the Si–Si–Si planes are denoted as δC.

The relaxation effects were estimated by an optimization of the geometric parameters for a number of fixed φ values in the range 0–50° with a step of 10°. The *ab initio* MO calculations were carried out at the Hartree–Fock level of the theory using the 6-311G** basis set with polarization functions and the GAUSSIAN-94 program.[9] It was found that the puckering potential of Si_4Me_8 is adequately described by the following quadratic-quartic function: $V(\varphi) = V_0[(\varphi/\varphi_e)^2 - 1]^2$, where V_0 = 0.65 kcal mol^{-1} and φ_e = 25.6°.

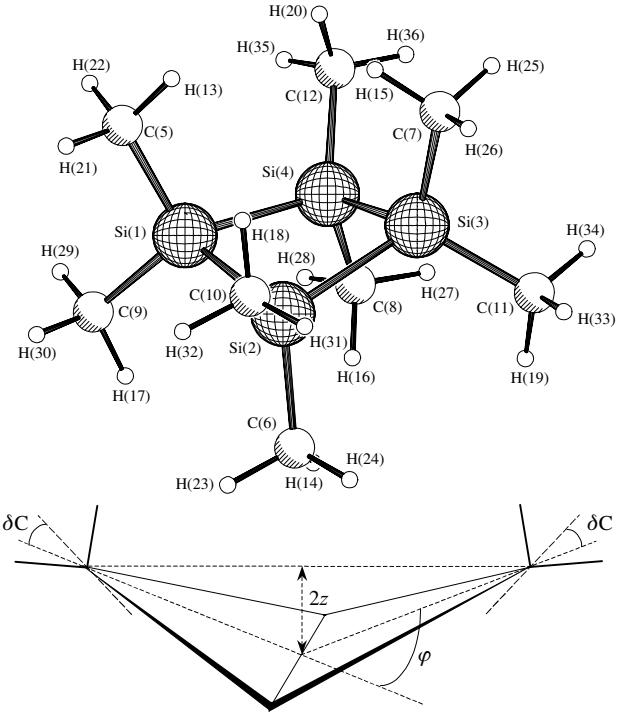

Figure 1 Molecular structure of Si_4Me_8; definition of the puckering coordinate z.

Table 1 Main geometric parameters of Si_4Me_8[a] (gas electron diffraction, GED, *ab initio* HF/6-311G** calculations, AI, and X-ray data).

Parameter	This work		GED[6]	X-ray[4]
	GED + AI[b]	AI		
Si–C	1.896(3)	1.903	1.893(3)	1.889
Si–Si	2.370(2)	2.398	2.362(4)	2.363
C–H	1.104(3)	1.087	1.096(11)	—
∠CSiC	109.5(6)	108.6	110.8(16)	110.0
∠SiSiSi	88.2(2)	88.6	88.1(5)	90.0
∠SiCH	111.7(6)	112.0	111.7(15)	—
δC	4.1[c]	4.1	0.8(17)	—
V_0/kcal mol^{-1}	1.0(5)	0.65	—	—
φ_e	28.3(19)	25.6	29.4(40)	0.0
R-factor (%)	4.8	—	10.3	—

[a]Distances, Å; angles, degrees; the GED parameters r_a and $\angle\alpha$; errors are given in parentheses as 3σ. [b]Joint analysis of GED and *ab initio* data. [c]Found from *ab initio* calculations.

The *ab initio* calculations showed that the bond lengths can change by 0.01 Ådur ing the puckering motion, and the valence and δ angles, by 2.5 and 4.2°, respectively. Thus, the relaxation effects in Si_4Me_8 are too large to be neglected in the description of the geometry of local conformers. To take into account these relaxation effects, the calculated geometric parameters $P(\varphi)$ were approximated by the third degree polynomials $P(\varphi) = a_0 + a_n\varphi^n$. The polynomial factors a_n were used in the structural analysis to compute the geometric parameters at a given value of φ, while the factors a_0 were variable parameters. For the angle δC, the factor a_0 is equal to zero by symmetry reasons because $\delta = 0°$ at $\varphi = 0°$. Therefore, these angles were parametrised by the function $\delta(\varphi) = k_0 \; a_n\varphi^n$, where k_0 is a variable parameter having the meaning of a scale factor.

For a complete description of the molecular geometry, the following six parameters were used: r(Si–C), r(Si–S i), ∠CSiC, δC, ∠SiCH, r(C–H). All of the parameters, with the exception of r(C–H), were parametrised as functions of the angle φ.

The frequencies and normal modes of Si_4Me_8 were calculated using the force field on Cartesian coordinates obtained in the full geometry optimization by the GAUSSIAN-94 program using the HF/6-311G** basis set. The transformation of the force field to symmetry coordinates and the optimization of scaling factors were carried out by the SHRINK4 program[10] using experimental frequencies.[5]

The results of normal coordinate calculations agree well with the frequency assignment of Si_4Me_8 made earlier in the 900–10 0 cm^{-1} region.[5] Normal coordinate analysis showed that the puckering mode has the lowest frequency, 33 cm^{-1} (A_1 symmetry). The nearest frequency of the same symmetry is the SiC_2 deformation, but it lies considerably higher than the ring puckering frequency at 161 cm^{-1}. Other low-frequency vibrations have different types of symmetry: SiC_2 twist, 87 cm^{-1} (A_2); SiC_2 rock, 74 cm^{-1} (B_1) and 73 cm^{-1} (E). Therefore, the puckering mode can be reliably separated from the framework vibrations, which were treated in a harmonic approximation.

The amplitudes and vibration corrections were calculated for the framework at fixed φ values (0, 10, 20, 30, 40, and 50°) using the optimised geometry for the corresponding φ values. The root-mean-square amplitudes (u) and vibration corrections ($\delta = r_\alpha - r_a$) were calculated using the technique[10] which applies a nonlinear transformation of internal coordinates into Cartesian displacements of atoms. This technique gives more reliable values of δ corrections than the standard method[11] if the molecule possesses low-frequency vibrations. For each internuclear distance, the functions $u(\varphi)$ and $\delta(\varphi)$ were interpolated during calculations of the reduced molecular intensity $sM(s)$ in the range φ = 0–5 0° wit h a step of 2.5° a ccording to the formula

$$sM(s) = \int_0^{\varphi_{max}} W(\varphi) sM(s,\varphi) d\varphi,$$

where $W(\varphi)$ is the classical probability density of the angle φ, $W(\varphi) = Q^{-1} \exp[-V(\varphi)/RT]$, where R is the gas constant, T is the absolute temperature, $V(\varphi)$ is the potential function and Q is the normalising factor.

The structural analysis was carried out using the modified ELED program[12] with the starting values of the parameters taken from the *ab initio* calculations. The refinement of the geometry was carried out using a conventional procedure.[7] At the first stage of the structural analysis, we varied the set of well-defined parameters (the Si–Si and Si–C bond le ngths and the ∠CSiC angles) as well as the parameters V_0 and φ_e for the potential function. The model with the planar ring configuration and the puckering potential function $V(\varphi) = A\varphi^4 + B\varphi^2$ was also tested. All starting approximations were shown to converge to the nonplanar ring conformation with the dihedral angle $\varphi_e = 28°$. After the background correction, the rest of geometric parameters and the amplitudes were sequentially added to the set of parameters under determination according to their contributions to the scattering. A variation in the scale factor k_0 for the angle δC leads to an extremely unstable solution. Therefore, we put $k_0 = 1$ for δC, *i.e.*, it was fixed at its *ab initio* value. The final results of the structural analysis are presented in Table 1 and compared with the data obtained from *ab initio* calculations and previous investigations.

As can be seen in Table 1, the dynamic model gives better agreement with the experimental data as compared to the static model:[6] the R-factor was halved, and this led to a decrease of the error limits. The parameters for both of the models are quite similar. However, this fact cannot be predicted beforehand. This situation can occur when the barrier height V_0 is high so that the most populated puckering vibrational levels lie under the barrier. In this case, the potential function can be approximated by a parabola near its minimum, and a simple harmonic approximation can be used for the puckering vibration. Thus, static and dynamic models will give essentially the same results.

The dihedral angle and the barrier height clearly indicate that the ring is puckered in the gas phase. This agrees with the vibrational spectra analysis. The planar ring in the solid phase found in an X-ray study[4] of Si_4Me_8 can apparently be explained by the crystal packing effect.

Note that cyclotetrasilane has also a puckered conformation according to *ab initio* calculations: $\varphi_e = 31.2°$ and V_0 = = 0.3–0.4 kcal mol^{-1}.[13] The replacement of hydrogen atoms with methyl groups increases the puckering barrier in Si_4Me_8 up to 1.0±0.5 kcal mol^{-1}, which is seemingly caused by an increase of the torsional strain energy. This is confirmed by the fact that the distances between the nearest nonbonded atoms C(8)···C(9) increase from 3.89 to 3.98 Åwhe n the conformation of the ring changes from planar to puckered with the angle φ_e. This means that in the equilibrium configuration the distance between adjacent methyl groups is equal to the sum of the van der Waals radii of the methyl groups, 4.0 Å.[14] The predominance of the torsional strain over the angular strain determines the puckered conformation of the ring in Si_4Me_8, as it is the case in cyclobutane, though the absolute values of angular and torsional strain energies decrease when carbon atoms of cyclobutane are replaced with silicon atoms.[15]

This work was supported by the Russian Foundation for Basic Research (grant nos. 99-03-32511a and 96-15-97469) and by the Research Council of Norway (Programme for Supercomputing).

References

1 A. C. Legon, *Chem. Rev.*, 1980, **80**, 231.
2 J. R. Koe, D. R. Powell, J. J. Buffy and R. West, *Polyhedron*, 1998, **17**, 1791.
3 (*a*) E. Hengge and D. Kovar, *Z. Anorg. Allg. Chem.*, 1979, **458**, 163; (*b*) K. Hassler, E. Hengge and D. Kovar, *J. Mol. Struct.*, 1980, **66**, 25.
4 C. Kratky, H. G. Schuster and E. Hengge, *J. Organomet. Chem.*, 1983, **247**, 253.
5 K. Hassler, *Spectrochim. Acta*, 1981, **A37**, 541.
6 V. S. Mastryukov, S. A. Strelkov, L. V. Vilkov, M. Kolonits, B. Rozsondai, H. G. Schuster and E. Hengge, *J. Mol. Struct.*, 1990, **238**, 433.
7 V. P. Novikov, S. A. Tarasenko, S. Samdal and L. V. Vilkov, *J. Mol. Struct.*, 1998, **445**, 207.
8 British Library Lending Division, Boston Spa, Wetherby, Yorkshire LS23 7BQ, Gr. Britain, Supplementary Publication No. SUP 26396.
9 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, *Gaussian 94 Program, Revision B.3*, Gaussian, Inc., Pittsburgh PA, 1995.
10 (*a*) V. A. Sipachev, *J. Mol. Struct.*, 1985, **121**, 143; (*b*) V. P. Novikov, V. A. Sipachev, E. I. Kulikova and L. V. Vilkov, *J. Mol. Struct.*, 1993, **301**, 29.
11 R. Stolevik, H. M. Seip and S. J. Cyvin, *J. Chem. Phys. Lett.*, 1972, **15**, 263.
12 V. P. Novikov, S. Samdal and L. V. Vilkov, *J. Mol. Struct.*, 1997, **413/414**, 279.
13 R. S. Grev and H. F. Schaefer, *J. Am. Chem. Soc.*, 1987, **109**, 6569.
14 Yu. V. Zefirov and P. M. Zorky, *Zh. Strukt. Khim.*, 1976, **17**, 745 [*J. Struct. Chem.* (*Engl. Transl.*), 1976, 644].
15 R. L. Rosas, C. Cooper and J. Laane, *J. Phys. Chem.*, 1990, **94**, 1830.

Received: 7th June 1999; Com. 99/1496