Silicon-29 and oxygen-17 relaxation in $H_8Si_8O_{12}$ in solution*

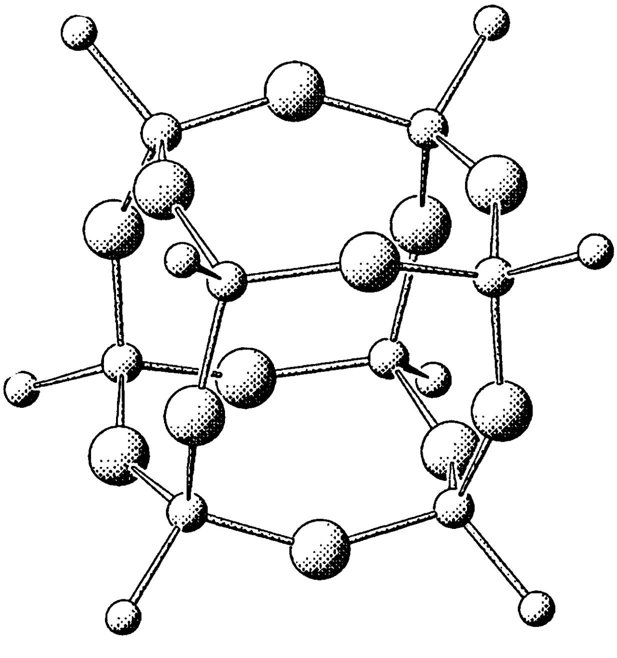
Jozef Kowalewski, Tomas Nilsson and Karl W. Törnroos

Department of Physical, Inorganic and Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden

Silicon-29 and oxygen-17 NMR relaxation data have been obtained for the spherosiloxane $H_8Si_8O_{12}$ in perdeuteriocyclohexane solution at 303 and 323 K. The spin–lattice relaxation rates and the nuclear Overhauser enhancement factors for silicon were used to determine the dipole–dipole contributions to the relaxation rates which, together with the known silicon–proton distance, yield the rotational correlation times for the silicon–proton axis. The oxygen linewidths provide the quadrupolar spin–spin relaxation rates, which were used to estimate a quadrupole coupling constant for oxygen-17 of 4.9 ± 0.5 MHz.

Spherosiloxanes are a group of molecular silicon acids which during recent years have been used extensively as model compounds within zeolite and silicate chemistry, as well as within the fields of catalytic and analytical chemistry. Of particular interest is the highly symmetrical (O_h) molecule $H_8Si_8O_{12}$, the electronic structure of which has been investigated theoretically,[1] as well as experimentally by means of elaborate spectroscopic research supplemented by normal coordinate analysis.[2] As we have earlier investigated open-framework structures such as the cyclic siloxanes,[3,4] it was of interest to expand our studies to include these more rigid closed cage structures.

Consequently, we describe here a nuclear spin-relaxation study of silicon-29 and oxygen-17 at natural abundance for the spherosiloxane $H_8Si_8O_{12}$ in perdeuteriocyclohexane solution. This compound is a nice example of a system where multinuclear relaxation studies can complement each other, allowing determination of the parameters characterising both the molecular dynamics and the static interaction strength, related to the structure. The examination of the relaxation of the silicon-29 nuclei carrying directly bonded protons, similar to an earlier study of chlorosilanes, allows us to determine the rotational correlation times for the molecule.[5] The oxygen-17 relaxation data in combination with these correlation times yield the oxygen-17 quadrupole coupling constant, which characterises the local electron distribution at the oxygen atom sites. The procedure used is sometimes denoted as the 'dual spin probe method', and has earlier been applied to determine the oxygen-17 quadrupole coupling constants in organic oxygen compounds, with carbon-13 relaxation measurements functioning as the source of the rotational correlation time.[6,7]



$H_8Si_8O_{12}$

Experimental

The $H_8Si_8O_{12}$ compound was synthesised according to Agaskar.[8] Deuteriated cyclohexane was obtained from Cambridge Isotope Laboratories. The NMR sample was prepared as a 6.8 mmol dm^{-3} solution of $H_8Si_8O_{12}$ in [$^2H_{12}$]cyclohexane, and was transferred to an NMR tube (outside diameter 10 mm) under a nitrogen atmosphere. Finally, the sample was degassed by several freeze–pump–thaw cycles and sealed under vacuum.

All the NMR experiments were performed at 30 and 50 °C. The silicon-29 experiments were carried out on a 9.4 T JEOL Alpha 400 spectrometer, while a Bruker MSL 200 spectrometer operating at 4.7 T was used for the oxygen-17 experiments. In both cases the standard broad-band 10 mm probe was used. The temperature was controlled using standard variable-temperature accessories provided by the instrument manufacturers, and the internal deuterium lock for field/frequency stabilisation was used in all measurements.

The ^{29}Si NMR experiments were carried out using two-level continuous-wave proton decoupling. The 90° pulse width was 22 μs, the digital resolution 1 Hz and the number of acquisitions typically 80–100. The spin–lattice relaxation times were measured using the fast inversion-recovery method[9] and eight different delays between the 180 and 90° pulses. The recycle delay was about 1.5–2 times the spin–lattice relaxation time. The spin–lattice relaxation times (T_1) were evaluated by three-parameter least-squares fitting[10] of line intensities (obtained after an exponential broadening by 5–10 Hz). The accuracy is estimated to be about 5–10%, even though the standard deviations of the non-linear fits were better. The heteronuclear nuclear Overhauser enhancement (NOE) factor was determined by taking a ratio, denoted 1 + NOE, of exponentially broadened line intensities obtained using the dynamic NOE sequence[11] with a long ($>5T_1$) and a short (10 ms) proton irradiation before the observe pulse. The accuracy of the

---

* *Non-SI unit employed:* cP = mPa s.

intensity ratio is 5–10%. In order to avoid temperature fluctuations, the continuous-wave decoupler was switched on all the time, and its frequency was set off-resonance by about 100 kHz during the recycle delay.

The 90° pulse width in the ^{17}O NMR experiments was 11 μs, the digital resolution was about 20 Hz and the number of scans was typically 2×10^6. The spin–spin relaxation time was determined from the linewidth by means of the relationship $T_2^{-1} = \pi\Delta\nu$. The linewidth $\Delta\nu$ was evaluated by fitting the spectra by a single Lorentzian, using the program FELIX from BIOSYM Inc (San Diego, CA). The uncertainty of the linewidth determination is 5–10%. All experiments were performed at least twice, and the mean values are reported.

The above-mentioned uncertainties in T_1, intensity ratio and linewidth are based on our experience of the variation of the results with respect to different parameter settings (in the experimental set-up and data processing), choice of the measuring method, *etc.*

Results and Discussion

The spin relaxation of low natural-abundance spin $\frac{1}{2}$ nuclei X carrying a directly bonded proton is often dominated by the dipole–dipole interaction with the proton magnetic moment. Under proton decoupling the relaxation is single exponential. For low-molecular-weight species in low-viscosity solution the extreme-narrowing conditions prevail and the spin–lattice relaxation rate due to the dipole–dipole interaction is given[12,13] by equation (1) where μ_0 is the permeability of

$$T_{1\mathrm{DD}}^{-1} = \left(\frac{\mu_0}{4\pi}\right)^2 \left(\frac{\gamma_X^2\gamma_H^2\hbar^2}{r_{XH}^6}\right)\tau_c^{\mathrm{eff}} \qquad (1)$$

vacuum, γ_X and γ_H are the magnetogyric ratios for nucleus X and the proton, respectively, r_{XH} is the internuclear distance and τ_c^{eff} is the effective correlation time for the reorientation of the internuclear axis. If other relaxation mechanisms contribute to the measured relaxation rate $T_{1\mathrm{obs}}^{-1}$, the dipole–dipole contribution can under extreme-narrowing conditions be isolated by measurement of the NOE factor[12,13] using equation (2) where $\mathrm{NOE_{obs}}$ is the observed nuclear Overhauser

$$T_{1\mathrm{DD}}^{-1} = T_{1\mathrm{obs}}^{-1} \frac{\mathrm{NOE_{obs}}}{(\gamma_H/2\gamma_X)} \qquad (2)$$

enhancement and $\gamma_H/2\gamma_X$ is the largest possible value of the NOE. For the $X = {}^{29}Si$ as in this study, $\gamma_H/2\gamma_X < 0$ and $\mathrm{NOE_{obs}}$ is always negative.

The ^{29}Si NMR spectrum of $H_8Si_8O_{12}$ is a doublet, with a splitting of 340 Hz corresponding to the one-bond silicon–proton coupling constant. Upon proton decoupling a single ^{29}Si line is obtained, the relaxation data for which are summarised in Table 1. The largest possible value of NOE for silicon is -2.52[13] and this value is indeed observed at 30 °C. This observation confirms that other relaxation mechanisms are not operative at this temperature and, in addition, that the extreme-narrowing conditions prevail. At 50 °C there is a small contribution from a non-dipole-dipole mechanism which, by virtue of increased efficiency at a higher temperature, is probably the spin-rotation interaction.[5] A silicon–proton distance in $H_8Si_8O_{12}$ of 146.1 pm has been obtained by single-crystal neutron-diffraction measurements.[14] Entering this value into equation (1) (and neglecting the fact that the vibrational corrections affect the neutron diffraction and NMR distances in a slightly different way) allows evaluation of the rotational correlation times, which are also given in Table 1, together with estimated error limits. The correlation times can be related to the estimated molecular volume, about 3.8×10^8 pm^3 (corresponding to a sphere with radius 450 pm[14]), for $H_8Si_8O_{12}$ and the solution viscosity (estimated to be 0.88 cP at 303 K and 0.65 cP at 323 K[15]), in the same way as in the work of Berggren and Kowalewski on octamethylcyclotetrasiloxane.[3] The conclusion is that the reorientation of $H_8Si_8O_{12}$ in perdeuteriocyclohexane, described in hydrodynamic terms, corresponds to a boundary condition close to the slipping limit.

Table 1 Relaxation data for ^{29}Si in $H_8Si_8O_{12}$

T/K	$T_{1\mathrm{obs}}^{-1}$/s^{-1}	$\mathrm{NOE_{obs}}$	$T_{1\mathrm{DD}}^{-1}$/s^{-1}	τ_c^{eff}/ps
303	0.038	−2.52	0.038	18 ± 3
323	0.033	−2.38	0.031	15 ± 3

Table 2 Relaxation data for ^{17}O in $H_8Si_8O_{12}$

T/K	Linewidth/Hz	T_2^{-1}/s^{-1}	Quadrupole coupling constant/MHz
303	133	420	4.9 ± 0.7
323	102	320	4.8 ± 0.7

The oxygen-17 NMR signal of $H_8Si_8O_{12}$ is a single, fairly broad line. The linewidths and derived quantities are shown in Table 2. Under extreme-narrowing conditions the $I = \frac{5}{2}$ oxygen-17 nuclei relax exponentially with the spin–lattice relaxation rate equal to the spin–spin relaxation rate, given by equation (3).[12,13] The relaxation rate is determined by a dynamic

$$T_{2Q}^{-1} = \frac{3\pi^2}{10}\left[\frac{2I+3}{I^2(2I-1)}\right]\left(1+\frac{\varepsilon^2}{3}\right)\left(\frac{e^2qQ}{h}\right)^2 \tau_c^{\mathrm{eff}} \qquad (3)$$

property, the effective rotational correlation time τ_c^{eff}, and the two static, structure-related molecular properties. The first of these is the quadrupole coupling constant, e^2qQ/h where Q is the nuclear electric quadrupole moment and q is the principal component of the field-gradient tensor at the site of the nucleus; the second is ε, the asymmetry parameter of the field-gradient tensor at the nuclear site. If the reorientational motion of the molecule is isotropic, a reasonable assumption for the essentially spherical $H_8Si_8O_{12}$, then the correlation times in equations (1) and (3) are identical. The correlation times from Table 1 can then be used, together with the oxygen-17 relaxation rates, to estimate the product of the square of e^2qQ/h and the factor $[1 + (\varepsilon^2/3)]$. For not-too-large asymmetry parameters the latter factor does not differ much from unity. An asymmetry parameter of about 0.2–0.3 was obtained for the oxygen-17 positioned between two silicon atoms in octamethylcyclotetrasiloxane.[3] At the level of accuracy of our determination of the rotational correlation time the correction of 1–3% due to an asymmetry parameter of this magnitude can be neglected. The oxygen quadrupole coupling constants at 30 and 50 °C are also presented in Table 2, where it can be seen that the two values agree well with each other. We therefore estimate the overall uncertainty of the determination of this parameter to be of the order of 0.5 MHz. It is noteworthy that the value for the present compound is significantly lower than those reported for octamethyl-[3] and octaphenyl-cyclotetrasiloxane[4] (6.3 and 6.2 MHz, respectively). In the octamethylcyclotetrasiloxane study it was suggested that the value should increase with increasing Si–O–Si angle. The Si–O–Si angle in $H_8Si_8O_{12}$[16] is 148.3°, compared to 142.5° in octamethylcyclotetrasiloxane,[17] so the lower value for the former compound cannot be explained by the angular change.

In conclusion, we have demonstrated that the silicon-29 relaxation in a Si–H fragment carries information on the reorientational dynamics in liquid solution. This information can be used in connection with oxygen-17 relaxation to provide structurally relevant quadrupole coupling constant data.

Acknowledgements

Thanks are due to Professor Gion Calzaferri for providing the compound. This work was supported by the Swedish Natural Science Research Council.

References

1 G. Calzaferri and R. Hoffmann, *J. Chem. Soc., Dalton Trans.*, 1991, 917.

2 M. Bärtsch, P. Bornhauser, G. Calzaferri and R. Imhof, *J. Phys. Chem.*, 1994, **98**, 2817 and refs. therein.

3 J. Kowalewski and E. Berggren, *Magn. Reson. Chem.*, 1989, **27**, 386.

4 J. Kowalewski and Z. Ali, *Acta Chem. Scand.*, 1995, **49**, 734.

5 K. M. Larsson, J. Kowalewski and U. Henriksson, *J. Magn. Reson.*, 1985, **62**, 260.

6 K. M. Larsson and J. Kowalewski, *Acta Chem. Scand., Ser. A*, 1986, **40**, 218.

7 C. Delseth and J.-P. Kintzinger, *Helv. Chim. Acta*, 1982, **65**, 2273.

8 P. A. Agaskar, *Inorg. Chem.*, 1991, **30**, 2707.

9 D. Canet, G. C. Levy and I. R. Peat, *J. Magn. Reson.*, 1975, **18**, 199.

10 J. Kowalewski, G. C. Levy, L. F. Johnson and L. Palmer, *J. Magn. Reson.*, 1977, **26**, 533.

11 J. Kowalewski, A. Ericsson and R. Vestin, *J. Magn. Reson.*, 1978, **31**, 165.

12 R. K. Harris, *Nuclear Magnetic Resonance Spectroscopy: a Physicochemical View*, Longmans, Harlow, 1986.

13 R. K. Harris and B. E. Mann, *NMR and the Periodic Table*, Academic Press, London, 1978, p. 75.

14 K. W. Törnroos, *Acta Crystallogr., Sect. C*, 1994, **50**, 1646.

15 Landolt-Börnstein, *Zahlwerten und Funktionen*, 6th edn., Springer, Berlin, 1969, vol. 5a.

16 T. P. E. Auf der Heyde, H.-B. Bürgi, H. Bürgy and K. W. Törnroos, *Chimia*, 1990, **45**, 38.

17 H. Steinfink, B. Post and I. Fankuchen, *Acta Crystallogr.*, 1955, **8**, 420.

Received 8*th November* 1995; *Paper* 5/07358H