CONTRIBUTION TO THE SEMIEMPIRICAL INTERPRETATION OF THE ANISOTROPY OF THE ^{29}Si NMR SHIELDING TENSOR IN SILICATES.

II. INFLUENCE OF CHANGES IN THE O–Si–O BOND ANGLE IN SiO_4^{4-} ION*

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The influence of variations in the OSiO bond angle α on the anisotropy of the ^{29}Si shielding tensor of the monosilicate anion SiO_4^{4-} in C_{3v} symmetry has been investigated by semiempirical CNDO/2 calculations. In the valence basis set of the silicon atom, no *d*-orbitals were employed. It could be shown that the terms characterizing the four Si–O bond contributions to $\Delta\sigma$ are of greatest importance for reproducing the experimentally observed trend of anisotropy signs in silicates. Both the increasing O(1)–Si–O(B) bond angle α, and the decreasing Si–O(1) bond length *r*(Si–O(1)) (and vice versa) exhibit an amplifying geometrical influence on $\Delta\sigma$.

In recent years, a number of ^{29}Si NMR studies were published concerned with the theoretical interpretation of the isotropic chemical shift $\delta_{iso}(^{29}Si)$ in silicate materials. Particular attention has been paid to the systematic investigation of various geometrical and substituent effects on the $\delta_{iso}(^{29}Si)$ (refs[2 – 4]). For describing the trends of these chemical shifts, semiempirical procedures of quantum chemistry were found to be well suited for the treatment even of relatively large molecular systems. However, an exact numerical reproduction of experimental chemical shifts requires a non-empirical calculation of the shielding of the considered ^{29}Si nucleus. Such non-empirical calculations have been carried out by Tossell and Lazzeretti by means of the *ab initio* "Coupled Hartree–Fock Perturbation Theory" (CHFPT)[5,6], and by Kutzelnigg and coworkers by means of the IGLO method ("Individual Gauge for Localized Orbitals")[7,8]. In their applications, these methods are limited to smaller molecular systems, as large basis sets must be used, greatly extending the computing requirements.

Besides the isotropic chemical shifts in ^{29}Si NMR, also the anisotropy of the chemical shifts has increasingly been measured[9,10], from which additional conclusions can be drawn on the respective structure and bonding type. So for example for the mono-

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* Part I, see ref.[1].

silicate component SiO_4^{4-}, partly considerable anisotropy values with opposite signs have been experimentally determined, although the corresponding isotropic chemical shifts exhibit but little difference[11]. Seeking theoretical interpretation of these pronounced anisotropies, in our first communication[1] we have studied the effect of the Si–O bond length on the shielding tensor, using semiempirical (CNDO/2) wave functions, without *d*-orbitals in the valence basis set of the Si atom. In combination with the magnetic shielding theory of Karplus and Pople[12], this semiempirical procedure provides a qualitative explanation of the connection between the geometrical structure of silicates on the one hand, and electronic quantities on the other hand, like Si netto-charges , α- or π-character of the Si–O bonds, distribution of electrons around the ^{29}Si nucleus or electronic excitation energies. These electronic quantities may affect both the isotropic chemical shifts, and the individual components of the shielding tensor in silicates.

The aim of this work is an analysis of the effect of changes in the O–Si–O bond angle on the shielding tensor and its anisotropy. In terms of the semiempirical all-valence-electron procedure CNDO/2, and of the magnetic shielding theory of Karplus and Pople[12], we tried to determine which components of the wave function strongly affect the anisotropy value and sign. The effects of the Si–O bond length (see ref.[1]) and of the O–Si–O bond angle on the tensor components and on the anisotropy were compared.

The theoretical results were compared with the experimental NMR data and with the geometrical parameters. This is rather difficult, as the various geometrical factors in real silicate structures cannot be mutually separated, and only few experimental data are presently available. The monosilicate model SiO_4^{4-}, with externally saturated four negative charges, as the smallest subunit of a silicate body, can only reflect the influence of the immediate neighbourhood of the ^{29}Si nucleus on its magnetic shielding.

The Shielding Tensor of the Monosilicate Component Unit SiO_4^{4-}

The shielding of the ^{29}Si nucleus in the SiO_4^{4-} anion by a magnetic field can mathematically be described as a tensor which can be visualized by means of an ellipsoid. The position of the SiO_4^{4-} ion of C_{3v} symmetry in the coordinate system is shown in Fig. 1, together with the orientation of the shielding tensor components with respect to the Si–O bonds. The component σ_{zz} in the *z* direction coincides with the threefold symmetry axis (along the Si–O(1) bond, and will further be designated as $\sigma_{\|}$. The shielding tensor is axially symmetric, i.e. in terms of the C_{3v} symmetry of the SiO_4^{4-} ion, the *xx* and *yy* components in the *x*/*y* plane are identical ($\sigma_{xx} = \sigma_{yy} \hat{=} \sigma_{\perp}$). The anisotropy $\Delta\sigma$ of the axially symmetrical shielding tensor then follows as

$$\Delta\sigma = \sigma_{\|} - \sigma_{\perp} . \qquad (1)$$

In the following we shall assume that the change in the diamagnetic part of the shielding constant is insignificant, and that the paramagnetic parts $\sigma_{\mathrm{para}\parallel}$ and $\sigma_{\mathrm{para}\perp}$ alone are sufficient to correctly describe the individual anisotropy components as well as the general anisotropy trend, i.e. its dependence on changes in the geometry of the unit. The effect of a change in the O–Si–O bond angle on the shielding tensor was investigated in the following way:

Starting from the ideal T_d symmetry of the SiO_4^{4-} ion, with four equivalent Si–O bonds, of length 160 pm, all three O(1)–Si–O(B) angles α were changed in the same sense in steps of 10° between 90° and 130°. In this process, all Si–O bond lengths remained unchanged. Such change in the geometry of the SiO_4^{4-} ion preserved the C_{3v} symmetry. Based on the LCAO–MO principle in ZDO approximation according to ref.[12], the paramagnetic part of the parallel component of the axially symmetric shielding tensor follows from

$$\sigma_{\mathrm{para}\parallel} = -\frac{e^2 h^2 \mu_0}{8 \pi^3 m^2} \langle r^{-3} \rangle_{3p} \, 2 \left[(\Omega_{AA})_{\parallel} + \sum_{B \neq A} (\Omega_{AB})_{\parallel} \right] \qquad (2)$$

with

$$(\Omega_{AA})_{\parallel} = \sum_{i}^{occ} \sum_{j}^{uno} (\varepsilon_j - \varepsilon_i)^{-1} \, (c_{ixA} c_{jyA} - c_{iyA} c_{jxA})^2 \qquad (3)$$

and

$$\sum_{B \neq A} (\Omega_{AB})_{\parallel} = \sum_{i}^{occ} \sum_{j}^{uno} (\varepsilon_j - \varepsilon_i)^{-1} \, (c_{ixA} c_{jyA} - c_{iyA} c_{jxA})$$

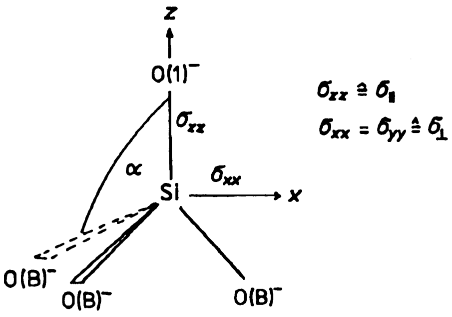

FIG. 1
Model of the monosilicate component unit SiO_4^{4-} in the coordinate system, and orientation of the tensor components with respect to Si–O bonds

$$\sum_{B \neq A} (c_{ixB}\, c_{jyB} - c_{iyB}\, c_{jxB}) \tag{4}$$

h, e, μ_0 and m are conventional universal constants. $\langle r^{-3} \rangle_{3p}$ is the expectation value of the reciprocal cubic radius of electron orbitals in the $3p$ atomic functions of the Si atom. The c_{ixA} etc. are the expansion coefficients of an LCAO–MO representation. The i and j designate the occupied and unoccupied MO's, A represents the considered Si atom and B the neighbouring oxygen atoms. The excitation energies were approximated as the difference of the molecular orbital energies ε. When all excitation energies are approximated by a common mean value ΔE, then the tensor components depend only on the elements of the charge density–bond order matrix $P_{\mu A \nu B}$ ($\hat{=}$ bonding order between the μ- or ν-th p atomic orbitals on atom A or B, respectively) of the ground state[13]. Thus the excited states need not be further considered.

In the "ΔE" approximation we have

$$\sigma_{\mathrm{parall}} = -\frac{e^2 h^2 \mu_0}{8 \pi^3 m^2} \langle r^{-3} \rangle_{3p} \, (\Delta E)^{-1} \frac{1}{2} [(Q_{AA})_{\|} + \sum_{B \neq A} (Q_{AB})_{\|}] \tag{5}$$

with

$$\frac{1}{2} (Q_{AA})_{\|} = P_{xAxA}\, P_{yAyA} - P_{xAxA}\, P_{yAyA} + P^2_{xAyA} \tag{6}$$

and

$$\frac{1}{2} (Q_{AB})_{\|} = -P_{xAxB}\, P_{yAyB} + P_{xAyB}\, P_{yAxB} \,. \tag{7}$$

By a cyclic coordinate interchange, analogous expressions are obtained for the vertical tensor component $\sigma_{\perp}$.

RESULTS AND DISCUSSION

The Effect of a Change in the O–Si–O Bond Angle on the Silicon netto Charges and the Isotropic Chemical Shifts

Any deviation from the ideal tetrahedral angle in SiO_4^{4-} at constant Si–O bond length leads to a reduction of the silicon netto charge q_{Si} (Fig. 2). Assuming that in the for alumosilicates typical range of isotropic chemical shifts $\delta(^{29}Si)$ and Si netto charges, the relation (see refs[2,3])

$$\delta_{\rm iso}(^{29}{\rm Si}) \approx -q_{\rm Si} \tag{8}$$

also holds in the considered case of changes in the O–Si–O bond angle, then any such change should lead to a low-filled shift (= reduction of $\sigma_{\rm para}$). In considerations of the substituent and bond-angle effects on the trend of the isotropic chemical shifts $\delta_{\rm iso}(^{29}{\rm Si})$ in silicates and alumosilicates[3] it was found as satisfactory and useful to apply the relative paramagnetic shielding constants $\sigma^*_{\rm para}$. Contrary to $\sigma_{\rm para}$, the relative quantity $\sigma^*_{\rm para}$ has the same sign as the chemical shift d which is defined as positive towards low field, see Eq. (9):

$$\sigma^*_{\rm para} = \frac{R^*_{3\rm p} P^*_{\rm u}}{\Delta E^*} \; . \tag{9}$$

In the investigation of the Si–O–Si bond-angle effect on the trend of isotropic chemical shifts in di- and polysilicates, the individual electronic factors affecting $\sigma^*_{\rm para}$ in terms of Eq. (9) have already been extensively discussed and compared as dimensionless relative quantities[3]. In analogy to these considerations, in this work the effect of the electronic factors $P^*_{\rm u}$, $R^*_{3\rm p}$ and $(\Delta E^*)^{-1}$ on the isotropic $\sigma^*_{\rm para}$ will be analyzed.

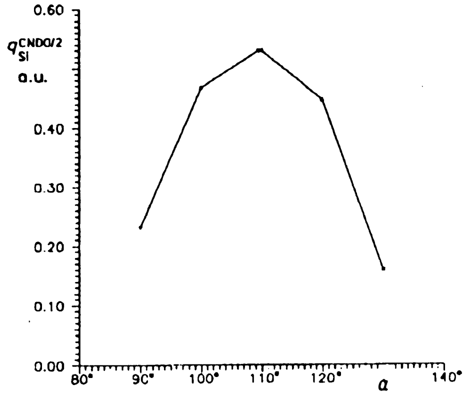

FIG. 2

Netto-charges on silicon, $q_{\rm Si}^{\rm CNDO/2}$, in a. u., in dependence on the O–Si–O bond angle α

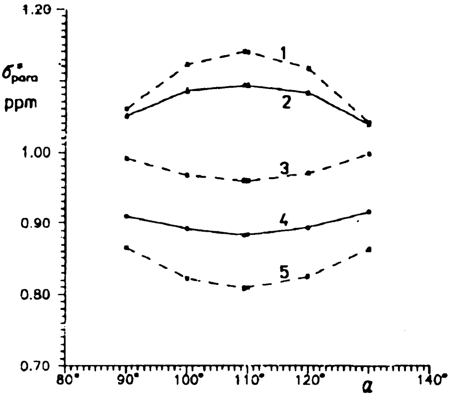

FIG. 3

Relative paramagnetic chemical shifts $\sigma^*_{\rm para}$ according to Eq. (9), and the corresponding electronic quantities $P^*_{\rm u}$, $R^*_{\rm p}$, and $(\Delta E^*)^{-1}$ in dependence on α; 1 $R^*_{3\rm p}$, 2 $\sigma^*_{\rm para}$ in "ΔE" approximation, 3 $P^*_{\rm v}$, 4 $\sigma^*_{\rm para}$ in "sum-over-states" approximation, 5 $(\Delta E^*)^{-1}$

In Fig. 3, the course of the named factors and of the resulting isotropic σ^*_{para} in the "ΔE" and "sum-over-states" approximation is shown. Only P^*_u, as a quantity describing the asymmetry of charge distribution about the nucleus reflects directly the trend of the isotropic chemical shifts with the O–Si–O bond angle, as expected from the course of the Si netto charges q_{Si} (see Fig. 2) and from the relations (*8*) and (*9*). For the factor $(\Delta E^*)^{-1}$, corresponding to the reciprocal of the electronic excitation energy, we obtain a course analogous to P^*_u. The trend of the reciprocal cubic radius of the electron orbits in the $3p$ atomic functions of the Si atom, R^*_{3p}, is uncorrected ($f = 1$, see ref.[3]), contrary to the course of P^*_u or $(\Delta E^*)^{-1}$.*

The explicit consideration of a change in the excitation energy within the "sum-over-states" approximation directly yields the expected trend of the isotropic σ^*_{para}. From Fig. 3 it can be seen that the isotropic chemical shifts are generally affected by a deformation of the tetrahedron, but a definite relation to the individual O–Si–O bond angles α in the silicate anion SiO_4^{4-} cannot be established.

The Effect of the O–Si–O Bond Angle on the Shielding Tensor

In our investigation of the effect of the Si–O bond length on the anisotropy $\Delta\sigma(^{29}Si)$ it was shown that the size and sign of $\Delta\sigma$ is determined by the contributions of the Si–O bonds[1]. Therefore in the discussion of the effect of the O–Si–O bond angle α on $\Delta\sigma(^{29}Si)$, the contributions $\Delta(\Omega_{AA})$ and $\Delta(Q_{AA})$, localized directly on the Si atom, and the Si–O bond contributions $\Delta(\Omega_{AB})$ and $\Delta(Q_{AB})$ will be considered separately, see Eqs (*10*) and (*11*):

$$\Delta(\Omega_{AA}) = [(\Omega_{AA})_{\parallel} - (\Omega_{AA})_{\perp}] , \qquad (10)$$

$$\Delta(\Omega_{AB}) = [\sum_{B \neq A} (\Omega_{AB})_{\parallel} - \sum_{B \neq A} (\Omega_{AB})_{\perp}] . \qquad (11)$$

The expressions for the Q terms in the "ΔE" approximation are analogous. According to Eqs (*1*) to (*7*), the anisotropy of an axially symmetric shielding tensor should be proportional to the following negative differences:

$$\Delta\sigma \approx -\Delta(\Omega_{AA}) \qquad \text{or} \qquad \Delta\sigma \approx -\Delta(Q_{AA}) \qquad (12)$$

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* The unrealistic trend of σ^*_{para} in the "ΔE" approximation (ΔE = const = 1) could be corrected by a suitable choice of the so called adjustment factor $f < 1$ in R^*. In such case the f factor would first of all correct the assumption underlying the "ΔE" approximation, namely that the electronic excitation energies do not change from molecule to molecule.

and

$$\Delta\sigma \approx -\Delta(\Omega_{AB}) \qquad \text{or} \qquad \Delta\sigma \approx -\Delta(Q_{AB})\,. \tag{13}$$

The results of the "ΔE" and "sum-over-states" approximation are visualized in Figs 4 and 5. In both representations it is evident that although the (AB) terms are numerically smaller than the local (AA) terms, the splitting of the perpendicular and parallel components and their contribution to the $\Delta\sigma$ anisotropy is considerable. While the splitting of the (Q_{AA}) term in the "ΔE" approximation is small, it does not differ considerably from the (Ω_{AB}) term in the "sum-over-states" approximation. As in ref.[1] the effect of the (Ω_{AB}) term was found as determining for the size of $\Delta\sigma$, we assume that the (Ω_{AA}) term (see Fig. 5) might be somewhat overstated owing to the use of uncorrected excitation energies in the "sum-over-states" approximation.

No simple correlation between the parallel and perpendicular components of the (Ω) and (Q) quantities and the O–Si–O bond angles α could be detected. The course of the $(Q_{AB})_\perp$ is evidently determined by the change in the σ bond order of the Si–O(1) bond, $P_{z\mathrm{Si}z\mathrm{O(1)}}$ (Fig. 6). The π bond orders of the Si–O(1) bond, $P_{x\mathrm{Si}x\mathrm{O(1)}}$ (or $P_{y\mathrm{Si}y\mathrm{O(1)}}$) do not significantly change, indicating that the $(p\text{–}p)_\pi$ character of this bond, established in ref.[1], is hardly affected by changes in the O–Si–O bond angles. Therefore the trend of

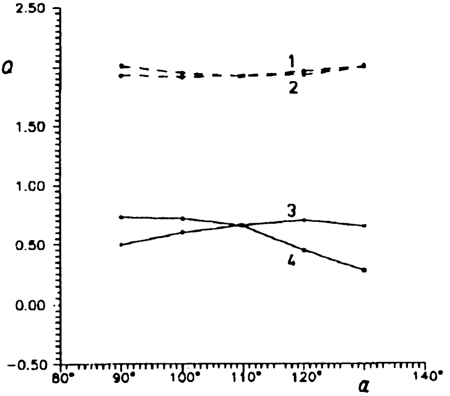

FIG. 4

Parallel and perpendicular components of (Q_{AA}) and $\sum_{B\neq A}(Q_{AB})$ terms of the "ΔE" approximation in dependence on the bond angle α, according to Eqs (6) and (7): 1 $(Q_{AA})_\parallel$, 2 $(Q_{AA})_\perp$, 3 $\sum_{B\neq A}(Q_{AB})_\perp$, 4 $\sum_{B\neq A}(Q_{AB})_\parallel$

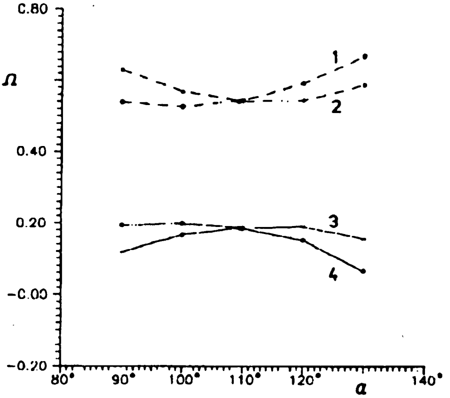

FIG. 5

Dependence of the (Ω) terms in the "sum-over-states" approximation according to Eqs (3) and (4), corresponding to Fig. 4 (smaller values correspond to stronger shielding of the resonating nucleus): 1 $(\Omega_{AA})_\parallel$, 2 $(\Omega_{AA})_\perp$, 3 $\sum_{B\neq A}(\Omega_{AB})_\perp$, 4 $\sum_{B\neq A}(\Omega_{AB})_\parallel$

$(Q_{AB})_{||}$ (see Eq.(*7*)) must be caused by the elements of the charge density–bond order matrix corresponding to the three Si–O(B) bonds (see Fig. 1).

In order to test the relevance of the presented results, and thus the suitability of the SiO_4^{4-} model for a semiempirical interpretation of the magnetic shielding of the ^{29}Si nucleus in silicate solids, some analogous calculations have also been carried out for the ortho-silicic acid model. Concerning the trend of the parallel and perpendicular components of the (Ω_{AA}) and (Ω_{AB}) quantities and the corresponding anisotropies in terms of Eqs (*10*) and (*11*), the results obtained for the monosilicate anion with four negative charges were confirmed. Thus for example an enhancement of the three bond angles α from 109.47° to 120° yields 0.048 and 0.027 for the $\Delta(\Omega_{AA})$ terms, and −0.038 and −0.046 for the $\Delta(\Omega_{AB})$ terms in the SiO_4^{4-} ion and in $Si(OH)_4$, respectively.*

Calculated and Experimental Relation between the O–Si–O Bond Angle α and the Anisotropy $\Delta\sigma(^{29}Si)$

In order to predict which of the calculated terms makes the most important contribution to the anisotropy, and to obtain a better theoretical understanding of the calculated quantities, it is useful to make a comparison with the experimental findings for the monosilicate component unit SiO_4^{4-}.

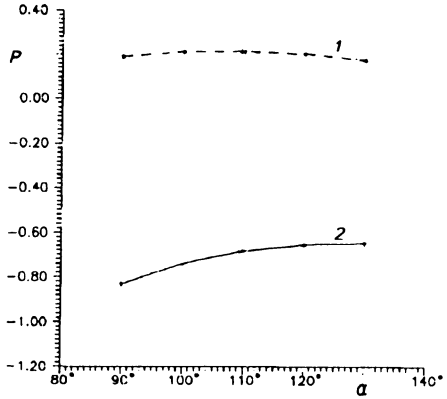

FIG. 6
Bond orders of the Si–O(1) bond in dependence on α: *1* π bond orders $P_{xSixO(1)}$ (= $P_{ySiyO(1)}$); *2* σ bond orders $P_{zSizO(1)}$

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* It is found that also for the change in the Si–O(1) bond length, the results for orthosilicic acid and those presented in ref.[1] for the monosilicate anion are analogous. The $\Delta(\Omega_{AA})$ and $\Delta(\Omega_{AB})$ terms agree in their sign trend and are also of similar size for the same change in bond length. As example let us present the results for an extension of $r_{Si-O(1)}$ from 160 to 164 pm: for SiO_4^{4-} and Si(OH), respectively, the corresponding values are $\Delta(\Omega_{AA})$ −0.0031 and −0.0035; $\Delta(\Omega_{AB})$ 0.0044 and 0.0036.

The experimental geometric and shielding data for tetramethylammonium silicate (TMAS) and for tricalcium silicate hydrate (TCSH) are summarized in Table I (ref.[10]). The paramagnetic parts of the shielding tensor components were calculated by means of Eq. (2). In comparison with the experimental values, $\sigma_{para\|}$ and $\sigma_{para\perp}$ are negative, nevertheless their change with geometry should correspond to the change in the experimental values of $\sigma_{\|}$ and $\sigma_{\perp}$ (see Tables I and II). The calculated values of $\sigma_{\|}$, $\sigma_{\perp}$ and $\Delta\sigma$ can be qualitatively referred to the experimental values of TMAS and TCSH, when only the $\sum_{B\neq A}(\Omega_{AB})$ term in Eq. (2) is taken into account in the calculation. As already indicated by the course of the (Ω_{AB}) components (see Fig. 5), a reduction of the three O–Si–O angles α to 100° or 90° leads to an enhancement of the shielding of the ^{29}Si nucleus perpendicular to the threefold axis with respect to the shielding of the resonating nucleus parallel to this axis (this means negative anisotropy values $\Delta\sigma_{calc}$). This type of angular geometry corresponds to that in TCSH, for which a negative anisotropy equal to –74 ppm has been experimentally determined (see Table I).

On the other hand, an opening of the O–Si–O angle α leads to a greater enhancement of the parallel tensor component $\sigma_{para\|}$ with respect to $\sigma_{para\perp}$, and thus to a positive anisotropy $\Delta\sigma_{(calc)}$, and this can be compared to the situation in TMAS (Table I).

Contrary to this, the quantities calculated from the local $(\Omega_{AA})_{\|(\perp)}$ components do not reproduce the experimentally found signs (Table II). Thus the shielding of the ^{29}Si nucleus is only correctly described by the parts of the molecular wave function that characterize the four bonds to the neighbouring O-atoms.

The Relation Between the O–Si–O Bond Angles, the Si–O Bond Lengths and the Anisotropy $\Delta\sigma(^{29}Si)$

In real silicate structures with the tetraedric monosilicate component unit SiO_4^{4-}, the O–Si–O bond angles vary between about 101° and 117°. The Si–O bond lengths lie between 155 and 169 pm (ref.[14]). From the results of semiempirical EHT–MO calculations of the SiO_4^{4-} ion[15] it is known that in the tetraedric unit the larger O–Si–O angles are enclosed by the shorter Si–O bonds, and the smaller O–Si–O angles by the

TABLE I
Experimental data on the geometry (r, pm) and NMR spectra (σ, ppm) of tricalciumsilicon hydrate (TCSH) and tetramethylammonium silicate (TMAS)

	α, °	$r_{Si-O(1)}$[a]	$r_{Si-O(B)}$[a]	$\sigma_{\|}$	$\sigma_{\perp}$	Δσ	$\sigma_{(iso)}$
TCSH[b]	104	167	161	35	109	–74	84
TMAS[c]	111	157	160	152	73	+78	99

[a] Ref.[10]; [b] structural data on the structurally analogous hemimorphite[19]; [c] structural data from ref.[18].

longer Si–O bonds. Experimentally observed steric details in various silicates (e.g. pyrosilicate in $Ba_3Si_4Nb_6O_{26}$ (ref.[16]), benitoit[17], TMAS[18] and hemimorphit[19]) confirm these results.

This experimentally and semiempirically proved connection between OSiO bond angles and Si–O bond lengths within the monosilicate component unit SiO_4^{4-} will in the following be related to the geometric factors discussed in ref.[1] and in this work as affecting the anisotropy $\Delta\sigma$ of the shielding tensor.

In Fig. 7 is shown the dependence of the anisotropy $\Delta\sigma_{(calc)}$ on the change in $r_{Si-O(1)}$ and <O(1)–Si–O(B) (see ref.[1]). $\Delta\sigma$ is evidently affected in the same direction by an opening of the three bond angles α and reduction of the Si–O(1) bond length, and vice versa. Assuming that these variations are linear in the whole considered angular and length range, we can quantitatively estimate and compare the effect of both these geometric factors on $\Delta\sigma(^{29}Si)$.

A linear regression analysis yields for the dependence of $\Delta\sigma$ (in ppm) on the Si–O(1) bond length (with constant O–Si–O angles)

$$\Delta\sigma^{+}_{(calc)} = +7.745 - 4.821 \cdot 10^{-2}\, r_{Si-O(1)} \quad [pm] \qquad (14)$$

and for the dependence on the O(1)–Si–O(B) angle (at constant bond lengths)

TABLE II

Calculated tensor components $\sigma_{para\|}$ and $\sigma_{para\perp}$, anisotropies $\Delta\sigma_{(calc)}$ and chemical shifts $\sigma_{(iso)}$ (all in ppm) in SiO_4^{4-} ; all Si–O bonds 160 pm long

α, °	$\sigma_{para\|}$	$\sigma_{para\perp}$	$\Delta\sigma_{(calc)}$	$\sigma_{(iso)}$ [a]
90	-7.74[b]	-4.65[b]	-3.09	-5.68
	-21.39[c]	-25.06[c]	+3.67	-23.84
100	-8.38[b]	-6.99[b]	-1.39	-7.45
	-22.19[c]	-23.96[c]	+1.77	-23.37
109.47	-7.94[b]	-7.94[b]	0	-7.94
	-23.18[c]	-23.18[c]	0	-23.18
110	-7.86[b]	-7.95[b]	+0.09	-7.92
	-23.26[c]	-23.15[c]	-0.11	-23.19
120	-6.35[b]	-7.96[b]	+1.61	-7.42
	-24.79[c]	-22.76[c]	-2.03	-23.44
130	-2.53[b]	-6.09[b]	+3.56	-4.90
	-26.17[c]	-22.95[c]	-3.22	-24.02

[a] $\sigma_{(iso)} = 1/3(\sigma_{\|} + 2\,\sigma_{\perp})$; [b] $\sigma_{para\|(\perp)}$ from ref.[2], only (Ω_{AB}) terms considered; [c] $\sigma_{para\|(\perp)}$ from ref.[2], only local (Ω_{AA}) terms considered.

$$\Delta\sigma^{++}_{(calc)} = -17.79 + 1.63 \,.\, 10^{-1}\alpha \quad [°] \,. \qquad (15)$$

From these equations it follows, for example, that a shortening of the Si–O(1) bond by ca 2 pm (from 160 to 158 pm), or an opening of the three bond angles α by ca 0.6° each (starting from the ideal tetrahedral angles), quite independently cause $\Delta\sigma_{(calc)}$ to increase from zero to about +0.1 ppm.

Besides the found qualitative agreement of the sign trend, and of the calculated and experimental anisotropies (vide supra) we have also tested whether there exists a semi-quantitative relation between the two quantities. Based on Eqs (*14*) and (*15*), theoretical $\Delta\sigma_{(calc)}$ were calculated for various real silicates. The necessary Si–O(1) bond lengths and O–Si–O bond angles were taken from the literature[18,19,20 – 25]. All results and geometric data are summarized in Table III. The correlation of the sum of the calculated anisotropies $\Delta\sigma^{+}_{(calc)}$ and $\Delta\sigma^{++}_{(calc)}$ with the corresponding experimental $\Delta\sigma_{(exp)}$ (refs[9 – 11,26]) is shown in Fig. 8. In spite of the great difference in the absolute values of the two quantities, the calculated anisotropies reproduce well the experimental sign trend. Considering that the anisotropies $\Delta\sigma_{(calc)}$ have been calculated on the assumption that

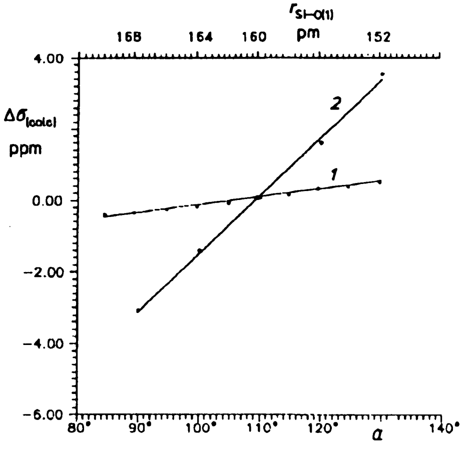

FIG. 7

Anisotropies $\Delta\sigma_{(calc)}$ calculated by means of Eqs (*2*) and (*1*), in dependence on $r_{Si-O(1)}$ (*1*) (see ref.[1]), and on O–Si–O angle α (*2*) (in Eq. (*2*) the (Ω_{AA}) terms were not included)

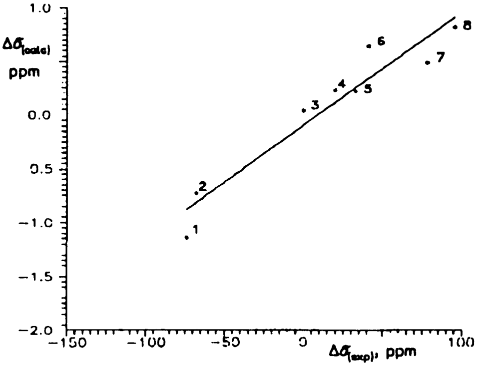

FIG. 8

Correlation of experimental anisotropies $\Delta\sigma_{(exp)}$ (refs[9 – 11,26]) with the corresponding $\Delta\sigma_{(calc)}$ values calculated by means of Eqs (*14*) to (*16*) (for numbering see Table III). Linear regression analysis yields:

$\Delta\sigma_{(calc)} = -9.82 \,.\, 10^{-2} + 1.05 \,.\, 10^{-2}\, \Delta\sigma_{(exp)}$ [pm] (*17*)

with maximum and minimum deviation 0.0305 and 0.208 ppm, respectively the remaining geometric parameters remain constant in each case (r_{Si-O} = 160 pm, or <O–S–O = 109.47°), then the correlation with $\Delta\sigma_{(exp)}$ is satisfactory, as such ideal geometric relations do not actually occur in the real silicate component units SiO_4^{4-} (see Table III).

CONCLUSIONS

The results of ref.[1] and of the present work indicate that a detailed understanding of the trends in the magnetic shielding of the ^{29}Si nucleus in silicate solids may serve as an additional source of information on the structure of the silicate and on the character of the respective bonds.

In the representation of the electron distribution in semiempirical (CNDO/2) wave functions, the experimental trend of the tensor components of the anisotropy $\Delta\sigma$ in dependence on the O–Si–O bond angle is qualitatively reproduced. The experimental finding[11] that silicates with the monosilicate component unit SiO_4^{4-} exhibit very diffe-

TABLE III
Variation with geometry (r in pm; α in °) of $\Delta\sigma_{(calc)}$ (in ppm), calculated for real silicate structures by means of Eqs (*14*) and (*15*)

No.	Silicate	$r_{Si-O(1)}$	$r_{Si-O(B)}$	$\Delta\sigma^{+}_{(calc)}$	α, °	$\Delta\sigma^{++}_{(calc)}$	$\Delta\sigma_{(calc)}$[a]
1	$Ca_6[Si_2O_7/(OH)]_6$ (TCSH, ref.[19])	167	161	-0.306	104	-0.835	-1.141
2	$Ca_3Si_2O_7$[b] (Rankinite, ref.[20])	166.7	160.5	-0.291	106.5	-0.439	-0.73
3	SiO_2 (T-Quartz, ref.[21])	160.9	160.9	-0.012	109.4	0.045	+0.033
4	β-Ca_2SiO_4[b] (β-Dicalciumsilicate, ref.[22])	161	164	-0.017	110.6	0.241	+0.224
5	$[(CH_3)_3Si]_8Si_8O_{20}$ (Q_8M_8, ref.[23])	158.8	160	0.089	109.9	0.124	+0.213
6	$Ca_5(OH)_2(SiO)_2$ (Calcio-Chondrodite, ref.[24])	162	164.7	-0.065	113.4	0.702	+0.637
7	$[N(CH_3)_4]_8Si_8O_{20} \cdot 69H_2O$ (TMAS, ref.[18])	157	160	0.181	111	0.306	+0.487
8	$Ba_2[Si_2O_6]$[b] (Sanbornite, ref.[25])	156.1	163.1	0.219	112.8	0.599	+0.818

[a] $\Delta\sigma_{(calc)} = \Delta\sigma^{+}_{(calc)} + \Delta\sigma^{++}_{(calc)}$ (*16*); [b] small deviations from C_{3v} point symmetry.

rent shift anisotropies, together with almost equal isotropic chemical shifts, becomes theoretically understandable on the basis of the discussed dependence of the molecular wave function and shielding tensor on geometric factors. Our results show that the components of the axially symmetric shielding tensor are to a different degree affected by the individual changes in the O–Si–O bond angles. Thus an opening of the three bond angles α leads to a greater enhancement of the component $\sigma_{\parallel}$ (parallel to the threefold symmetry axis), as compared to the perpendicular component $\sigma_{\perp}$, i.e. the resulting anisotropy is positive (and vice versa). At the same time it was found that the (Ω_{AB}) and (Q_{AB}) terms characterizing the contribution of the four Si–O bonds to $\Delta\sigma$ are determining for the reproduction of the experimental trend of the anisotropy sign.

From the independent calculations concerning the effect of Si–O bond lengths and O–Si–O bond angles on $\Delta\sigma(^{29}Si)$ it can be concluded that the two mutually coupled geometric factors synergistically affect $\Delta\sigma$. According to Eq. (*17*), a change of 10 ppm in experimental anisotropy corresponds to a calculated value of about 0.1 ppm (see Fig. 8). The influence on $\Delta\sigma$ of a change in the O–Si–O bond angle is usually at least twice larger than the effect of the simultaneously changing Si–O(1) bond length (see in Table III $\Delta\sigma^{+}$ and $\Delta\sigma^{++}$). This means that for example an enhancement of $\Delta\sigma_{(exp)}$ by ca 10 ppm would be caused by an opening of the three bond angles α by 0.4° each, and by a shortening of $r_{Si-O(1)}$ by ca 0.65 pm within the monosilicate component unit.

These results demonstrate that from a knowledge of the tensor components and their anisotropy, it is possible to recognize small deviations from ideal tetrahedral symmetry, i.e. to draw a relation to the individual Si–O bond lengths, O–Si–O bond angles and character of the Si–O bond in the SiO_4^{4-} ion.

The aim of further calculations of magnetic shielding of the ^{29}Si nucleus in silicate solids therefore should be a systematic study of various geometric effects on the shielding tensor by means of non-empirical methods. As indicated by CHFPT and IGLO calculations of the shielding tensor in inorganic Si compounds for some selected geometries[5 - 8], it might then be possible to obtain a good quantitative reproduction of the measured tensor components and anisotropies. For the interpretation of shielding tensors and anisotropies, the IGLO method seems to be of advantage. As the chemical shifts σ are obtained as a sum of contributions of localized orbitals, conclusions concerning the individual MO contributions to the anisotropy $\Delta\sigma(^{29}Si)$ can be directly drawn and compared with the results of semiempirical (CNDO/2) calculations discussed in ref.[1]. Our own *ab initio* calculations by means of the IGLO method investigating various geometric effects on the ^{29}Si shielding tensor are in preparation.

In connection with the discussed studies on silicates, a study of the influence of geometric changes on the shielding tensor of ^{31}P in solid phoshates would be of interest. Recently by means of a simple tensor model, the experimentally observed dependence of the tensor components of the ^{31}P shielding tensor on the P–O bond length was related by Olivieri[27] to differences in (P–O) bond orders. An analysis of the influence of P–O bond lengths on the ^{31}P shielding tensor might, in analogy to the influence of Si–O bond length on the magnetic shielding tensor in silicates, as discussed in ref.[1], bring information also on the nature of the P–O bond, i.e. on the relevant orbitals.

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