J. Am. Chem. Soc. 1986, 108, 192-195

^{33}S Quadrupole Coupling Tensor of Sulfolane

B. H. Ruessink, W. J. van der Meer, and C. MacLean*

Contribution from the Department of Physical Chemistry, Free University, 1081 HV Amsterdam, The Netherlands. *Received July 11, 1985*

Abstract: The ^{33}S quadrupole coupling tensor components in sulfolane are measured from the NMR spectrum of the dielectrically aligned liquid and from spin-lattice relaxation (T_1) measurements. The assignment of the principal tensor components to molecular axes follows straightforwardly from the NMR experiments for one of the components. The other two are assigned on the basis of Hartree-Fock-Slater MO calculations. The major principal ^{33}S quadrupole coupling tensor component is +1.34 MHz and is found perpendicular to the five-membered molecular ring; the one of intermediate magnitude (-1.05 MHz) is along the C_2 molecular symmetry axis. From the T_1 measurements, the molecular reorientation is found to be essentially isotropic. Decoupling experiments indicate that the $^2J(^{33}S-^1H)$ scalar-coupling constant is 4-5 Hz.

Tetrahydrothiophene 1,1-dioxide (trivially called sulfolane) is a dipolar aprotic solvent which is frequently used in both pure and applied chemistry. Striking properties of sulfolane are its high polarity (dipole moment ~16.2 × 10^{-30} cm), its high dielectric constant (ϵ ~40), and its low autoprotolysis constant (pK_s ~25.5). Important applications of the solvent are found in extraction processes in the petrochemical industry. The properties and applications of sulfolane have been comprehensively reviewed by Martinmaa.[1] For completeness, the structural formula of sulfolane is represented in Figure 1.

Nuclear magnetic resonance studies of sulfolane are scarce and have predominantly dealt with carbon-13,[2,3] hydrogen,[4] and deuterium.[5] NMR relaxation investigations have also been undertaken for sulfolane in the plastic crystalline phase just below the melting point. Oxygen-17 NMR, generally not observed easily (the nucleus has a small magnetogyric ratio, a low natural abundance, and fast quadrupolar relaxation), has, nevertheless, been reported for sulfolane.[6] Neither is sulfur-33 a favorable nucleus for NMR, for the same reasons as oxygen-17. In spite of this, ^{33}S NMR of sulfolane and other sulfones has been reported a few years ago,[7,8] and chemical shifts, line widths, and substituent effects[9] were tabulated. Very recently the first ^{33}S T_1 study on sulfolane as a function of solvent and temperature appeared.[10]

As ^{33}S is a quadrupolar nucleus (I = 3/2), its T_1 is dominated by quadrupolar relaxation, i.e., the modulation of the interaction between the nuclear quadrupole moment and the electric field-gradient at the nucleus. It is, therefore, of interest to obtain information about the quadrupole coupling tensor (QCT), describing this interaction. To this end, we investigated the ^{33}S NMR spectrum of liquid sulfolane, aligned by a strong electric field (EF NMR). The results, together with ^{2}H and ^{33}S relaxation measurements, are now reported.

Experimental Section

Sulfolane (Fluka A. G.) was destilled just before use. To obtain the EF NMR sample, it was mixed with 20% volume of sulfolane-d_8 (Merck, Sharp, and Dohme, used without further purification) and 10% volume of benzene. The latter was added to ensure a liquid sample at ambient probe temperature. All NMR experiments were performed with a Bruker WM 250 spectrometer, operating (in quadrature detection) at 38.4 MHz for ^{2}H and at 19.2 MHz for ^{33}S, with a 15-mm broad-band tunable probehead. Apart from the actual dimensions, the EF NMR sample-cell was of the same design as described before,[11] as is the case for the high voltage equipment. The electrode distance was 3.0 mm.

The ^{33}S EF NMR spectrum was recorded under proton decoupling, sampling the free induction decay (fid) following a 90° pulse (190 μs) for 0.1 s and storing it in 1K data points. The preacquisition delay was 50 μs, and no recycle delay was used. In total 400 000 scans were accumulated. Before Fourier transformation, the fid was weighted by a Lorentz-Gauss function (maximum at 15% of the fid, with a line broadening of -10 Hz) and was zero-filled to a digital resolution of 1.2 Hz/pt. The acoustic ringing, though hardly present, could be removed by deleting the first few data points of the fid. The ^{2}H EF NMR spectrum was obtained by accumulating 300 fids for 2.7 s each after a 60 μs 90° pulse, and subsequent storage was in 4K data points. The preacquisition delay was half the dwell time. The fid was weighted by a Lorentz-Gauss function (having its maximum at 10% of the fid, with a line broadening of -4 Hz) and zero-filled to a digital resolution of 0.18 Hz/pt. The T_1 relaxation times were measured by the inversion recovery pulse sequence, with pure sulfolane-d_8 sealed in a 5-mm o.d. tube.

Theory

A strong external electric field will partially orient a polar molecule by interaction with the permanent molecular dipole moment. In principle, the interaction of the electric field is with the anisotropic molecular polarizability, but in the case of small, strongly polar molecules like sulfolane, the orientation by the permanent dipole is the dominant mechanism.[11] The effect of the partial orientation may become apparent in the NMR spectra through anisotropic spin interactions. For quadrupolar nuclei (e.g., ^{2}H and ^{33}S) the Hamiltonian describing the anisotropic interaction between the nuclear quadrupole moment and the electric field gradient at the nucleus, treated as a first-order perturbation to the Zeeman energy, is [12]

$$\mathcal{H}_Q = \frac{3}{2}\,\frac{eQ}{6I(2I-1)}V_{z'z'}[3I^2_{z'} - I^2] \qquad (1)$$

eQ is the nuclear quadrupole moment, I the nuclear spin quantum number, $I_{z'}$ the component of the nuclear spin along the magnetic field direction (z'), and $V_{z'z'}$ the electric field gradient along the z' axis. The latter term may also be expressed in terms of gradients in a molecular frame of reference (x,y,z). In the present case, the orientation mechanism leads to a simple expression[11]

$$V_{z'z'} = \left\langle \frac{3}{2}\cos^2\theta_{z'z} - \frac{1}{2}\right\rangle_E V_{zz} \qquad (2)$$

---

[1] Martinmaa, J. "The Chemistry of Nonaqueous Solvents"; Academic Press: New York, 1979; Vol. IV, pp 247-287.

[2] Barbarella, G.; Dembech, P.; Garbesi, A.; Fava, A. *Org. Magn. Reson.* **1976**, *8*, 108-114.

[3] Fawkett, A. H.; Ivin, K. J.; Stewart, C. D. *Org. Magn. Reson.* **1978**, *11*, 360-369.

[4] Biscarini, P. et al. *Boll. Sci. Fac. Chim. Ind. Bologna* **1963**, *21*, 169. Strom, E. T. et al. *J. Org. Chem.* **1968**, *33*, 2555-2557. Kydon, D. W.; Sharp, A. R.; Hale, M. E.; Watton, A. *J. Chem. Phys.* **1980**, *72*, 6153-6157.

[5] Peemoeller, H.; Sharp, A. R.; Watton, A.; Kydon, D. W. *J. Chem. Phys.* **1983**, *78*, 4337-4340.

[6] Block, E. et al. *J. Org. Chem.* **1980**, *45*, 4807-4810.

[7] Faure, R.; Vincent, E. J.; Ruiz, J. M.; Lēna, L. *Org. Magn. Reson.* **1981**, *15*, 401-403.

[8] Harris, D. L.; Evans, S. A. *J. Org. Chem.* **1982**, *47*, 3355-3358.

[9] Cassidei, L.; Fiandanese, V.; Sciacovelli, O. *Org. Magn. Reson.* **1984**, *22*, 486-487.

[10] (a) Hinton, J. F. *J. Magn. Reson.* **1984**, *59*, 469-473. (b) Belton, P. S.; Cox, I. J.; Harris, R. K. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 63-75.

[11] Van Zijl, P. C. M.; Ruessink, B. H.; Bulthuis, J.; MacLean, C. *Acc. Chem. Res.* **1984**, *17*, 172-180.

[12] Slichter, C. P. "Principles of Magnetic Resonance"; Springer: Berlin, 1980.

0002-7863/86/1508-0192$01.50/0

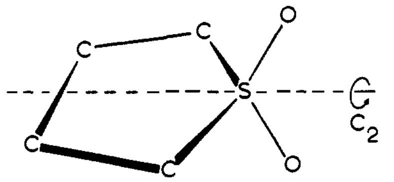

Figure 1. The structural formula of sulfolane. The protons attached to carbon are omitted for clarity.

V_{zz} is the electric field gradient along the molecular dipole moment and $\langle {}^3/_2 \cos\theta - {}^1/_2\rangle_E$ is the socalled alignment, with $\theta_{z'z}$ the instantaneous angle between dipole moment and magnetic field, the brackets indicating averaging over the molecular tumbling in the liquid. The quadrupole interaction leads to line-splittings in the NMR spectrum. For parallel electric and magnetic fields, the frequency difference between adjacent lines of the (in total) $2I$ lines is (in Hz)

$$\Delta\nu = \frac{3}{2I(2I-1)}\frac{eQV_{zz}}{h}\left\langle\frac{3}{2}\cos^2\theta_{z'z} - \frac{1}{2}\right\rangle_E \quad (3)$$

As can be seen from this equation, the ratio of line-splittings for ^{33}S and ^{2}H is related to the ratio of the corresponding eQ/hV_{zz} terms. Fortunately, of these terms the one for deuterium is often known. Taking the asymmetry parameter (η) of the electric field gradient zero (a good approximation for deuterons[13]), $(eQ/h)V_{zz}$ can be calculated from

$$(eQ/h)V_{zz} = \left(\frac{3}{2}\cos\alpha_{zz''} - \frac{1}{2}\right)\frac{eQ}{h}V_{z''z''} \quad (4)$$

$\alpha_{zz''}$ is the angle between the dipole moment and the z'' axis, $(eQ/h)V_{z''z''}$ is the major principal component of the quadrupole coupling tensor, commonly called the quadrupole coupling constant (QCC) and found along the C–^{2}H bond. If the ^{2}H QCC and $\alpha_{zz''}$ are known, the ratios of ^{2}H and ^{33}S line-splittings and of the terms in I (eq 4) permit the calculation of $(eQ/h)V_{zz}$ for the sulfur atom.

Additional information about the ^{33}S QCT can in principle be obtained from spin–lattice relaxation time measurements. For quadrupolar nuclei T_1 generally is dominated by quadrupolar relaxation. The relaxation rate may then be written as[14a]

$$\frac{1}{T_1} = \frac{1}{T_{1Q}} = \frac{12\pi^2(2I+3)}{40I^2(2I-1)}\left(1 + \frac{\eta^2}{3}\right)\left(\frac{eQ}{h}V_{z''z''}\right)^2\tau_c \quad (5)$$

η is the asymmetry parameter of the electric field gradient tensor ($\eta = (V_{x''x''} - V_{y''y''})/V_{z''z''}$) and τ_c the correlation time for isotropic molecular tumbling. Again, the deuterium QCC and η are known, and the ^{33}S QCC can be calculated from the ratio of relaxation times, if $\eta(^{33}\text{S})$ is known, and isotropic molecular tumbling is taking place. Extreme values for η are 0 and 1, making the term $(1 + \eta^2/3)^{-1/2}$ contribute factors 1.00 and 0.87 respectively to $(eQ/h)V_{z''z''}$. Consequently, a fair indication of the ^{33}S QCC is obtained. To check whether the tumbling in liquid sulfolane is indeed isotropic, the temperature dependence of the ^{2}H and ^{33}S T_1's was measured, and activation energies for the reorientation were calculated from an Arrhenius plot. Isotropic tumbling should lead to the same activation energy for deuterium and sulfur reorientation.

Results and Discussion

The ^{2}H and ^{33}S EF NMR spectra recorded at an electric field of 8.3×10^6 V m^{-1} are shown in Figure 2. The outer lines of the ^{33}S triplet are broader than the central transition. This effect is real and can be understood by evaluating the Redfield expression for quadrupolar relaxation.[14b] The quadrupolar line-splittings are 17.8 ± 0.2 and 73.9 ± 1.2 Hz for the α-deuteron and sulfur, respectively. No splitting is observed for the β-deuteron, reflecting the unfavorable orientation of the C–^{2}H$_\beta$ bond with respect to the molecular dipole moment. The ^{33}S spectrum was recorded under broad-band proton decoupling, thus removing the line-broadening caused by the $^2J(^1\text{H}–^{33}\text{S})$ scalar coupling. From the broadening, which was noticed before by Hinton,[10a] the indirect coupling was estimated to be 4.5 Hz. This observation is in good agreement with the directly measured value of 6 Hz in a closely related compound.[10b]

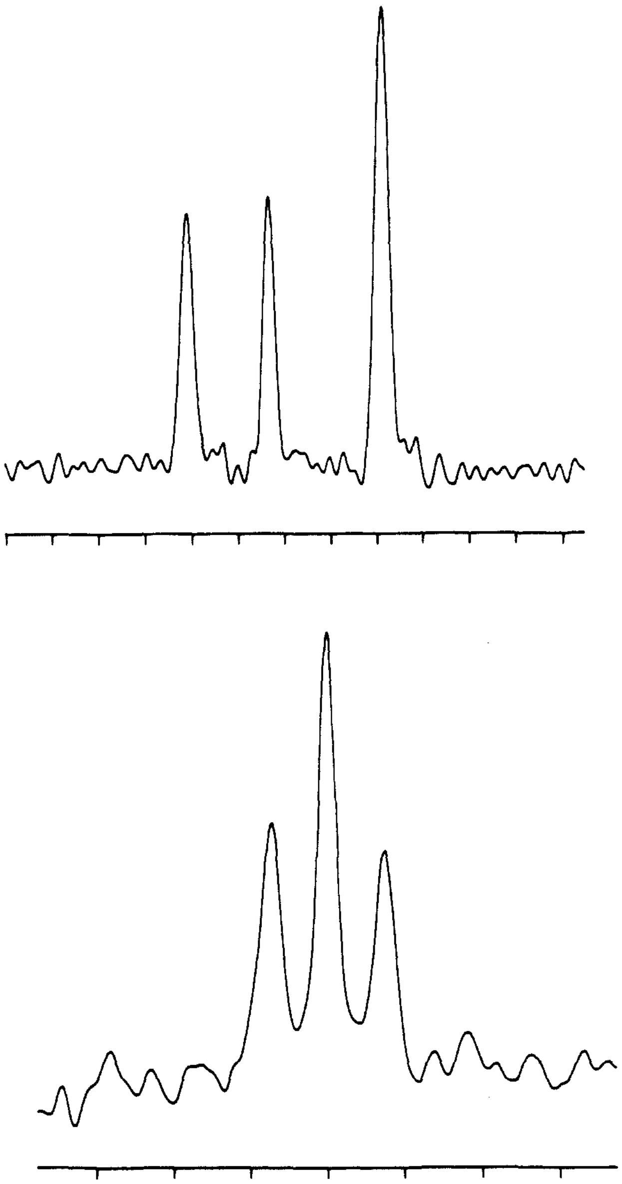

Figure 2. EF NMR spectra of sulfolane, obtained with an applied electric field of 8.3×10^6 V m^{-1}. Top trace: ^{2}H spectrum (10 Hz div^{-1}); bottom: ^{33}S spectrum (100 Hz div^{-1}). The frequency decreases from left to right in the spectra.

To calculate $(eQ/h)V_{zz}$ for sulfur, $\alpha_{zz''}$ (eq 4) and, hence, the molecular structure should be known. There has been disagreement in the literature about the structure of sulfolane. An electron diffraction study[15] was said to be incompatible with a planar structure of the five-membered ring. Later, microwave spectra could be interpreted with two models: a bent, nonplanar structure and an essentially planar one,[16] the latter of which was afterwards confirmed from additional evidence and a reinterpretation of the early electron diffraction results.[17] Apart from

---

(13) Mantsch, H. H.; Saitō, H.; Smith, I. C. P. "Progress in NMR Spectroscopy"; Pergamon: Oxford, 1977; Vol. 11, pp 211–271.

(14) (a) Abragam, A. "The Principles of Nuclear Magnetism"; Clarendon Press: Oxford, 1961. (b) Werbelow, L.; Pouzard, G. *J. Phys. Chem.* **1981**, *85*, 3887–3891.

(15) Naumov, V. A.; Semashko, V. N.; Shuidulin, S. A. *Zh. Strukt. Khim.* **1973**, *14*, 555–559.

(16) Alonso, J. L. *J. Mol. Struct.* **1981**, *73*, 71–78.

(17) Hargittai, I. *J. Mol. Struct.* **1981**, *77*, 313–314.

Table I. Structural Parameters of Sulfolane[a]

angles	degrees	distances	nm
OSO	115.3	OS	0.1450
CSC	102.0	SC	0.1800
SCC	105.0	C_1C_2	0.1540
CCC	114.0	C_2C_3	0.1545
SC_1H_1	107.8	C_1H_1	0.1105
$C_1C_2H_3$	109.0	C_2H_3	0.1112
$H_1C_1H_2$	109.4		
$H_3C_2H_4$	106.2		

[a] The numbering of atoms is as follows: H_1 and H_2 are attached to C_1; H_3 and H_4 to C_2.

the planarity of the skeleton, the complete structure of sulfolane is not known, however. We, therefore, performed a MNDO MO calculation[18] for optimization of the positions of the protons, keeping the skeleton and the two oxygens fixed in the planar electron diffraction structure.[15] The results indicate that the C–H_α bond is inclined 54.7° to the molecular plane, with its plane projection deviating 70.9° from the C_2 axis (dipole moment direction) and hence $\alpha_{zz''}$ (eq 4) is 79.1°. For the C–H_β bond the angles are 53.1°, 146.9°, and 59.8°, respectively. Indeed the orientation of the C–H_β bond is less favorable for the observation of a quadrupolar line splitting ($(^3/_2 \cos^2 \alpha - {}^1/_2)$ in eq 4 is 0.12 for H_β, vs. −0.45 for H_α). For clarity the final structure from electron diffraction plus MNDO optimization is given in Table I. A second quantity to be known in eq 4 is the ^{2}H QCC. From the measured T_1 relaxation times and the observed isotropic reorientation (see below), the QCC's for the two deuterons obviously differ by about 15%. The average value observed for the QCC of deuteron attached to sp_3 hybridized carbons is 165 kHz.[19] We prefer to attribute this value to the β deuterons, since for the α deuterons, the nearby SO_2 fragment probably leads to a deviation from the quoted value. From the relaxation times, the $^2H_\alpha$ QCC then is calculated to be 190 kHz, a rather high, but not an impossible value for a deuteron bonded to a sp_3-like carbon atom.

With the calculated $\alpha_{zz''}$ and $^2H_\alpha$ QCC the value of $(eQ/h)V_{zz}$ in eq 4 can be calculated and $(eQ/h)V_{zz}(^{33}S)$ follows from the ratio of deuteron and sulfur quadrupolar line splittings: $(eQ/h)V_{zz}(^{33}S) = (\pm)1.05 \pm 0.03$ MHz. Since the z axis coincides with the C_2 symmetry axis, one of the principal components of the ^{33}S QCT is known now.

The activation energies, calculated from the T_1 measurement as a function of temperature, are 15.4 ± 1.5, 14.5 ± 1.5, and 17.2 ± 2.5 kJ mol^{-1} for the $^2H_\alpha$, $^2H_\beta$, and ^{33}S reorientation, respectively. For sulfur this is in good agreement with the result of ref 10a: 17.0 and 18.1 kJ mol^{-1} for sulfolane in Me_2SO and $CDCl_3$ solution, respectively. The results indicate that the molecular tumbling is isotropic or very nearly so. This might appear unlikely at first sight, since sulfolane is a polar molecule with low symmetry, both unfavorable properties for isotropic reorientation. It should be noted, however, that sulfolane forms a plastic crystalline phase in a small temperature range just below its melting point.[1] This, again, is unexpected: normally only highly symmetrical "globular" molecules do so; NMR relaxation studies have revealed isotropic reorientation of sulfolane in the plastic phase,[4,5] indicating that one may speak of an effectively globular molecule. These observations in the (solid) plastic phase make our conclusions of isotropic tumbling in the liquid phase not as unexpected as might seem at first sight. Consequently, applying eq 5, the T_1 of $^2H_\alpha$ and ^{33}S (0.28 and 0.019 s, respectively, at 303 K) allows the calculation of the ^{33}S QCC as a function of η. The extreme values are 1.41 and 1.22 MHz, found for $\eta = 0$ and 1, respectively. The correct choice of QCC and η should, however, reproduce the principal component of the ^{33}S QCT measured in the EF NMR experiment (±1.05 MHz). The result is the following: QCC(^{33}S) = (±)1.34 MHz, $\eta = 0.56$. (Use has been made of the Laplace condition that the QCT is traceless.) The zz component of the tensor has to be identified with the C_2 axis of sulfolane, so two possibilities are left for the orientation of the major principal component: perpendicular to either the five-membered ring or to the SO_2 plane. Of course it would be of interest to indicate the most probable solution. The first idea is to refer to literature data on molecules closely resembling sulfolane in electronic structure as far as the SO_2 moiety is concerned. To our knowledge no such data are available. Another approach to obtain an unambiguous assignment is a theoretical determination of the EFG tensor at the sulfur nucleus.

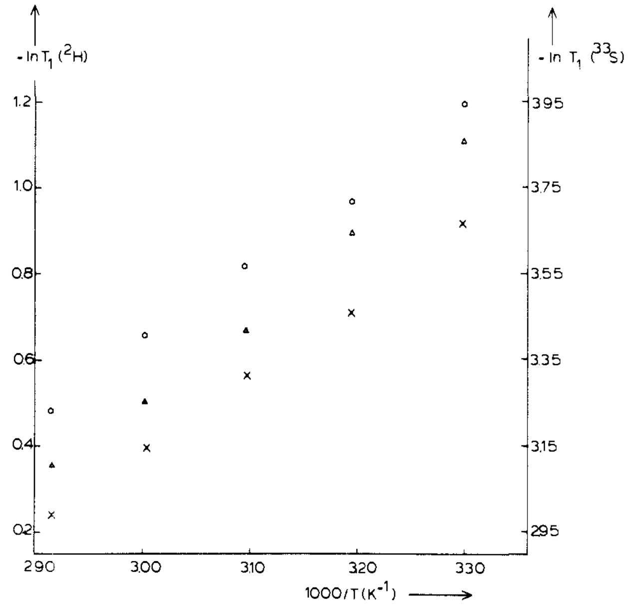

Figure 3. Plots of ln T_1 vs. T^{-1} for $^2H_\alpha$ (○), $^2H_\beta$ (×), and ^{33}S (△).

Theoretical Calculation of the EFG Tensor. A reliable determination of the EFG tensor elements requires essentially electronic structure calculations on an ab initio level. To this end LCAO Hartree–Fock–Slater (HFS) calculations have been performed by using the discrete variational method (DVM) developed by Baerends and Ros,[20,21] in which the molecular orbitals are calculated in a self-consistent manner. The method is relatively efficient and thus can be used to deal with comparatively large systems on an ab initio level. Characteristic of the HFS method is the replacement of the Hartree–Fock (HF) exchange operator by a simple local potential as proposed by Slater[22]

$$V_{x_\alpha}(r) = -3\alpha(\tfrac{3}{4}\pi)(\tfrac{1}{2}\rho(r))^{1/3} \qquad (6)$$

The scaling parameter α was taken to be 0.7, which has been shown to be the optimal value.[23] The basis set used in the calculations consisted of Slater type orbitals (STO's) and was of optimized double-ζ quality.[24] On the sulfur nucleus, on which the field gradient tensor components are evaluated, extra 3d polarization functions have been added. the elements of the Fock matrix, needed to solve the one-electron equations, were evaluated by numerical integration. To simplify the integrals for Coulomb and exchange potentials, a least-squares fit of the electron density was used

$$\rho(r) \simeq \sum_i a_i f_i \qquad (7)$$

in which the fitting functions are again STO's. On the sulfur nucleus an extended fit set (10 s; 8 p; 5 d; 3 f an 1 g type STO) was used in order to describe the electron density in this part of the molecule as accurately as possible. Again it should be em-

---

(18) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899–4907.

(19) Rinne, M.; Depireux, J. "Advances in Quadrupole Resonance"; Heydon: London, Vol. 1, 1974; pp 357–374.

(20) Baerends, E. J.; Ros, P. *Int. J. Quantum Chem.* **1978**, *12*, 169–190.

(21) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41–51.

(22) Slater, J. C. *Phys. Rev.* **1951**, *81*, 385–390. Slater, J. C. *Adv. Quantum Chem.* **1972**, *6*, 1–92.

(23) Baerends, E. J.; Ros, P. *Chem. Phys.* **1973**, *2*, 52–59.

(24) Snijders, J. G.; Vernooijs, P.; Baerends, E. J. *At. Data Nucl. Data Tables* **1981**, *26*, 483–509.

Table II. Principal Components of the ^{33}S Quadrupole Coupling Tensor of Sulfolane (Calculated and Experimental Values)

tensor	HFS/MHz[a]	experimtl/MHz
$(eQ/h)V_{aa}$	−1.65	(±)0.29[b]
$(eQ/h)V_{bb}$	+3.55	(±)1.34[b]
$(eQ/h)V_{cc}$	−1.90	(±)1.05

[a] Calculated with $eQ(^{33}S) = -6.4 \times 10^{-30}$ m^2. [b] Assignments interchangeable on the basis of experimental evidence alone.

phasized that the accuracy of both density fitting and numerical integration is such that with this method essentially ab initio quality solutions to the HFS one-electron equations can be obtained. Determination of the EFG tensor elements requires calculation of integrals of the form

$$\int \rho(r) \frac{Z_{lms}(\hat{r}_N)}{r_N^{3}} dr \ (l = 2) \qquad (8)$$

where $\rho(r)$ is the electron density from the MO calculation, r_N is the vector with respect to nucleus N, and $\hat{r}_N$ is the unit vector in this direction. $Z_{lms}(m \geq 0)$ is a real spherical harmonic. Evaluation of the electric field gradient from the fitted electron density (eq 7) yielded reliable results for hydrogen and methane.[25] An improvement, that offers a circumvention of the problems associated with possible errors due to the incompleteness of the fitset in eq 7, can be obtained by replacing the expression of $\rho(r)$ in a set of fitfunctions by an expression obtained from the squared eigenfunctions of the HFS one-electron equations. One-electron properties can then be calculated with the package of the POLYATOM program.[26] Since this program is based on GTO's, the eigenvectors from HFS (STO's) should be expanded in a sum of GTO's. The interface program described by Ravenek[27] was used for this purpose. The number of GTO's used in the expansion was increasaed until a stable value for the EFG was obtained. The calculated ^{33}S quadrupole coupling tensor (adopting -6.4×10^{-30} m^2 for the ^{33}S nuclear quadrupole moment[28]) is given in Table II in terms of tensor components in the principal axes system (a,b,c) at sulfur. The b axis is perpendicular to the plane formed by the five-membered ring; the c axis is parallel to the C_2 symmetry axis.

The HFS calculation indicates that the EFG component of intermediate absolute magnitude is along the C_2 axis (dipole moment direction). This result is in agreement with the experimental observation. It should be noted that the component along the dipole moment direction is the one that can be assigned explicitly, due to the nature of the EF NMR experiment. The aim of the HFS calculation was to discriminate between the two possible solutions left for the assignment of the components perpendicular to the C_2 axis. If it is assumed that the calculated values are at least relatively confident, and adopting their signs, only the assignment which puts the major principal tensor component (+1.34 MHz) perpendicular to the molecular five-membered ring is justified by the calculation.

A question that still needs consideration is the discrepancy between the absolute values of the calculated and experimental results (the calculated values are 2–5 times the experimental ones, see Table II). A possible explanation is the use of the frozen-core approximation in the HFS calculation. Computational time can be saved if the core electrons, generally not involved in the chemical bond, are kept frozen. This means, in the presence case, that 1s, 2s, and 2p electrons on sulfur and 1s electrons on carbon and oxygen are treated as if they originate from atomic calculations. Because of the spherical symmetry the frozen core of sulfur does not give a contribution to the one-center part of the EFG tensor. This effect is expected to be dominant over the change in the two-center contribution to the tensor due to the frozen core on carbon and oxygen. In principle, Sternheimer factors could be used to correct for the assumption of a frozen core. These factors have been calculated for atoms and their ions,[29] but for molecules they are not very reliable.[30] Another explanation might be the use of a not sufficiently extended basis set. The set chosen in the present case should, however, be regarded as a fair compromise between reliability and computational time.

Finally it should be noted that nuclear quadrupole moments are often not known very accurately: uncertainties of 20–30% are not unusual.[31] For the ^{33}S quadrupole moment two values have been reported -6.4×10^{-30} (ref 28) and -5.5×10^{-30} m^2.[32] By adopting the latter, the more recent one, the difference between calculated and experimental values, is reduced but by no means removed. We are, therefore, left with a discrepancy which is most probably caused by the frozen core approximation used in the HFS calculation. To check this thoroughly, a new calculation with an all-electron treatment, at least on sulfur, is needed. In view of the extreme calculational efforts involved with such an approach and considering the fact that, in spite of the deviation of absolute field gradient values, the relative figures can be expected to be reasonably reliable, we decided that it was not appropriate to proceed with the all-electron calculations.

Conclusions

Electric field NMR, in combination with T_1 relaxation measurements and Hartree–Fock–Slater MO calculations, was applied to measure the ^{33}S quadrupole coupling tensor in liquid sulfolane. The major principal component of the tensor, the quadrupole coupling constant, is found perpendicular to the five-membered ring and has a value of 1.34 ± 0.03 MHz. The component along the molecular dipole moment is −1.05 ± 0.03 MHz. Hence, the asymmetry of the tensor is 0.56.

Acknowledgment. The investigations were supported by the Netherlands Foundation for Chemical Research (S.O.N.) with financial help from the Netherlands Organization for the Advancement of Pure Research (Z.W.O). The authors appreciate the assistance of Dr. F. J. J. de Kanter in performing the MNDO calculations. They are indebted to professor E. J. Baerends for helpful discussions and his interest in this work. The help of Dr. W. Ravenek in making the properties program accessable to us is gratefully acknowledged.

Registry No. ^{33}S, 14257-58-0; sulfolane, 126-33-0; deuterium, 7782-39-0.

---

(25) Snijders, J. G.; van der Meer, W.; Baerends, E. J.; de Lange, C. A. *J. Chem. Phys.* **1983**, *79*, 2970–2974.

(26) Neumann, D. B. et al. *QCPE.* **1971**, *11*, 199.

(27) Ravenek, W.; Jacobs, J. W. M.; van der Avoird, A. *Chem. Phys.* **1983**, *78*, 391–404.

(28) Bird, G. R. *Phys. Rev.* **1954**, *94*, 1203–1208.

(29) Sternheimer, R. M. *Phys. Rev.* **1967**, *164*, 10–20.

(30) Engström, S. et al. *Mol. Phys.* **1977**, *34*, 813–821.

(31) Harris, R. K. "Nuclear Magnetic Resonance Spectroscopy"; Pitman: London, 1983; pp 232–233.

(32) Fuller, G. H. *J. Phys. Chem. Ref. Data* **1976**, *5*, 835–1092.