$^{33}$S, $^{17}$O, and $^{13}$C Relaxation and Nuclear Quadrupole Coupling Constants in Thiophene, Tetrahydrothiophene, Furan, and Tetrahydrofuran

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$^{13}$C and $^{17}$O or $^{33}$S relaxation time measurements for 1 M solutions of furan, tetrahydrofuran, thiophene and tetrahydrothiophene in $\text{C}_4\text{D}_8$ at 30°C permit estimation of the $^{13}$C and $^{33}$S quadrupole coupling constants. These measurements yield $^{33}$S QCC(thiophene) = 26 MHz, QCC(tetrahydrothiophene) = 48 MHz, and $^{17}$O QCC(furan) = 11 MHz and QCC(tetrahydrofuran) = 13 MHz.

The magnetic isotopes of oxygen and sulphur, $^{17}$O and $^{33}$S, have rather unfavourable NMR characteristics: low natural abundance and low magnetogyric ratios which lead to very low receptivities. In spite of the difficulties, $^{17}$O NMR is used almost routinely, while $^{33}$S investigations of organosulphur compounds are scarce. One of the reasons for this difference is probably to be sought in the fact that $^{33}$S lines are usually considerably broader than the $^{17}$O signals.

In this communication, we wish to elucidate the differences in the $^{17}$O and $^{33}$S relaxation properties by combining $^{13}$C spin-lattice relaxation time measurements with $^{17}$O/$^{33}$S line width studies for two pairs of analogues: furan/thiophene and tetrahydrofuran/tetrahydrothiophene. In this way, we can also estimate and compare the $^{17}$O and $^{33}$S quadrupole coupling constants (QCC); in the case of $^{33}$S, such a procedure has in the past been applied only once, by Vold et al. for $\text{CS}_2$.

**Experimental**

**Compounds.** Furan, tetrahydrofuran, thiophene and tetrahydrothiophene were of commercial origin and distilled immediately before sample preparation. 3.2 ml samples of 1 M solutions in $\text{C}_4\text{D}_8$ were prepared directly in 10 mm NMR tubes. Dissolved oxygen was removed by applying several freeze-pump-thaw cycles before sealing.

**NMR measurements.** The $^{13}$C experiments were run on a Varian XL-100 spectrometer at 25.14 MHz. $T_1$ was measured by FIDRT and the Overhauser enhancement by dynamic NOE (DNOE). $T_1$ and NOE were obtained from three- and two-parameter nonlinear fits, respectively, and the reported values are weighted averages from several measurements. $^{33}$S and $^{17}$O spectra were recorded on a Jeol GX-400 instrument at 30.68 and 54.23 MHz, respectively. The $^{17}$O experiments were run in 10–15 min, $^{33}$S spectra for thiophene in 1–1.5 h and overnight for tetrahydrothiophene. The line widths were obtained from a Lorentzian curve-fitting routine. All types of experiments were repeated at least three times, and the error in a single experiment was estimated to be less than 10%. In all cases, the temperature was 30°C. Field/frequency lock was set at the deuterium signal in $\text{C}_4\text{D}_8$ for the $^{13}$C and $^{17}$O experiments. The $^{33}$S spectra were recorded without lock in order to avoid possible interference between the lock and observe channels (the deuterium frequency is almost exactly twice the sulphur frequency).
Results and discussion

The quadrupole coupling constant, QCC, can, under favourable conditions, be estimated from multinuclear NMR relaxation time measurements, using the so-called dual-spin probe technique.22-24 The general idea of this method is to determine the molecular correlation time from \(^{13}C\) \(T_1^{\text{DD}}\) and use it to extract the QCC from the line width for the quadrupolar nucleus. Under \(^1H\) decoupling and in the motional region of extreme narrowing, \(\omega \tau \ll 1\), the \(^{13}C\) dipolar relaxation rate can be described by\(^{25}\)

\[
\frac{1}{T_1^{\text{DD}}} = \left(\frac{h_0}{4\pi}\right)^2 n H \gamma_C^2 \gamma_H^2 h^2 r_{C-H}^6 \tau_{\text{DD}}^0,
\]

where the dipolar relaxation rate is determined from the observed relaxation rate and the nuclear Overhauser enhancement, using standard equations.\(^{26}\) Bond lengths are taken from electron diffraction studies and the following values have been used: \(r_{C-H}(\text{furan}) = 1.075\ \text{Å}, r_{C-H}(\text{thiophene, α-carbon}) = 1.115\ \text{Å}, \) and \(r_{C-H}(\text{tetrahydrofuran}) = 1.120\ \text{Å}.\) The quadrupolar relaxation rate, which is given from the line width at half height, \(\Delta v_i\), is in the extreme narrowing described by\(^{31}\)

\[
\frac{1}{T_1^0} = \frac{1}{T_2^0} = \frac{3\pi^2}{10 \bar{f}(2I-1)} \left(1 + \frac{\epsilon^2}{3}\right) \left(\epsilon^2 q_z Q / h\right)^2 \tau_{\text{DD}}^0,
\]

where \(I(\text{^{13}O}) = 5/2\), \(I(\text{^{33}S}) = 3/2\), \(\epsilon\) is the asymmetry parameter, and \((\epsilon^2 q_z Q / h)\) is the quadrupole coupling constant. Relaxation times, NOE values, and line widths are collected in Table 1. All the \(^{13}C\) relaxation times are fairly similar, while there are large differences in line widths between oxygen and sulphur.

The two correlation times in Eqs. (1) and (2) are identical if the molecular tumbling is isotropic. The \(^{13}C\) correlation times (Table 2) show that this is approximately the case, and an average value of \(\tau_{\text{DD}}^0\) can be used. For \(\epsilon = 0.6\) seems to be a reasonable estimate for both oxygen and sulphur.\(^{32,33}\) The estimated quadrupole coupling constants are collected in Table 2, and the errors are estimated from 20\% error in \(\tau_{\text{DD}}^0\), 10\% in line widths and 10\% in \([1 + (\epsilon^2/3)]\). The QCC values

| \(^{13}C\) Relaxation Times, \(T_1(\text{s})\), and Overhauser Enhancement; \(^{17}O\) and \(^{33}S\) Line Widths (Hz) |
|---------------------------------|----------|----------|----------|----------|
|                                 | \(\alpha\)-carbon | \(\beta\)-carbon | \(\gamma\)-carbon | \(\delta\)-carbon |
| \(T_1^{\text{obs}}\) | \(\eta^{\text{obs}}\) | \(T_1^{\text{obs}}\) | \(\eta^{\text{obs}}\) | \(\Delta v_i\) | \(\Delta v_i\) |
| furan                          | 31.4±0.4 | 1.15±0.07 | 29.6±0.9 | 1.06±0.02 | 34 | - |
| THF                            | 29.4±0.2 | 1.84±0.04 | 28.8±0.8 | 1.69±0.03 | 48 | - |
| thiophene                      | 29.2±0.3 | 1.60±0.08 | -^a     | -^a     | - | 1165 |
| THF                            | 21.6±0.2 | 1.70±0.04 | 20.6±0.4 | 1.83±0.03 | - | 3657 |

^a^Not measurable due to overlapping solvent lines.

| Reorientational correlation times, \(\tau_c^{20}\) (ps), and quadrupole coupling constants, QCC (MHz) |
|---------------------------------|----------|----------|----------|----------|
|                                 | \(\tau_c^{20}(\alpha)\) | \(\tau_c^{20}(\beta)\) | \(\tau_c^{20}(\gamma)\) | \(\tau_c^{20}(\delta)\) |
| \(^{17}O\) QCC | \(^{33}S\) QCC |
| furan                          | 0.79±0.04 | 0.77±0.03 | 0.78±0.03 | 11±1 | - |
| THF                            | 0.84±0.02 | 0.79±0.03 | 0.82±0.02 | 13±2 | - |
| thiophene                      | 1.18±0.04 | -         | 1.18±0.04 | -   | 26±3 |
| THT                            | 1.08±0.03 | 1.22±0.03 | 1.15±0.03 | -   | 48±6 |
obtained for furan and tetrahydrofuran are representative for ether oxygens (9–14 MHz). The sulphur compounds show a much more pronounced effect on QCC than their oxygen analogues when going from saturated to unsaturated species. Thus, the increasing relative change in the QCC between the saturated and unsaturated compounds follows the increasingly aromatic character of thiophene compared to furan. This observation can be rationalized as follows. The principal z axis of the field gradient tensor at the heteroatom X can be expected normal to the CXC plane (shown theoretically to be the case for ethers). Upon the delocalization of the lone pair in the heteroaromatic species, the field gradient decreases due to a more uniform charge distribution around the heteronucleus.

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References


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