

^{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 C_6D_6 at 30°C permit estimation of the ^{17}O 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 receptivities¹. In spite of the difficulties, ^{17}O NMR is used almost routinely^{2–4}, while ^{33}S investigations of organosulphur compounds are scarce^{5–16}. 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 $^{17}\text{O}/^{33}\text{S}$ 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.*⁷ for 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 C_6D_6

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 FIRFT¹⁷ and the Overhauser enhancement by dynamic NOE (DNOE)¹⁸. T_1 and NOE were obtained from three- and two-parameter nonlinear fits, respectively¹⁹, and the reported values are weighted averages²⁰ 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 routine²¹. 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 C_6D_6 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 ¹³C T_1^{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, $\omega\tau_c \ll 1$, the ¹³C dipolar relaxation rate can be described by²⁵

$$\frac{1}{T_1^{\text{DD}}} = \left(\frac{\mu_0}{4\pi}\right)^2 n_{\text{H}} \gamma_{\text{C}}^2 \gamma_{\text{H}}^2 h^2 r_{\text{C-H}}^{-6} \tau_c^{\text{DD}}, \quad (1)$$

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: $r_{\text{C-H}}$ (furan) $r_{\text{C-H}}$ (thiophene, α -carbon) = 1.075 Å,^{27,28} $r_{\text{C-H}}$ (tetrahydrofuran) = 1.115 Å,²⁹ and $r_{\text{C-H}}$ (tetrahydrothiophene) = 1.120 Å.³⁰ The quadrupolar relaxation rate, which is given from

the line width at half height, $\Delta\nu_{\frac{1}{2}}$, is in the extreme narrowing described by³¹

$$\frac{1}{T_1^{\text{Q}}} = \frac{1}{T_2^{\text{Q}}} = \frac{3\pi^2}{10} \frac{2I+3}{I^2(2I-1)} \left(1 + \frac{\epsilon^2}{3}\right) \left(\frac{e^2 q_{zz} Q}{h}\right)^2 \tau_c^{\text{Q}}, \quad (2)$$

where $I(^{17}\text{O}) = 5/2$, $I(^{33}\text{S}) = 3/2$, ϵ is the asymmetry parameter, and $(e^2 q_{zz} Q/h)$ is the quadrupole coupling constant. Relaxation times, NOE values, and line widths are collected in Table 1. All the ¹³C 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 ¹³C correlation times (Table 2) show that this is approximately the case, and an average value of τ_c^{DD} can be used. For ϵ , 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 τ_c^{DD} , 10% in line widths and 10% in $[1 + (\epsilon^2/3)]$. The QCC values

Table 1. ¹³C relaxation times, T_1 (s), and Overhauser enhancement; ¹⁷O and ³³S Line Widths (Hz)

	¹³ C				¹⁷ O	³³ S
	α -carbon		β -carbon			
	T_1^{OBS}	η^{OBS}	T_1^{OBS}	η^{OBS}		
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

^aNot measurable due to overlapping solvent lines.

Table 2. Reorientational correlation times, τ_c^{DD} (ps), and quadrupole coupling constants, QCC (MHz)

	$\tau_c^{\text{DD}}(\alpha)$	$\tau_c^{\text{DD}}(\beta)$	$\tau_c^{\text{DD}}(\text{av})$	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),^{22,33–35} and tetrahydrothiophene is in fairly good agreement with the value for hydrogen sulphide (48 versus 40 MHz).³² The sulphur compounds show a much more pronounced effect on QCC than their oxygen analogues when going from saturated to unsaturated species, (48 to 27 versus 13 to 11 MHz). Thus, the increasing relative change in the QCC between the saturated and unsaturated compounds follows the increasingly aromatic character of thiophene compared to furan.³⁶ 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 ethers³⁷). 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

- Lambert, J. B. and Riddell, F. G., eds. *The multinuclear approach to NMR spectroscopy*. NATO ASI Ser., Ser. C 103, Reidel, Dordrecht 1983, p. xi.
- St. Amour, T. E. and Fiat, D. *Bull. Magn. Reson.* 1 (1980) 118.
- Kintzinger, J. P. In: Diehl, P., Fluck, E. and Kosfeld, R., eds., *NMR basic principles and progress*. Springer, Heidelberg 1981, Vol. 17, p 1.
- Klemperer, W. G. In: Lambert, J. B. and Riddell, F. G., eds. *The multinuclear approach to NMR spectroscopy*. NATO ASI Ser., Ser. C 103, Reidel, Dordrecht 1983, p. 245.
- Retcofsky, H. L. and Friedel, R. A. *Appl. Spectrosc.* 24 (1970) 379.
- Retcofsky, H. L. and Friedel, R. A. *J. Am. Chem. Soc.* 94 (1972) 6579.
- Vold, R. R., Sparks, S. W. and Vold, R. L. *J. Magn. Reson.* 30 (1978) 497.
- Faure, R. and Vincent, E. J., Ruiz, J. M. and Léna, L. *Org. Magn. Reson.* 15 (1981) 401.
- Harris, D. L. and Evans Jr., S. A. *J. Org. Chem.* 47 (1982) 3355.
- Annunziata, R. and Barbarella, G. *Org. Magn. Reson.* 22 (1984) 250.
- Hinton, J. F. and Buster, D. *J. Magn. Reson.* 57 (1984) 494.
- Hinton, J. F. *J. Magn. Reson.* 59 (1984) 469.
- Cassidei, L., Fiandanese, V., Marchese, G. and Sciacovelli, O. *Org. Magn. Reson.* 22 (1984) 486.
- Belton, P. S., Cox, I. J. and Harris, R. K. *J. Chem. Soc., Faraday Trans. 2* 81 (1985) 63.
- Farrar, T. C., Trost, B. M., Tang, S. L. and Springer-Wilson, S. E. *J. Am. Chem. Soc.* 107 (1985) 262.
- Cassidei, L. and Sciacovelli, O. *J. Magn. Reson.* 62 (1985) 529.
- Martin, M. L., Delpuech, J.-J. and Martin, G. J. *Practical NMR spectroscopy*. Heyden, London 1980, p. 256.
- Martin, M. L., Delpuech, J.-J. and Martin, G. J. *Practical NMR spectroscopy*. Heyden, London 1980, p. 231.
- Kowalewski, J., Levy, G. C., Johnson, L. R. and Palmer, L. *J. Magn. Reson.* 26 (1977) 533.
- Topping, J. *Errors of observation and their treatment*. Chapman and Hall, London 1972, p. 72.
- Levy, G. C. "NMR", NMR Laboratory, Syracuse University, Syracuse, NY 1984.
- Delseth, C. and Kintzinger, J.-P. *Helv. Chim. Acta* 65 (1982) 2273.
- Kintzinger, J.-P. and Lehn, J.-M. *J. Am. Chem. Soc.* 96 (1974) 3313.
- Dechter, J. J., Henriksson, U., Kowalewski, J. and Nilsson, A.-C. *J. Magn. Reson.* 48 (1982) 503.
- Harris, R. K. *Nuclear magnetic resonance spectroscopy*. Pitman, London 1983, p. 89.
- Harris, R. K. *Nuclear magnetic resonance spectroscopy*. Pitman, London 1983, p. 108.
- Almenningen, A., Bastiansen, O., Hansen, L. *Acta Chem. Scand.* 9 (1955) 1306.
- Harshbarger, W. R. and Bauer, S. H. *Acta Cryst. B* 26 (1970) 1010.
- Geise, H. J., Adams, W. J. and Bartell, L. S. *Tetrahedron* 25 (1969) 3045.
- Náhlovská, Z., Náhlovský, B. and Seip, H. M. *Acta Chem. Scand.* 23 (1969) 3534.
- Harris, R. K. *Nuclear magnetic resonance spectroscopy*. Pitman, London 1983, p. 133.
- Lucken, E. A. C. *Nuclear quadrupole coupling constants*. Academic Press, London 1969, p. 287.
- Hsieh, Y., Koo, J. C. and Hahn, E. L. *Chem. Phys. Lett.* 13 (1972) 563.
- Butler, L. G., Cheng, C. P. and Brown, T. L. *J. Phys. Chem.* 85 (1981) 2738.
- Eliasson, B., Larsson, K. M. and Kowalewski, J. J. *Phys. Chem.* 89 (1985) 258.
- Cordell, F. R. and Boggs, J. E. *J. Mol. Struct.* 85 (1981) 163.
- Gready, J. E. *J. Phys. Chem.* 88 (1984) 3497.

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