117. Determination of the Quadrupolar Coupling Constant and the Asymmetry Parameter of Oxygen-17 in Acetone by ^{17}O- and ^{1}H-NMR in Nematic Phases

by **Yves Tricot**[1]) and **Werner Niederberger**[2])*

Institut de Chimie Organique de l'Université, Rue de la Barre 2, CH–1005 Lausanne

(9.III.84)

Summary

Linear relationships between the inverse of the quadrupolar coupling constant, $1/\chi$ and the asymmetry parameter η are obtained for the ^{17}O-nucleus of acetone oriented in four different nematic phases, using the information contained in ^{1}H- and ^{17}O-NMR spectra. The absence of a unique intersecting point of these relations shows that the quadrupolar constants differ slightly between polar and apolar nematic phases, while the orientation remains similar. By combination of the experimentally derived relations with predictions from the theory of *Townes* and *Dailey*, values for $\chi = 11.15$ MHz and $\eta = 0.47$ in polar media and $\chi = 11.35$ MHz and $\eta = 0.51$ in an apolar medium are obtained, which are similar to those found in the gas and solid phases.

Introduction. – Direct determination of quadrupolar coupling constants for ^{17}O is usually performed in the solid state by nuclear quadrupole resonance (NQR) [1–8] or in the gas phase by microwave spectroscopy [9] [10]. In isotropic liquids, an indirect method based on quadrupolar relaxation yields the quadrupolar coupling constant from the linewidth of the ^{17}O-NMR signal, using the asymmetry parameter predicted by theory [11]. In this work, a method based on the orientation of host molecules by nematic phases is used. This technique has been applied to the ^{14}N- and ^{2}H-nuclei [12], but not yet to the ^{17}O-nucleus. Knowledge of the quadrupolar coupling constants and the asymmetry parameter gives an insight into the electronic repartition in a molecule and provides a test for the theoretical calculations of molecular orbitals and electric field gradients [13] [14].

Experimental. – Na_2SO_4, decanol and *Phase IV* were of analytical grade (*Merck*, Darmstadt, GFR) and used as purchased. ^{17}O-enriched water (26.5% ^{17}O and 46.3% ^{18}O) was purchased from *Biogenzia Lemania*, Lausanne, Switzerland. *Phase ZLI 1167 (Merck)* and purified sodium decylsulfate (SDS) were a gift from Prof. *P. Diehl*, Basel. ^{17}O-enriched acetone was prepared by oxygen exchange in ^{17}O-enriched water.

Lyotropic nematic phases were prepared by vortex-mixing and centrifuging weighted amounts of the components at r.t. until an optically clear and fluid mixture was obtained. 1.5 to 2.0 wt-% of acetone was injected into the nematic phases, then further mixed and centrifuged (table-top model, 3000 rpm). The nematic solutions

---

[1]) Present address: Department of Chemistry, Clarkson College, Potsdam, N.Y. 13676, USA.

[2]) Present address: Biopharmaceutical Department, *Sandoz Ltd.*, CH–4002 Basel.

were transferred into 5-mm outer diameter NMR tubes and sealed with a teflon anti-vortex plug and a parafilm cork directly on top of the plug, thus preventing acetone evaporation and further mixing of the phase. Measurements were made several days after preparation. Solutions in thermotropic nematic phases were obtained by vortex-stirring mixtures of 3–4% of previously ^{17}O-enriched acetone in *ZLI 1167* or *Phase IV*, and glass-sealing the samples in NMR tubes.

^{17}O-NMR spectra were recorded at 54.4 MHz on a *Bruker WH-400* or at 36.6 MHz on a *Bruker CXP-270* (for acetone in *Phase IV*). For acetone in SDS I, SDS II and *ZLI 1167*, the ^{1}H-NMR spectra were recorded with the same samples in the same spectrometer. ^{1}H-NMR spectra were found to be identical immediately before and after the ^{17}O-NMR measurement. For samples in *Phase IV*, the ^{1}H-NMR spectra were recorded on a *WH-400* and repeated on lower field spectrometers. No significant difference was observed. All measurements were made at r.t. in the NMR probe (22–23°).

Results and Discussion. – In a macroscopically oriented nematic phase, the ^{17}O-nucleus gives rise to five equidistant NMR transitions with an intensity ratio of 5:8:9:8:5 [15] due to the interaction between the ^{17}O quadrupolar moment and the electric field gradient (efg) of the molecule at the position of the ^{17}O-nucleus. This splitting has been previously observed for the water molecules of the lyotropic nematic phases [16–18].

Lyotropic and thermotropic nematic phases are also used to orient host molecules and in several studies interatomic distances have been determined from the ^{1}H-NMR spectra of oriented molecules [19–23].

In this work, we combine the information derived from the ^{17}O- and ^{1}H-NMR spectra of acetone oriented in several nematic phases in order to determine the quadrupolar coupling constant χ and the asymmetry parameter η of the ^{17}O-nucleus in acetone. This molecule has been chosen since the large chemical shift (538 ppm downfield from water) allows us (at a field strength of 94.1 kG) to separate completely the quintuplets arising from acetone and water in lyotropic phases, as shown in *Fig. 1a*.

In thermotropic phases, a very large spectral width is necessary due to the stronger orientation, as shown in *Fig. 1b* for acetone in *Phase IV*. The ^{1}H-NMR spectrum of oriented acetone has been reported and analysed [24–26] and contains sufficient infor-

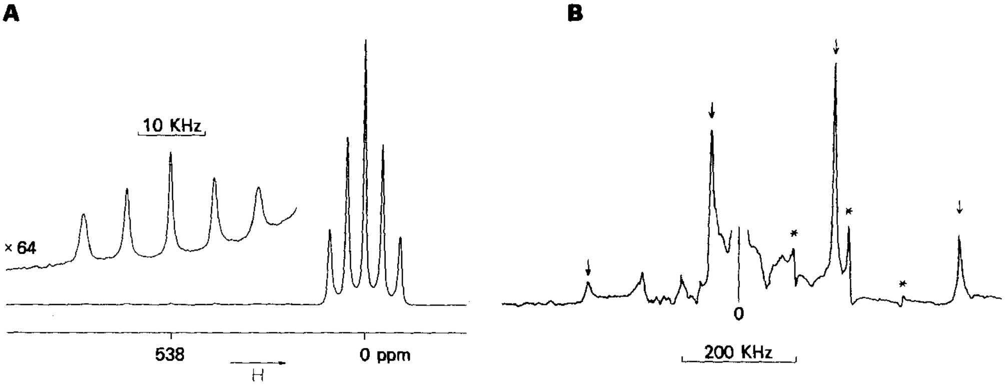

Fig. 1. A) *^{17}O-NMR spectrum at 54.4 MHz of acetone oriented in lyotropic nematic phase SDS II* (26.5% ^{17}O, 1.5 wt-%). Temperature 22°, spectral width 125 KHz, 1.5 × 10^6 scans, total acquisition time 1 h 40 min; B) *^{17}O-NMR spectrum at 36.6 MHz of acetone oriented in thermotropic nematic phase* Phase IV (20% ^{17}O, 3 wt-%). Arrows indicate the four visible peaks from the acetone quintuplet. Stars show three peaks from the water (impurity resulting from the oxygen exchange), also oriented. Temperature 23°, spectral width 1 MHz, 10^6 scans, total acquisition time 7 h.

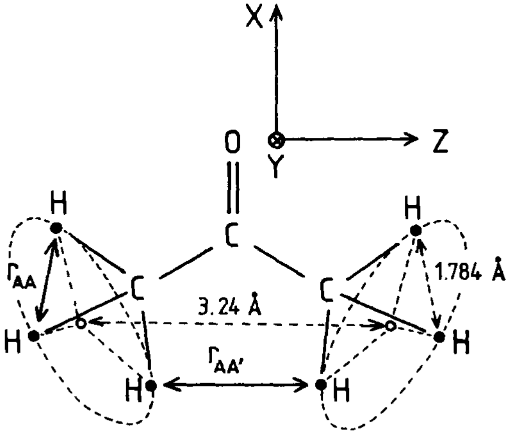

Fig. 2. *The acetone molecule represented with the principal axis system of the electric field gradient tensor at the* ^{17}*O-nucleus* (as determined in gaseous formaldehyde [9]) *and with the interatomic distances used to calculate the order parameters* [25]

mation to derive the two order parameters necessary to fully describe the orientation of the acetone molecule, using the interatomic distances cited in the literature.

In the principal axis system of the efg-tensor of ^{17}O in acetone, as determined in gaseous formaldehyde [9], and shown in *Fig. 2*, χ and η are related by an expression containing the residual quadrupolar splitting Δ (frequency difference between two adjacent lines in the quintuplet) and the two order parameters S_{xx} and S_{zz} with respect to the magnetic field [27]:

$$\eta = \frac{1}{2S_{xx} + S_{zz}}\left(\frac{20 \cdot \Delta}{\chi} - 3S_{zz}\right) \qquad (1)$$

where the numerical factor 20 is the value of a spin function (spin 5/2 for ^{17}O). The order parameters S_{xx} and S_{zz} are derived from the ^{1}H-NMR spectrum according to the procedure described by *Courtieu & Gounelle* [25] using the ^{1}H,^{1}H direct coupling constants D_{AA} (within the same CH$_3$-group) and $D_{AA'}$ (from one CH$_3$-group to the other). The values of D_{AA} and $D_{AA'}$ were determined by an iterative simulation of the experimental spectra, using the programme PANIC [28] and are summarized, together with the indirect coupling constant $J_{AA'}$ in *Table 1.*

Using the values derived for Δ, S_{xx} and S_{zz}, *Eqn. 1* yields a linear relationship for each phase (see *Fig. 3*). A common intersecting point of the four straight lines would yield directly χ and η. However, no such point is found. The slope of the three straight lines for SDS I and II and *ZLI 1167* is similar, as is evident from the almost proportional order parameters. Only *Phase IV* results in a markedly different orientation. The intersecting region of the *Phase IV* relation with the others corresponds to $\chi \cong 14$ MHz and $\eta \cong 0.35$. This value seems unrealistic, since the quadrupolar constants of several other carbonyl compounds have been found to be $\chi \cong 11$ MHz and $\eta \cong 0.5$, either by NQR at 77 K [4–6] or by NMR in isotropic liquid [11]. Therefore, we cannot derive directly the couple χ and η from the experimental results. An explanation is the slight variation of the quadrupolar constants from one phase to another according to the

Table 1. *Residual ^{17}O Quadrupolar Splitting Δ of Acetone and Water* (when present), *Direct (D) and Indirect (J) $^1H,^1H$ Coupling Constants, and Order Parameters* S *of Acetone Oriented in Four Nematic Phases*

Phase[a])	Type	Δ(acetone) [KHz]	Δ(water) [KHz]	D_{AA}[b]) [Hz]	$D_{AA'}$[c]) [Hz]	J [Hz]	RMS Error	S_{xx}	S_{zz}[d])
SDS I[e])	Lyotropic[f])	2.99 ± 0.01	3.40 ± 0.01	– 13.81	+ 2.91	+ 0.65	0.041	-3.51×10^{-3}	-5.72×10^{-4}
SDS II[e])	Lyotropic[g])	6.56 ± 0.01	2.66 ± 0.01	– 30.80	+ 6.51	+ 0.78	0.033	-7.81×10^{-3}	-1.28×10^{-3}
ZLI 1167	Thermotropic[f])	43.80 ± 0.05	–	– 190.51	+ 41.38	+ 0.58	0.088	-4.74×10^{-2}	-8.22×10^{-3}
Phase IV	Thermotropic[g])	214.8 ± 0.5	–	+ 828.03	– 310.47	+ 0.76	0.306	$+1.05 \times 10^{-1}$	$+6.94 \times 10^{-2}$

[a]) Measurements at room temperature (22–23°).

[b]) Protons in the same CH_3-group.

[c]) Protons in different CH_3-groups.

[d]) $S_{yy} = -(S_{xx} + S_{zz})$.

[e]) Composition: SDS I = Na-decylsulfate (SDS), decanol, $D_2{}^{17}O$ (26.5% ^{17}O) 33.9:6.7:59.4 wt-%; SDS II = SDS, decanol, Na_2SO_4, $D_2{}^{17}O$ 32.8:6.5:6.3:54.4 wt-%.

[f]) Orients parallel to the magnetic field.

[g]) Orients perpendicular to the magnetic field.

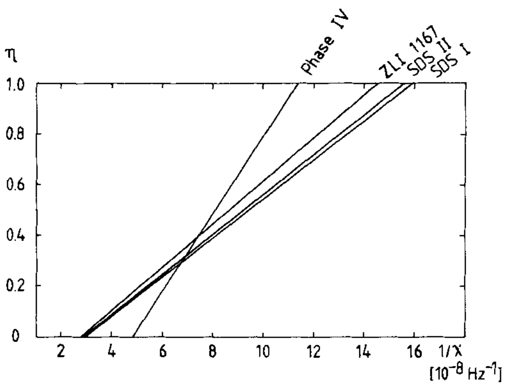

Fig. 3. *Experimental linear relations between* $1/\chi$ (inverse of the quadrupolar coupling constant) *and* η (asymmetry parameter) *of the* ^{17}*O-nucleus in the acetone molecule, oriented in four nematic phases*

polarity of the medium, which affects the polarization of the C=O bond due to formation of H-bonds. This variation can be quantified by comparing the experimental relations with a theoretical prediction derived from the theory of *Townes & Dailey* [29]. In a series of carbonyl compounds, *Cheng & Brown* [4] have used this theory to correlate χ and η with the population $P\pi$ of the atomic orbital of the oxygen participating in the π-bond of the carbonyl group. The variation of this single parameter appears to explain qualitatively the variations of quadrupolar constants in this series of compounds. Recently, *Suhara & Smith* [8] have extended this model, but the small variations found in acetone can already be explained in terms of the simpler model.

Fig. 4 shows the theoretical relation derived from the theory of *Townes & Dailey* together with the experimental relations from *Fig. 3* in a linear scale for χ and η. Well-defined intersecting points are found, giving values of χ, η and the corresponding value of $P\pi$ which are listed in *Table 2*. *Fig. 4* shows also literature values of χ and η of solid dichloroacetone (DA) [5] and gaseous formaldehyde (F) [9]. It is evident from *Fig. 4* that the values of χ and η for acetone in various nematic phases are between the ones found for solid dichloroacetone [5] and gaseous formaldehyde [9].

In polar media (lyotropic phases) the parameter $P\pi$ is larger than in an apolar medium *(Phase ZLI 1167)*. This corresponds, according to [29], to a more polarized π-bond, which is expected from the formation of H-bonds. However, the value obtained in *Phase IV* is not in agreement with this effect since *Phase IV* is more polar than *ZLI 1167*. A specific interaction between *Phase IV* and acetone could explain this discrepancy. This is in line with other observations that *Phase IV* distorts the geometry of host molecules [20] [21] and cannot therefore be regarded as an 'inert' solvent.

Conclusion. – Simple and precise experimental relations between χ and η can be derived from ^{17}O- and ^{1}H-NMR spectra of acetone dissolved in nematic phases. However, the determination of a unique couple (χ, η) requires some additional information, because the orientations obtained in the nematic phases investigated are very similar and the constants χ and η are slightly dependent on the polarity of the orienting phase. This solvent or polarity effect observed with acetone should be less pronounced for less

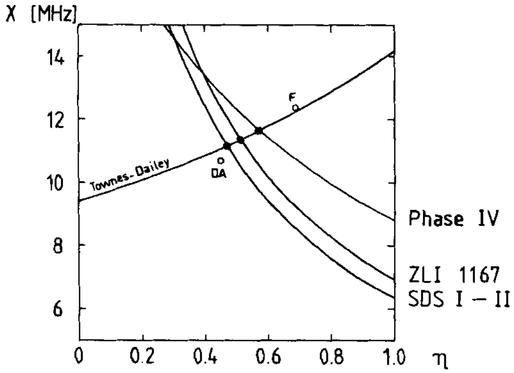

Fig. 4. *Comparison of the experimental relations shown in* Fig. 3 *with the theoretical relation according to the model of* Townes & Dailey [4]. The intersecting points yield the values of χ (quadrupolar coupling constant) and η (asymmetry parameter) of the ^{17}O-nucleus in acetone oriented in four nematic phases given in *Table 2.* Experimental values found in solid dichloroacetone (DA) [25] and gaseous formaldehyde (F) [9] are also shown.

Table 2. *^{17}O Quadrupolar Coupling Constant χ and Asymmetry Parameter η with Corresponding* $P\pi$ (population of the oxygen atomic orbital in the carbonyl π-bond) *Obtained by Combining the Experimental Relations Determined in Four Nematic Phases with the* Townes-Dailey *theory*

Phase	χ [MHz]	η	$P\pi$
SDS I and II[a])	11.15 ± 0.05	0.47 ± 0.01	1.375
ZLI 1167	11.35 ± 0.05	0.51 ± 0.01	1.358
Phase IV	11.65 ± 0.05	0.57 ± 0.01	1.331

[a]) Composition given in *Table 1.*

polar functional groups like esters or ethers. However, the differences between orientations in various nematic phases will probably remain small, which inherently limits the applicability of the described method.

The authors wish to thank Prof. *P. Diehl* (University of Basle) for the gift of *Phase ZLI 1167* and of purified sodium decylsulfate, Dr. *H.-P. Kellerhals* (*Bruker-Spectrospin,* Zürich) for the use of the *Bruker WH-400,* Dr. *B. Knüttel* (*Bruker,* Karlsruhe) for measurements on the *Bruker CXP-270,* Prof. *J. Lauterwein* and Dr. *C. Delseth* for helpful discussion and Prof. *H. Dahn* for financial support under Grant 2.633-0.76 of the *Swiss National Science Foundation.*

REFERENCES

[1] *E.A.C. Lucken,* 'Nuclear Quadrupole Coupling Constants', Academic Press, New York, 1969.
[2] *H.W. Spiess, B.B. Garett, K. Sheline & S.W. Rabideau,* J. Chem. Phys. *51,* 1201 (1969).
[3] *D.T. Edmonds, S.D. Goren, A.A.L. White & W.F. Sherman,* J. Magn. Reson. *27,* 35 (1977).
[4] *C.P. Cheng & Th.L. Brown,* J. Am. Chem. Soc. *101,* 2327 (1979).
[5] *R. Kado & Y. Takarada,* J. Magn. Reson. *32,* 89 (1978).
[6] *Y. Hsieh, J.C. Koo & E.L. Hahn,* Chem. Phys. Lett. *13,* 563 (1972).
[7] *C.R. Bretts & D.T. Edmonds,* J. Magn. Reson. *49,* 304 (1982).
[8] *M. Suhara & J.A.S. Smith,* J. Magn. Reson. *50,* 237 (1982).
[9] *W.H. Flygare & J.T. Lowe,* J. Chem. Phys. *43,* 3645 (1965).

[10] *J. Verhoeven, A. Dynamus & H. Bluyssens,* J. Chem. Phys. *50,* 3330 (1969).

[11] *C. Delseth,* Ph.D. Thesis, University of Lausanne, 1977.

[12] *E.T. Samulski & H.J.C. Berendsen,* J. Chem. Phys. *56,* 3920 (1972).

[13] *J.E. Gready,* Chem. Phys. *55,* 1 (1981).

[14] *J. Clymer, N.S. Goldstein, J.L. Ragle & E.L. Reed Jr.,* J. Chem. Phys. *76,* 4535 (1982).

[15] *A. Abragam,* 'The Principles of Nuclear Magnetism', Oxford University Press, London, 1961.

[16] *M.M. Civan & M. Shporer,* Biophys. J. *12,* 404 (1972).

[17] *F. Fujiwara, L.W. Reeves, A.S. Tracey & L.A. Wilson,* J. Am. Chem. Soc. *96,* 5249 (1974).

[18] *W. Niederberger & Y. Tricot,* J. Magn. Reson. *28,* 313 (1977).

[19] *P. Diehl & C.L. Khetrapal,* 'NMR Studies of Molecules Oriented in the Nematic Phase of Liquid Crystals', 'NMR Basic Principles and Progress', Vol. 1, chap. 1, eds. P. Diehl, E. Fluck and R. Kosfeld, Springer-Verlag, Berlin, 1969.

[20] *P. Diehl, H. Bösiger & H. Zimmermann,* J. Magn. Reson. *33,* 113 (1979).

[21] *S. Sykora, J. Vogt, H. Bösiger & P. Diehl,* J. Magn. Reson. *36,* 53 (1979).

[22] *W. Bechtold, G.B. Magruder & J.L. Goldstein,* Org. Magn. Reson. *19,* 173 (1982).

[23] *J. Courtieu, Y. Gounelle, J. Jullien, J.P. Barnier, J.M. Conia & S.K. Kan,* Org. Magn. Reson. *19,* 63 (1982).

[24] *J. Lindon & B.P. Dailey,* Mol. Phys. *20,* 937 (1971).

[25] *J. Courtieu & Y. Gounelle,* Org. Magn. Reson. *3,* 533 (1971).

[26] *M.S. Gopinathan & P.T. Narashima,* J. Magn. Reson. *6,* 147 (1972).

[27] *C.L. Khetrapal, A. Kunwar, A.S. Tracey & P. Diehl,* 'Lyotropic Liquid Crystals', 'NMR Basic Principles and Progress', Vol. 9, eds. P. Diehl, E. Fluck and R. Kosfeld, Springer-Verlag, Berlin, 1975.

[28] *Bruker*-Report *3* (1979).

[29] *C.H. Townes & B.P. Dailey,* J. Chem. Phys. *17,* 782 (1949).

[30] *R.C. Long Jr.,* J. Magn. Reson. *12,* 216 (1973).