Solid state ^{13}C and ^1H MAS NMR investigations of $\text{C}_{60}(\text{ferrocene-d}_{10})_2$ complex

E. Shabanova, K. Schaumburg and F.S. Kamounah *

*CISMI, Department of Chemistry, University of Copenhagen, Universitetsparken 5,
DK-2100 Copenhagen, Denmark*

Abstract. The article presents NMR investigations of a molecular crystalline material $\text{C}_{60}(\text{ferrocene-d}_{10})_2$, which consists of two highly mobile molecules. ^{13}C and ^1H NMR line shapes and T_1 relaxation times are discussed and compared with results obtained for the undeuteriated compound. The mobilities of C_{60} and ferrocene molecules were found to increase in the complex in comparison with the two components as crystalline materials.

Keywords: Molecular crystal, plastic crystal, C_{60} , ferrocene, ^{13}C and ^1H NMR

1. Introduction

Molecules in crystalline C_{60} [1,2] and ferrocene [2–5] have been shown to carry out a rapid rotations at room temperature. The mobilities of the molecules have been found to be changed when they are combined in the crystalline complex $\text{C}_{60}(\text{ferrocene})_2$ [2] (Fig. 1). A more complete description of the molecular mobility can be obtained by extension of the NMR investigations to include the deuteriated material $\text{C}_{60}(\text{ferrocene-d}_{10})_2$. Here it is possible to neglect nuclear dipolar interactions. Therefore, comparing the results for deuteriated and undeuteriated complexes it should be possible to separate dipolar ^1H contributions from other interactions.

To explore the dynamical properties of the ferrocene molecules in greater detail, the ^2H NMR [3,6] investigations should be performed. The corresponding results will be published elsewhere. The present article describes ^{13}C and ^1H NMR results obtained in $\text{C}_{60}(\text{ferrocene})_2$ and $\text{C}_{60}(\text{ferrocene-d}_{10})_2$.

2. Experimental

The $\text{C}_{60}(\text{ferrocene-d}_{10})_2$ complex [7] was prepared from C_{60} (99.99%) [8] and ferrocene-d₁₀ [9] according to the procedure described elsewhere [2]. As a result, 95% of protons has been exchanged with deuterium in ferrocene-d₁₀. Statistically, the molecule investigated is composed of: 57% ferrocene-d₁₀, 36% ferrocene-d₉ and 7% ferrocene-d₈. Other isotopomers are present in negligible amounts [9].

The NMR results reported have been obtained at a room temperature. Most of the NMR experiments were performed on a Bruker MSL300 spectrometer in a magnetic field of 7.4 T, which corresponds to a ^{13}C Larmor frequency of 75.5 MHz and ^1H Larmor frequency of 300.130 MHz. ^{13}C and ^1H 90° pulses

*Corresponding author. Tel: +45 35 32 18 24; Fax: +45 39 27 12 07; E-mail: f.kamounah@symbion.ki.ku.dk; URL: <http://www.cismi.dk>.

Fig. 1. Schematic representation of the $\text{C}_{60}(\text{ferrocene})_2$ packing arrangement. The black and white sites of ferrocene molecules are not crystallographic equivalent due to the $P\bar{1}$ symmetry.

were adjusted to $6\ \mu\text{s}$. The investigations were carried out on a Bruker MAS HPWP73A probehead at 5 kHz MAS rate.

Spin–lattice relaxation time (T_1) measurements were performed using the magnetization saturation recovery with proton decoupling applied during r.f. pulses and acquisition in order to eliminate additional line broadening from ^{13}C interactions with protons. ^{13}C and ^1H chemical shifts are reported relative to tetramethylsilane.

To determine the field-dependent contributions to the NMR lines, some experiments were performed on a Varian INOVA-600 spectrometer using the similar parameters.

3. Results and discussion

3.1. ^{13}C MAS NMR

The pure crystalline C_{60} and undeuterated ferrocene have chemical shifts at 143 ppm [1] and 69.4 ppm [10], respectively. Since both molecules undergo fast reorientational motion, their chemical shifts in a complex should mainly be determined by the intrinsic properties of the molecules. The ^{13}C MAS NMR spectrum of $\text{C}_{60}(\text{ferrocene})_2$ (**1**) was observed to consist of two lines: a high intensity narrow C_{60} line at

Fig. 2. 300 MHz spectrometer: ^{13}C MAS (5 kHz) NMR spectrum of ferrocene line in **1** $\text{C}_{60}(\text{ferrocene})_2$ **2** $\text{C}_{60}(\text{ferrocene-}d_{10})_2$.

143 ppm and a lower intensity ferrocene signal at 68–72 ppm. No change in appearance of the C_{60} line has been observed in comparison with the pure C_{60} . A single line of $\Delta 1/2$ (width at $1/2$ height) = 94 Hz has been observed for pure ferrocene, while a broad double line appeared for ferrocene in **1**. The double ferrocene signal (Fig. 2a) is due to the two crystallographically unequivalent sites of the ferrocene in the compound. An X-ray study has reported [7], that the compound has a triclinic symmetry $P\bar{1}$ where the C_{60} molecule lies in the crystallographic inversion centre (Fig. 1). The two rings of one ferrocene molecule are situated differently in the structure with respect to the C_{60} molecules. As a result, the ring, which is situated closer to C_{60} should have a stronger charge transfer interactions with C_{60} and, consequently, it should display a signal at higher ppm. The two maxima at 69.8 ppm and 71.2 ppm are observed for ferrocene in **1** (Fig. 2a). $\Delta 1/2$ for each maxima can be estimated as 70 ± 2 Hz. Both maxima have the same integral intensities, as expected for equal amounts of nuclei in the two rings. Due to a small change in ferrocene chemical shift it can be concluded that no strong charge transfer is taking place in **1**.

A similar spectrum has been observed for $\text{C}_{60}(\text{ferrocene-}d_{10})_2$ (**2**). Here, the two ferrocene maxima (Fig. 2b) are situated at 69.5 ppm and 70.8 ppm with $\Delta 1/2$ of 80 ± 2 Hz each. These maxima are 0.35 ± 0.1 ppm shifted to the higher field, reflecting weaker charge-transfer interactions in the deuteriated compound.

In comparison with **1** the following changes in the ferrocene line shape should appear in **2**: (i) the line should become more narrow due to the almost complete replacement of ^1H and the consequently reduced ^{13}C – ^1H spin–spin couplings and dipole–dipole interactions [11]; (ii) the line should be broadened due to ^{13}C – ^2H spin–spin coupling [11] and residual ^{13}C – ^2H dipolar interactions [12] – these can be estimated to contribute a maximum 35 Hz broadening. Interactions should be averaged due to fast ferrocene rotation around the C_5 axis and due to MAS. The chemical shift anisotropy (CSA) broadening should be substantially the same in **1** and **2**. Comparison of the two spectra (Fig. 2a,b) reflects no significant difference in the line shapes. Therefore, it can be expected, that the line shape of ferrocene in **1** and **2** is inhomogeneous and it is due to the anisotropic chemical shift distribution, while other interactions are averaged out. To support this assumption, both spectra were acquired with and without high power proton decoupling. This did not have any influence on the appearance of the spectra.

Analogous spectra have been acquired at 600 MHz spectrometer with similar settings. Experimental results are shown in Fig. 3a,b. Here, the positions of the maxima in ppm are identical with the 300 MHz results. This is in accordance with the two chemical shifts for the two nonequivalent ferrocene rings (Fig. 1). The high field ferrocene maximum of **1** has a broadening $\Delta 1/2$ of 110 ± 2 Hz, while the low

Fig. 3. 600 MHz spectrometer: ^{13}C MAS (5 kHz) NMR spectrum of ferrocene line in **1** $\text{C}_{60}(\text{ferrocene})_2$ **2** $\text{C}_{60}(\text{ferrocene-}\text{d}_{10})_2$.

Table 1
 ^{13}C T_1 (s) of **1** and **2** at 75.5 MHz

Compound	1	2
C_{60}	5.9 ± 0.2	10.0 ± 1.0
Low field maximum	0.16 ± 0.05	1.0 ± 0.3
High field maximum	0.36 ± 0.05	4.0 ± 0.5

field maximum shows $\Delta 1/2$ of 140 ± 2 Hz. The integral intensities of the lines are still 1 : 1. In **2** both maxima have changed $\Delta 1/2$ to 110 ± 2 Hz. This observation rules out CSA as the dominant factor in describing the line broadening. The difference in line widths reflects that different spectral densities are implied at the double field strength and that the lines are broadened due to lifetime.

Additional information about molecular mobility can be obtained from T_1 measurements. Results are presented in Table 1. As a consequence of the high deuteration of **2** the difference in C_{60} magnetization recovery in **1** and **2** can be considered to be due to relaxation contribution from intermolecular $^{13}\text{C}(\text{C}_{60})\text{--}^1\text{H}(\text{ferrocene})$ dipole–dipole interactions. The dipole–dipole contribution $T_{1,dd}$ equal to 15 s can be estimated according to the expression: $R_\Sigma = R_{dd} + R_{CSA}$. Here, $R_{(x)} = 1/T_{1(x)}$ is the relaxation rate. It is known, that the T_1 relaxation in pure crystalline C_{60} is due to CSA and the relaxation time is about 45–50 s [13]. The $T_{1,CSA}$ of 10 s in **1** and **2** is consistent with a much higher mobility of C_{60} .

Nonequivalence of the two ferrocene rings (Fig. 1) are also reflected in spin–lattice relaxation times T_1 of the ferrocene (Table 1). The relaxation rates for the low (l) and high (h) field maxima in **1** and **2** are due to CSA and due to the $^{13}\text{C}\text{--}^1\text{H}$ dipole–dipole interactions. Neglecting the dipole–dipole interactions in **2** the corresponding relaxation rates can be expressed as:

$$R_\Sigma^{1,l} = R_{dd}^{1,l} + R_{CSA}^l,$$

$$R_\Sigma^{1,h} = R_{dd}^{1,h} + R_{CSA}^h,$$

$$R_\Sigma^{2,l} = R_{CSA}^l,$$

$$R_\Sigma^{2,h} = R_{CSA}^h.$$

Because of high $R_\Sigma = R_{dd} + R_{CSA}$ deuteration in **2** the difference in the relaxations between **1** and **2** can be considered as a relaxation contribution due to $^{13}\text{C}(\text{ferrocene})\text{--}^1\text{H}(\text{ferrocene})$ dipole–dipole

interactions. Using the experimental data from the Table 1 these contributions can be estimated as $T_{1,dd}^{1,l} = 0.19 \pm 0.08$ s for the low field maximum and $T_{1,dd}^{1,h} = 0.4 \pm 0.06$ s for the high field maximum. The low field maxima, which are corresponding to the ferrocene rings situated closer to C_{60} , have faster relaxation times. From the experimental data in Table 1, the T_1 's of low and high field maxima differ with almost the same ratio 4 for both **1** and **2**, namely:

$$R_{\Sigma}^{1,l}/R_{\Sigma}^{2,l} \approx R_{\Sigma}^{1,h}/R_{\Sigma}^{2,h},$$

$$R_{\Sigma}^{1,l}/R_{\Sigma}^{1,h} \approx R_{\Sigma}^{2,l}/R_{\Sigma}^{2,h}.$$

Both ratios lead to the condition, that in the compound **1**:

$$R_{dd}^{1,l}/R_{CSA}^l \approx R_{dd}^{1,h}/R_{CSA}^h.$$

In comparison with the $T_1 = 16$ s for the pure crystalline ferrocene, a faster relaxation in **1** and **2** is due to higher molecular mobility in the complex [2].

3.2. ^1H MAS NMR

Strong dipolar decoupling due to high molecular mobility was expected to yield relatively narrow lines in a proton spectrum of **1**. The small amount (5%) of ^1H in **2** was expected to substantially reduce dipole–dipole interactions between the protons and, consequently, to course a further narrowing of ^1H NMR lines.

^1H MASNMR spectrum of pure crystalline ferrocene have been acquired as a reference. This spectrum represents a broad Gaussian-shaped line with $\Delta 1/2$ of 1.4 kHz (4.6 ppm) at a chemical shift of 4.3 ± 0.2 ppm. In **1** the ^1H line became almost twice narrower with $\Delta 1/2$ of 750 Hz (2.5 ppm) at 4.3 ± 0.1 ppm. This reflects the dilution of ferrocene molecules and an increased molecular mobility in the complex yielding an increased averaging of ^1H – ^1H dipole–dipole interactions. In the “absence” of ^1H – ^1H dipole–dipole interactions, **2** shows a ^1H line at 4.4 ppm with $\Delta 1/2$ of 270 Hz (0.9 ppm). 600 MHz spectra showed a line with $\Delta 1/2$ of 840 Hz (1.4 ppm) for **1** and a line with $\Delta 1/2$ of 540 Hz (0.9 ppm) for **2**. Here, the line width of **1** includes the influence of residual ^1H – ^1H dipole–dipole interactions. The line width in **2** is identical in ppm for the both magnetic fields, which is likely due to chemical shift distribution. The width of 0.9 ppm is still not sufficiently small to observe any isotope effect on chemical shift. No change of the width have been observed for **2** at higher rotation frequencies up to 12 kHz.

Spin–lattice relaxation times at 300.13 MHz were found as follows: $T_1 = 0.94 \pm 0.05$ s for **1**, and $T_1 = 1.56 \pm 0.06$ s for **2**. The major contributions to the relaxation are due to CSA and due to the ^1H – ^1H dipole–dipole interactions. Thus, the relaxation rates can be described by expression $R_{\Sigma} = R_{dd} + R_{CSA}$. Taking into account that ^1H – ^1H dipole–dipole interactions in **2** are negligibly small the ^1H – ^1H dipolar contribution to T_1 can be estimated as 2.4 ± 0.5 s.

4. Conclusions

Higher mobilities of C_{60} and ferrocene molecules were observed in the molecular crystalline complexes $\text{C}_{60}(\text{ferrocene})_2$ and $\text{C}_{60}(\text{ferrocene-}d_{10})_2$ in comparison with the crystalline C_{60} and ferrocene

materials. The nonequivalence of the two ferrocene rings in the complexes was reflected in two chemical shifts for ferrocene. It was found that due to the high molecular mobility a major part of the dipole–dipole interactions have been averaged out. Therefore, T_1 relaxation of the $\text{C}_{60}(\text{ferrocene})_2$ and $\text{C}_{60}(\text{ferrocene-}\text{d}_{10})_2$ are mainly due to CSA. A slow dipolar contributions to the relaxation due to interactions with protons were determined for $\text{C}_{60}(\text{ferrocene})_2$ by comparison with $\text{C}_{60}(\text{ferrocene-}\text{d}_{10})_2$.

The results would stimulate further structural and dynamic studies of $\text{C}_{60}(\text{ferrocene-}\text{d}_{10})_2$ by ^2H NMR.

Acknowledgements

The authors would like to acknowledge H.J. Jacobsen and R. Johansen from NMR Instrument Centre, Aarhus University, for useful discussions and possibility to use the Varian INOVA-600 spectrometer.

References

- [1] C.A. Pennington and V.A. Stenger, *Reviews of Modern Physics* **68** (1996), 855.
- [2] E. Shabanova, K. Schaumburg and F. Kamounah, *Can. J. Appl. Spectroscopy* **43**(2) (1998), 53.
- [3] S.J. Heyes and C.M. Dobson, *Magn. Res. Chem.* **28** (1990), s37.
- [4] A.E. Aliev, K.M. Harris, I.J. Shannon, C.J. Glidewel, C.M. Zakaria and P.A. Schofeld, *J. Phys. Chem.* **99** (1995), 12008.
- [5] A.M. Orendt, J.C. Facelli, Y.J. Jiang and D.M. Grant, *J. Phys. Chem. A* **102** (1998), 7692.
- [6] D. O'Hare, S.J. Heyes, S. Barlow and S. Mason, *J. Chem. Soc., Dalton Trans.* (1996), 2989.
- [7] J.D. Crane, P.B. Hitchcock, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc., Chem. Commun.* (1992), 1764.
- [8] Molecules prepared by M. Plotniece, Riga Technical University, Faculty of Chemical Technology, Dept. of Organic Chemistry, Azenes 14, Riga, LV-1048.
- [9] E. Shabanova, K. Schaumburg and F.S. Kamounah, *J. Chem. Res. (S)* (1998), 364.
- [10] S.J. Heyes, N.J. Clayden and C.M. Dobson, *J. Phys. Chem.*, **95** (1991), 1547.
- [11] D.L. Pavia, G.M. Lampman and G.S. Kriz, *Introduction to Spectroscopy*, Saunders College Publishing, 1979.
- [12] S.D. Swanson, S. Ganapathy and R.G. Bryant, *J. Magn. Res.* **73** (1987), 239.
- [13] M. Kanowski, G. Buntkowsky, H. Werner, M. Wohlers, R. Schloegl, H.-M. Vieth and K. Lueders, *Mol. Cryst. Liq. Cryst.* **245** (1994), 271.