J. Phys. Chem. A **1997,** *101,* 1793−1797

Anisotropy of Molecular Reorientation in Pure Liquid Benzene Using Nuclear Relaxation of the Longitudinal ^{13}C−^{1}H Two-Spin Order

Hélène Python, Pierre Mutzenhardt, and Daniel Canet*

Laboratoire de Méthodologie RMN,† Université Henri Poincaré, Nancy I,
B.P. 239-54506 Vandoeuvre-lès-Nancy (Cedex), France

Received: October 11, 1996; In Final Form: December 29, 1996⊗

Simple pulse sequences have been used to determine and isolate most carbon-13 and proton longitudinal relaxation parameters in pure liquid benzene (carbon-13 in natural abundance). The derived parameters include specific longitudinal proton and carbon-13 relaxation rates, direct and remote proton−carbon cross-relaxation rates, proton−proton cross-relaxation rates, and the cross-correlation rate involving direct proton−carbon dipolar interaction and carbon shielding anisotropy (the latter being derived from the evolution of the initially created longitudinal spin order). From these data, it was possible to estimate the dipolar intermolecular contributions to proton and carbon longitudinal nuclear relaxations and the anisotropy of molecular reorientation (the two relevant correlation times are found to be at 25 °C: $\tau_{\|} = 0.58$ ps and $\tau_{\perp} = 1.62$ ps; $\tau_{\perp}$ associated with the tumbling of the symmetry axis perpendicular to the molecular plane and $\tau_{\|}$ associated with rotation around this axis).

Introduction

Reorientation of the benzene molecule in the liquid state has been the subject of numerous studies. In addition to this abundant literature, reference can be made to the two most recent works dealing with nuclear spin relaxation techniques.[1,2] Only two correlations times are needed for describing this rotational motion: $\tau_{\perp}$ associated with the tumbling of the symmetry axis perpendicular to the molecular plane, and $\tau_{\|}$ associated with rotation around that axis. It turns out that most relaxation parameters arising from dipolar interactions or quadrupolar interactions (in the case of deuterated benzene) are related to reorientation of in-plane vectors for which the effective correlation time τ_i can be expressed as

$$\tau_i = \frac{1}{4}\left(\tau_{\perp} + 9\frac{\tau_{\|}\tau_{\perp}}{2\tau_{\perp} + \tau_{\|}}\right) \tag{1}$$

Clearly, the measurement of a relaxation parameter involving an out-of-plane vector is required so as to reach the reorientation anisotropy defined usually by the parameter $\chi = \tau_{\perp}/\tau_{\|}$. A good candidate is the relaxation mechanism arising from shielding anisotropy, usually called CSA (for chemical shift anisotropy) mechanism. ^{13}C shielding anisotropy is especially appealing because it is important (182 ppm) and because the main direction of the shielding tensor is perpendicular to the molecular plane. As a matter of fact, it is essentially the ^{13}C CSA mechanism which has been used[1,2] in order to detemine the parameter χ. However, there seems to be some inconsistencies in the values of χ found in the literature[1−3] and it may be worth attempting further derivation of this parameter possibly through novel experimental procedures capable of yielding accurate values for the dipolar and CSA contributions (which should provide τ_i for the former and essentially $\tau_{\perp}$ for the latter). In this respect, the present paper deals with pulse sequences aiming at the determination of dipolar cross relaxation (i) between carbon-13 and its directly bound proton, (ii) between carbon-13 and remote protons including intra- and intermolecular contributions. The discrimination between those two types of protons will be performed by selectivity procedures based on the existence of a J coupling between directly bonded ^{13}C and ^{1}H. On the other hand, the CSA mechanism will be evaluated by the so-called interference term which arises from a cross-correlation spectral density involving the C−H dipolar interaction and the ^{13}C CSA mechanism. Coupry et al.[2] obtained this parameter by following the creation of the so-called longitudinal spin order from longitudinal magnetization. Let us recall that the longitudinal spin order, represented by the product operator $2I_z^{\mathrm{C}}I_z^{\mathrm{H}}$, can be converted into an observable antiphase doublet of splitting J_{CH}, for example, a carbon antiphase doublet by applying a $(\pi/2)_x$ pulse to ^{13}C; this yields a state represented by $2I_y^{\mathrm{C}}I_z^{\mathrm{H}}$. The longitudinal order is zero at thermal equilibrium and can be created in two ways: (i) by relaxation through a coupling term with longitudinal magnetization, which is precisely the dipolar−CSA interference, (ii) by a special pulse sequence whose goal is first to produce an antiphase doublet which is then converted into the longitudinal order by an appropriate selective pulse (in a way inverse to that described above for its observation). The longitudinal spin order so created should then decay to zero according to its own relaxation rate with a possible contribution arising again from the CSA−dipolar interference term which induces the buildup of some longitudinal magnetization. This buildup will manifest itself at the observation stage by a in-phase doublet superposed to the antiphase doublet due to the longitudinal order. While Coupry et al.[2] used approach (i), we shall be dealing here with approach (ii) with the additional motivation of studying the relaxation behavior of longitudinal order, considered only in rare instances[4] for small molecules while recognized as very useful in the case of large biomolecules.[5]

Theory

The first set of experiments to be presented below will be exclusively devoted to the determination of cross-relaxation rates between a carbon-13 whose longitudinal magnetization will be denoted by I_z^{C} and (i) its directly bonded proton (longitudinal magnetization denoted by I_z^{H}), (ii) the two protons in ortho position with respect to the considered carbon (dubbed in the

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† URA CNRS 406-LESOC; FU CNRS E008-INCM.

⊗ Abstract published in *Advance ACS Abstracts,* February 15, 1997.

S1089-5639(96)03130-1 CCC: $14.00

following as "remote" protons) with the sum of their longitudinal magnetizations denoted by $I_z^{H'}$. It can be mentioned that contributions from other protons, especially the ones of other molecules, are included in H′ due to the impossible discrimination among all these protons and to the necessarily simplified interpretation which is based on the following enlarged Solomon equations

$$\frac{d}{dt}I_z^C = -R_1^C(I_z^C - I_{eq}^C) - \sigma_{CH}(I_z^H - I_{eq}^H) - \sigma_{CH'}(I_z^{H'} - 2I_{eq}^H)$$

$$\frac{d}{dt}I_z^H = -R_1^H(I_z^H - I_{eq}^H) - \sigma_{CH}(I_z^C - I_{eq}^C) - \sigma_{HH'}(I_z^{H'} - 2I_{eq}^H)$$

$$\frac{d}{dt}I_z^{H'} = -R_1^{H'}(I_z^{H'} - 2I_{eq}^H) - 2\sigma_{CH'}(I_z^C - I_{eq}^C) - 2\sigma_{HH'}(I_z^H - I_{eq}^H) \quad (2)$$

In these equations, I_{eq}^C and I_{eq}^H are the equilibrium magnetization for carbon-13 and for *one* proton, respectively; R_1^C, R_1^H, and $R_1^{H'}$ are the specific relaxation rates; σ_{CH} is the cross-relaxation rate between the carbon-13 and its directly bonded proton; $\sigma_{CH'}$ and $\sigma_{HH'}$ are cross-relaxation rates with *one* H′ proton. Actually, we shall focus on cross-relaxation rates whose interpretation is unambiguous since they depend solely on the dipolar mechanism. Moreover, as extreme narrowing conditions certainly apply here and as the correlation time τ_i (see eq 1) prevails for all in-plane vectors, their general expression is given by

$$\sigma_{AX} = (1/2)(\mu_0/4\pi)^2(\gamma_A\gamma_X\hbar/r_{AX}{}^3)^2\tau_i \quad (3)$$

where the various symbols have their usual meaning, r_{AX} being the distance between the two nuclei A and X. Moreover, the specific relaxation rate $R_1^{H'}$ differs from R_1^H by the $^{13}C-^{1}H$ dipolar contribution (which, compared to the cross-relaxation rate, is twice as large in the relaxation rate) so that

$$R_1^{H'} = R_1^H - 2\sigma_{CH} \quad (4)$$

Finally, R_1^C can be determined independently from a classical ^{13}C inversion-recovery experiment in the presence of proton decoupling. Experiments based on eqs 2 should be devised so as to yield the remaining unknowns which are R_1^H, σ_{CH}, $\sigma_{CH'}$, and $\sigma_{HH'}$. It can be noticed that the whole set of eqs 2 governs carbon-13 longitudinal relaxation provided that protons H′ are effectively perturbed. Suppose, for instance, that protons H′ are selectively inverted while the proton H remains at thermal equilibrium. Carbon-13 longitudinal relaxation can be affected via two possible relaxation pathways: (i) directly through $\sigma_{CH'}$, and (ii) in a relayed manner, first through $\sigma_{HH'}$ which will perturb I_z^H; the latter will then act on I_z^C through σ_{CH}. Conversely, if H′ magnetization is left at thermal equilibrium, the above mechanisms would be active only at very long times since this would require a further cross-relaxation step, namely the perturbation of H′ via $\sigma_{HH'}$ (or $\sigma_{CH'}$). Clearly, in the case where the proton H is selectively inverted, carbon-13 data can be safely treated in the two-spin approximation:

$$\frac{d}{dt}I_z^C = -R_1^C(I_z^C - I_{eq}^C) - \sigma_{CH}(I_z^H - I_{eq}^H)$$

$$\frac{d}{dt}I_z^H = -R_1^H(I_z^H - I_{eq}^H) - \sigma_{CH}(I_z^C - I_{eq}^C) \quad (5)$$

where cross relaxation with proton H′ has been ignored.

So far, the CSA relaxation mechanism has been only implicitly considered by its contribution to specific relaxation rates. However, at the magnetic fields considered in this paper, it can be neglected (in the specific relaxation rates R_1^H and R_1^C) with respect to other contributions (dipolar and/or spin rotation[1]). It turns out that the CSA mechanism is nevertheless prone to act via an interference term, arising from cross correlation with the dipolar interaction. This phenomenon has been known for a long time[6] and, in a two-spin system, amounts to coupling simple longitudinal magnetizations to the so-called longitudinal spin order represented in the present situation by the product operator $2I_z^CI_z^H$, so that eqs 5 have to be appended as follows[7]

$$\frac{d}{dt}I_z^C = -R_1^C(I_z^C - I_{eq}^C) - \sigma_{CH}(I_z^H - I_{eq}^H) - \sigma_{CSA(C),d}(2I_z^CI_z^H)$$

$$\frac{d}{dt}I_z^H = -R_1^H(I_z^H - I_{eq}^H) - \sigma_{CH}(I_z^C - I_{eq}^C) - \sigma_{CSA(H),d}(2I_z^CI_z^H)$$

$$\frac{d}{dt}(2I_z^CI_z^H) = -R_1^{C,H}(2I_z^CI_z^H) - \sigma_{CSA(C),d}(I_z^C - I_{eq}^C) - \sigma_{CSA(H),d}(I_z^H - I_{eq}^H) \quad (6)$$

where the interference term can be expressed as

$$\sigma_{CSA(X),d} = (1/5)(\mu_0/4\pi)\gamma_X B_0 \Delta\sigma_X(\gamma_A\gamma_X\hbar/r_{AX}{}^3)\tau_{CSA(X)} \quad (7)$$

(7) is expressed within the extreme narrowing hypothesis: $\Delta\sigma_X$ is the shielding anisotropy of nucleus X and $\tau_{CSA(X)}$ is an effective correlation time which depends on the shielding asymetry parameter $\eta_{CSA(X)}$, and on quantities already defined ($\tau_\perp$ and χ), thus providing additional data for the determination of rotational correlation times:

$$\tau_{CSA(X)} = \frac{1 + 3\eta_{CSA(X)} + 2\chi}{1 + 2\chi}\tau_\perp \quad (8)$$

Still in extreme narrowing conditions, $R_1^{C,H}$, the specific relaxation rate of the longitudinal spin order, is simply related to relaxation rates already defined

$$R_1^{C,H} = R_1^C + R_1^H - (14/5)\sigma_{CH} \quad (9)$$

Although interference terms involving proton shielding anisotropy have been determined in some instances,[2,8−12] in spite of the small value of the latter quantity, we shall rather focus on $\sigma_{CSA(C),d}$ which should lead to more pronounced effect due to the relatively large value of benzenic carbon shielding anisotropy (182 ppm). As can be seen in eqs 6, $\sigma_{CSA(C),d}$ can be measured either from the creation by relaxation of $(2I_z^CI_z^H)$ and its superposition to the evolution of I_z^C or, in a reverse way, from the creation by relaxation of I_z^C and its superposition to the evolution of $(2I_z^CI_z^H)$. We shall prefer the latter approach because, for the former, the desired effect, which anyway must occur at long mixing times, might be obscured by cross relaxation with remote protons (protons H′, see eqs 2). Conversely, this should not affect the evolution of the longitudinal spin order (at least to a very good order of approximation).

Experimental Section

Almost all measurements were carried out at 25 °C with the help of a Bruker DRX 400 spectrometer operating at 100 MHz for carbon-13 measurements. The only exception concerns a

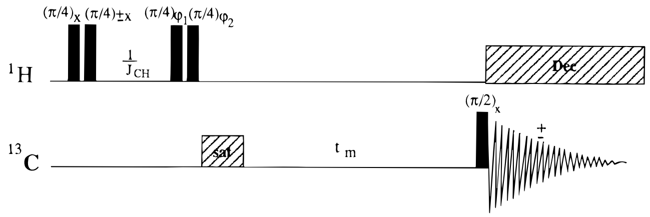

Figure 1. Pulse sequence used to measure cross-relaxation rates in the case of proton spectrum involving a single line and its associated ^{13}C satellites. The proton carrier frequency is set at the frequency of this single line so that the heteronuclear coupling governs exclusively the evolution during the interval $1/J_{CH}$. The phase cycle affecting the second $(\pi/4)$ pulse, φ_1, φ_2 and the acquisition is such that the second experiment corresponds to a reference (without, in principle, any disturbance of proton magnetizations), subtracted from the first experiment which involves a selective inversion. The interval denoted by "sat" is composed of two long pulses $(2\alpha)_x(\alpha)_y$ aimed at destroying any ^{13}C magnetization. t_m is the mixing time during which transfers by cross relaxation take place. The phase cycles for the selective inversion of (i, top) ^{13}C satellites in the proton spectrum (the directly bonded proton), (ii, bottom) the main line in the proton spectrum (remote protons denoted H′ in the text) are as follows: (i) $\varphi_1 = \mp x$, $\varphi_2 = -x$ and (ii) $\varphi_1 = \pm x$, $\varphi_2 = x$.

proton experiment, aimed at following the evolution of the longitudinal spin order, performed at the same temperature with a home-made spectrometer operating at 200 MHz.

The pulse sequence sketched in Figure 1 is devised either to measure the direct cross-relaxation σ_{CH} or to probe the effects of both $\sigma_{CH'}$ and $\sigma_{HH'}$ (see eqs 2). This is acheived by choosing the proper phases for the last pair of $(\pi/4)$ pulses of the proton channel. For the first phase setup, ^{13}C satellites in the proton spectrum are selectively inverted whereas the second one leaves these satellites unchanged and inverts the main signal in the proton spectrum (which corresponds to protons H′). This very simple sequence, derived from X filtered HOESY experiments,[13] works provided that the main benzene proton signal is set on resonance, the precession interval $1/J_{CH}$ leading to a situation where both ^{13}C satellites on the one hand and the main signal on the other hand are opposite along the y axis of the rotating frame. Phases of the last proton pulse pair take them along $+z$ or $-z$ accordingly. Furthermore, the phase cycling allows for the production of a reference experiment which is subtracted from the experiment where a selective inversion was applied. In this way, carbon magnetization measured at the end of the mixing time t_m reflects solely transfers by cross relaxation, this procedure removing carbon-13 magnetization which would reconstruct through its specific longitudinal relaxation subsequently to the saturation stage. Some caution must be exercized concerning initial conditions prior to the mixing interval (which must be effectively used in the exploitation of Solomon equations). This is because ^{13}C proton satellites spread over a finite frequency range due to proton−proton coupling constants (magnetic equivalence no longer prevails). As a consequence, inversion or recovery (along $+z$) may be imperfect and it is important to determine the actual state of all proton magnetizations. This is accomplished via the control experiments performed on the proton channel:

$$(\pi/4)_x(\pi/4)_x - 1/J_{CH} - \text{Acq} \qquad \text{(first step of the phase cycle)}$$

$$(\pi/4)_x(\pi/4)_{-x} - 1/J_{CH} - \text{Acq} \qquad \text{(second step of the phase cycle)}$$

$$(\pi/2)_x - \text{Acq} \qquad \text{(reference experiment)}$$

Finally, in order to check the consistency of the experimental data, a global one-dimensional HOESY experiment was carried out. It amounts to replace the proton preparation period, up to the beginning of the mixing interval, by $(\pi/2)_x(\pi/2)_{\pm x}$. Again, for this experiment, initial conditions have been controlled by means of separate experiments of the same kind as those described above.

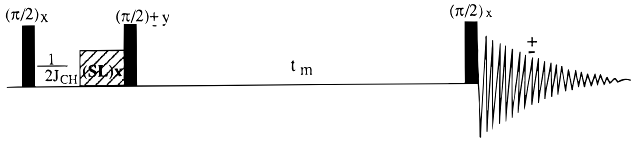

Figure 2. Pulse sequence used to measure the relaxation of the longitudinal spin order. It can be applied indifferently to proton or carbon-13. The first part of the sequence is aimed at creating the longitudinal spin order prior to the mixing interval t_m. Its state is read by the last $(\pi/2)$ pulse.

We turn now to the experiment aimed at measuring relaxation of the longitudinal spin order. It is homonuclear in essence and can be applied indifferently to proton or carbon-13 provided again that on-resonance conditions prevail (Figure 2). By the end of the interval $1/2J_{CH}$, an antiphase configuration exists which can be represented by $2I_x^CI_z^H$ or $2I_z^CI_x^H$ for a carbon-13 or a proton experiment, respectively. The spin lock period, $(SL)_x$ in Figure 2, purges out all unwanted magnetization whereas the $(\pi/2)_{\pm y}$ converts the antiphase configuration into the desired longitudinal spin order $\pm 2I_z^CI_z^H$ (in both experiments), which is then allowed to decay during the mixing time t_m. The last $(\pi/2)_x$ pulse is a read pulse which probes any kind of longitudinal magnetization, including of course the longitudinal spin order which reappears in the form of an antiphase doublet. The phase cycling removes longitudinal magnetization which would have reconstructed through its specific relaxation. Again, the actual initial conditions prior to the mixing interval are determined by means of the two separate experiments

$$(\pi/2)_x - 1/2J_{CH} - (SL)_x - \text{Acq}$$

$$(\pi/2)_x - \text{Acq} \qquad \text{(reference experiment)}$$

Results and Discussion

The first cross-relaxation experiment (Figure 1(i)) which relies upon the selective inversion of ^{13}C satellites in the proton spectrum is dominated by the two parameters σ_{CH} and R_1^H (the true proton relaxation rate), in addition to R_1^C determined from a separate experiment. Indeed, the corresponding data were fitted very satisfactorily by using eq 2 without the need to recourse either to remote dipolar interactions (with H′) or to the coupling with longitudinal spin order (through the CSA−dipolar inteference term). The influence of these two latter mechanisms is actually negligibly small with respect to σ_{CH} and R_1^H even at long mixing times (this feature can be checked by numerical simulations). Thus, from this first experiment, we obtain the following parameters whose accuracy is believed to be better than 5% (R_1^C has been determined from the classical inversion-recovery experiment):

$$R_1^C = 4.3 \times 10^{-2}\ \text{s}^{-1} \qquad \sigma_{CH} = 1.04 \times 10^{-2}\ \text{s}^{-1}$$
$$R_1^H = 7.15 \times 10^{-2}\ \text{s}^{-1}$$

The second cross-relaxation experiment (Figure 1(ii)), which relies upon the selective inversion of the main proton signal (remote protons H′), requires a three-spin analysis as explained in the previous section. In fact, the carbon-13 magnetization buildup is rather weak, reflecting the weakness of (i) the cross relaxation rate $\sigma_{CH'}$ and/or (ii) the relayed relaxation pathway

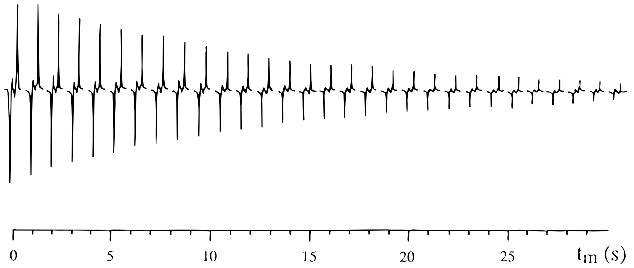

Figure 3. Decay of the longitudinal spin order as probed by the experiment of Figure 2 applied to proton in a field of 4.7 T (200 MHz proton resonance frequency). The central line in each trace corresponds to the residual main signal in the benzene proton spectrum.

$H' \rightarrow H \rightarrow C$. Nevertheless, inserting in eq 2 the parameters previously determined (i.e., R_1^C, σ_{CH}, R_1^H), it proved possible to determine the two remaining parameters with an accuracy comparable to that indicated above (according to an algorithm described elsewhere[14]):

$$\sigma_{CH'} = 5.4 \times 10^{-4}\ s^{-1} \qquad \sigma_{HH'} = 2.1 \times 10^{-3}\ s^{-1}$$

In passing, it can be emphasized that this approach yields nicely the proton−proton cross-relaxation rate, a parameter difficult to obtain by other means. The presently available results (R_1^C, σ_{CH}, R_1^H, $\sigma_{CH'}$, and $\sigma_{HH'}$) can be considered as reliable since they perfectly fit the experimental data obtained by the global one-dimensional HOESY experiment described in the previous section (data not shown). However, they are not in agreement with the conventional NOE factor (whose experimental value, determined by the classical gated decoupling method, is 1.28). Usually, one extracts the dipolar contribution to R_1^C from the confrontation of the NOE factor and the carbon-13 relaxation rate. We find here $2.77 \times 10^{-2}\ s^{-1}$, which, although of the same order of magnitude, is in excess with respect to the expected value of $2.30 \times 10^{-2}\ s^{-1}$ ($2(\sigma_{CH} + 2\sigma_{CH'})$). This is not too surprising, because the approach using the NOE factor strictly applies to a two-spin system and ignores, among other things, dipolar cross relaxation among the proton spin system as well as all dipolar cross-correlation terms.[7,15] Another point of interest is the possible intermolecular contribution to $\sigma_{CH'}$ and $\sigma_{HH'}$. From σ_{CH} and $r_{CH} = 1.08$ Å, we find 0.94 ps for τ_i, which leads to the intramolecular contributions to $\sigma_{CH'}$ and $\sigma_{HH'}$ ($r_{CH'} = 2.15$ Å):

$$(\sigma_{CH'})_{intra} = 1.81 \times 10^{-4}\ s^{-1} \qquad (\sigma_{HH'})_{intra} = 1.22 \times 10^{-3}\ s^{-1}$$

It can be seen that intermolecular dipolar interactions contribute for $^2/_3$ of $\sigma_{CH'}$ and for $^1/_2$ of $\sigma_{HH'}$. Further interpretation of these figures would require molecular dynamics calculation in order to estimate (i) the number of interacting protons and to modify accordingly eqs 2, and (ii) the relative influence of rotational and translational motions.[16]

We turn now to the evolution of the so-called two-spin longitudinal order ($2I_z^C I_z^H$) which can be created from an antiphase configuration as explained in the previous section. The first experiment shown in Figure 3 starts from a *proton* antiphase configuration, meaning that only proton longitudinal magnetization has been disturbed from its equilibrium state. Consequently, as seen from eqs 6, only $\sigma_{CSA(H),d}$ would be able to affect the decay of the longitudinal spin order in addition to the specific relaxation rate $R_1^{C,H}$. Due to the fact that the actual experiment has been carried out at low field (4.7 T, 200 MHz proton resonance frequency) and due to the relatively small proton shielding anisotropy, such an effect is not expected and is not indeed observed (the antiphase doublet which reflects the longitudinal two-spin order remains unaffected, i.e., with two branches of equal intensity). Furthermore, the decay is perfectly monoexponential and can be safely assigned to the sole influence of $R_1^{C,H}$ which is found to be identical to the value determined from the ^{13}C experiment analyzed below. Of course, it would have been more satisfactory to determine the $\sigma_{CSA(H),d}$ interference term which is smaller than $\sigma_{CSA(C),d}$ by a factor of less than 4.[2] This would imply to run the experiment at 400 MHz or more without anyway the warranty of sufficient accuracy. Actually, this measurement was not performed because it was not mandatory to access to motional anisotropy.

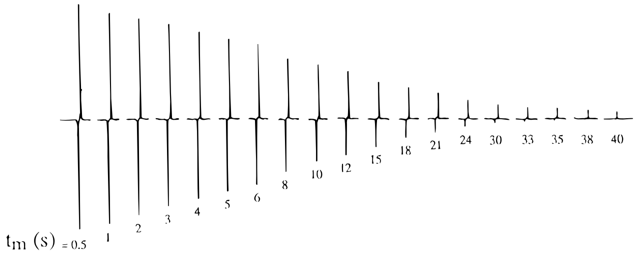

Figure 4. Decay of the apparent longitudinal spin order as probed by the experiment of Figure 2 applied to carbon-13 in a field of 9.4 T (100 MHz carbon resonance frequency). Notice the disappearance of the antiphase doublet at long mixing times which indicates a contribution from the in-phase doublet arising from the CSA−dipolar interference term.

Conversely, the ^{13}C experiment leading to the evolution of the longitudinal two-spin order, because it starts from a carbon antiphase configuration, is dependent on $\sigma_{CSA(C),d}$ and therefore involves primarily the carbon shielding anisotropy much larger than the proton shielding anisotropy, and should lead to stronger effects as far as the interference term is concerned. Moreover, this experiment has been carried out in a field twice as large as the previous one (9.4 T) and should exhibit visible effects. As a matter of fact, Figure 4 exemplifies such a behavior: the antiphase doublet which is a measurement of the longitudinal order evolution exhibits a gradual dissymmetry indicating the appearance of an in-phase contribution arising from the carbon longitudinal magnetization created by the CSA−dipolar interference term. Of course, this can only occur at long mixing times and is effective here because other possible dipolar contributions are not prone to act on the longitudinal spin order. This is in contrast with the simple longitudinal magnetization behavior for which remote dipolar interactions would possibly hinder this effect and this is presumably the reason for which Coupry et al.[2] studied 1,3,5-deuterobenzene rather than normal benzene. Data analysis is better performed by considering (i) the algebraic difference in intensity of the two lines, and (ii) their algebraic sum,[17] both plotted in Figure 5. From eqs 6, it can be seen that the former is dominated by $R_1^{C,H}$, the specific relaxation rate of longitudinal spin order, whereas the latter arises primarily from $\sigma_{CSA(C),d}$. The sum of doublet intensities represents the buildup of the longitudinal magnetization by the CSA−dipolar interference term. Data has been fitted in each case according to eqs 6 (although in the case of $2I_z^C I_z^H$ the decay is monoexponential to a very good approximation and can be simply fitted according to $R_1^{C,H}$) and yield $R_1^{C,H} = 8.33 \times 10^{-2}\ s^{-1}$ and $\sigma_{CSA(C),d} = 7.32 \times 10^{-3}\ s^{-1}$. Concerning $R_1^{C,H}$ it is reassuring to find a value of $8.54 \times 10^{-2}\ s^{-1}$ by inserting into eq 9 the values of $R_1^{C,H}$, R_1^H, and σ_{CH} deduced from pure “cross-relaxation experiments” (see above); this demonstrates the consistency of the whole experimental data set and was in fact one of the goals of the present study.

When dealing with CSA−dipolar interference terms, a point of interest concerns the absolute sign of the indirect coupling

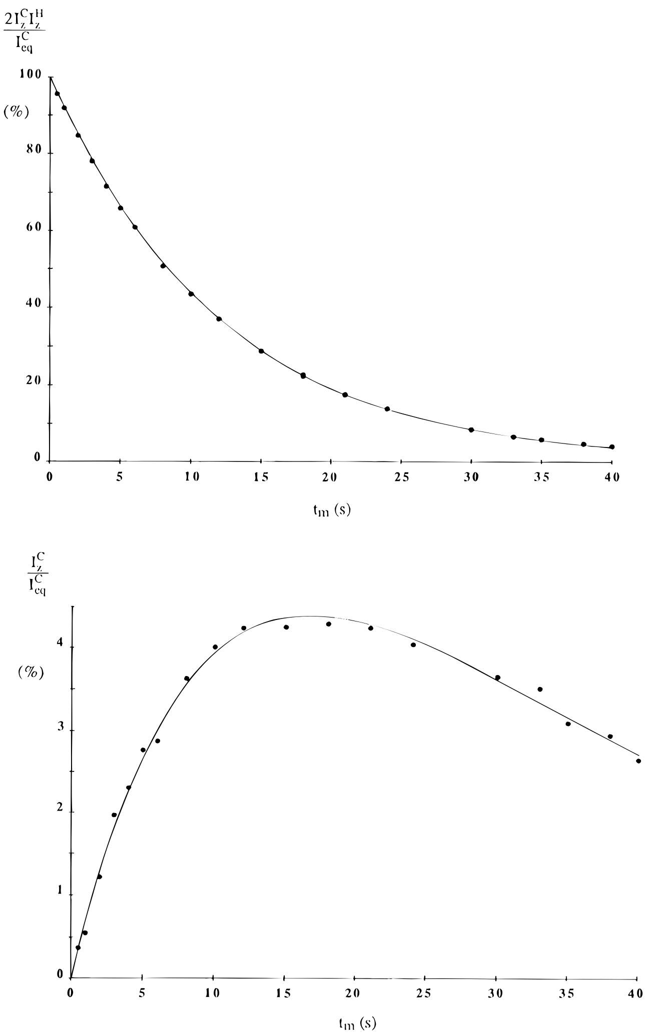

Figure 5. (Top) Evolution of the pure longitudinal spin order as obtained by taking the algebraic difference of the two lines shown in Figure 4. The decay is monoexponential and leads to $R_1^{C,H}$ (see text). (Bottom) Buildup of the pure longitudinal carbon magnetization as obtained by taking the algebraic sum of the two lines shown in Figure 4. This curve depends essentially on the interference term $\sigma_{CSA(C),d}$ (see text). In each case, dots represent experimental data whereas the solid line has been recalculated from the fitted relaxation parameters.

(J_{CH}, which is known to be positive), provided that the sign of the shielding anisotropy $\Delta\sigma$ is available (see eq 7). Here $\Delta\sigma$ is positive so that $\sigma_{CSA(C),d}$ is positive thus leading to a negative contribution of I_z^C which adds to the longitudinal spin order. This can be seen very simply by a first-order expansion:

$$I_z^C(t_m) = I_z^C(0) + t_m\left(\frac{d}{dt}I_z^C\right)_{t=0} = -t_m\sigma_{CSA(C),d}2I_z^CI_z^H(0)$$

Now, when converted into transverse magnetization by a $(\pi/2)_x$ pulse acting on carbon-13, $-I_z^C$ and $2I_z^CI_z^H$ become $-I_y^C$ and $2I_y^CI_z^H$, respectively. If, with the usual convention (retained in Figure 4), frequency increases from right to left, the leftmost line in the carbon-13 doublet is associated with $I_z^H = 1/2$ provided that J_{CH} is positive and should be positive for $2I_y^CI_z^H$ (by contrast with the phasing of spectra in Figure 4). Nevertheless, the fact that this line disappears upon the superposition of $-I_y^C$ and $2I_y^CI_z^H$ demonstrates the consistency of all the above assumptions (J_{CH} and $\sigma_{CSA(C),d}$ both positive).

Finally, we can derive $\tau_{CSA(C)}$ by inserting $\Delta\sigma_C = 182$ ppm into eq 7. With $\eta_{CSA(C)} = 0.72$,[1] combining $\tau_{CSA(C)}$ and τ_i deduced from the cross relaxation rate σ_{CH}, we arrive at $\tau_\perp = 1.62$ ps and $\chi(=\tau_\perp/\tau_\parallel) = 2.8$, this latter value being in good agreement with the results of Coupry et al.[2] The fact that their $\tau_\perp$ is significantly larger (2.2 ps) should be ascribed to the different temperature (10 °C) at which their experiments are carried out.

As a conclusion, we can emphasize the potentiality of longitudinal spin order in view of determining CSA−dipolar interference terms. Because this quantity is purely two-spin in nature, it is expected to be especially sensitive to relaxation parameters involving the two relevant spins (as this is the case for CSA−dipolar interference term). Indeed, this has been nicely verified in the present study where the influence of such a mechanism is clearly demonstrated at long mixing times without any contribution from other (remote) dipolar interactions.

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