^{1}H NMR Study of Molecular Motions in Thiourea Pyridinium Halide Inclusion Compounds

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The proton NMR second moment and spin-lattice relaxation time have been studied for polycrystalline inclusion compounds of thiourea pyridinium chloride, bromide, iodide and their perdeuterated analogues in a wide temperature range. The pyridinium cation reorientation around the pseudohexagonal C_6' symmetry axis over inequivalent barriers and hindered rotation of the thiourea molecule around its C=S bond have been revealed. The activation parameters of the both motions have been found.

Key words: NMR; Molecular Motion; Inclusion Compounds.

1. Introduction

Thiourea inclusion compounds exhibit a wide range of interesting and important fundamental physicochemical properties [1]. In the classical thiourea inclusion host lattice, a channel system is formed by a double helix of hydrogen-bonded thiourea ribbons. Usually the structure has hexagonal channels, which fit together in a honeycomblike system of hexagonal or rhombohedral symmetry. Neutral molecular guests such as medium-sized alicyclic, highly branched hydrocarbons, ketones, esters, halides, or organometalics can be accomodated within each channel [2, 3].

Recently, a substantial amount of research has been focused on the structural and dynamic properties and phase transitions in thiourea solid organic inclusion compounds. Much less is known about the properties of solid organic salts inclusion compounds. Therefore we have chosen such compounds for a study of the molecular dynamics by ^{1}H NMR methods. This paper is focused upon thiourea pyridinium chloride, bromide and iodide inclusion compounds. All the halides were first prepared by Phillips [4]. Although the room-temperature structure of one of the halides was already determined in 1972 by Truter and Vickery [5], the complex single-crystal X-ray experiment for all three halides has been performed quite recently by Prout et al. [6]. The study performed in a wide temperature range has led to the identification of the different phases of these compounds: two in chloride and iodide and three in bromide. The authors did not give the precise temperatures of the phase transitions, giving only the temperature range of each phase change. The recent dielectric study of the halides has revealed more precisely the temperatures of the phase transitions, namely 233 K in chloride, 149 and 180 K in bromide and 165 K in iodide [7].

Prout et al. have found that the halides in all their phases crystallize in the orthorhombic system. At room temperature the compounds belong to the space group Cmcm (chloride: $a = 14.563$ Å, $b = 10.561$ Å, $c = 8.398$ Å; bromide: $a = 14.771$ Å, $b = 10.897$ Å, $c = 8.368$ Å; iodide: $a = 15.119$ Å, $b = 11.230$ Å, $c = 8.237$ Å; $Z = 4$). The pyridinium cation is disordered. In the low temperature phase the chloride crystallises in the space group Pbca with a doubled a axis ($a = 29.021$ Å, $b = 10.418$ Å, $c = 8.374$ Å; $Z = 8$), and the pyridinium cations is partially ordered. The bromide, in the intermedium phase, changes the space group to Cmc2_1 ($a = 44.128$ Å, $b = 10.789$ Å, $c = 8.351$ Å; $Z = 12$), and the a axis is tripled. In the low temperature phase the bromide (space group P2_1cn, $a = 14.431$ Å, $b = 10.984$ Å, $c = 8.291$ Å; $Z = 4$) is fully ordered and isomorphous with the iodide (space group P2_1cn, $a = 14.869$ Å, $b = 11.312$ Å, $c = 8.305$ Å; $Z = 4$).

It has been established that the thiourea molecules are bound via hydrogen bonds into four ribbons, which form a channel parallel to the c axis with an approximately square section. In each channel there is a stack of pyridinium cations, the planes of which are inclined

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at an angle of $\sim 60°$ to the channel axis. Where four channels meet, a second type of channel is formed, in which anions are located.

Besides the X-ray diffraction study, Prout et al. also performed a variable-temperature ^{2}H NMR study of the perdeuteriopyridinium salts in order to obtain information about the molecular dynamics of the compounds. They found a similar dynamic behaviour in all the halides, namely a complex motion involving in-plane libration of the pyridinium ions at low temperatures and additional out-of-plane motion at the higher temperatures.

The aim of our paper is to throw more light on the problem of the motional behavior of the pyridinium cation as well as the thiourea molecules. Accordingly, measurements of the proton NMR second moment and spin-lattice relaxation time T_1 were made as function of temperature of

1.) thiourea pyridinium chloride, bromide and iodide, denoted as T_2(PyH)Cl, T_2(PyH)Br and T_2(PyH)I, respectively, and their partially perdeuterated analogues,

2.) $T_2(d_5PyH)Cl$, $T_2(d_5PyH)Br$, $T_2(d_5PyH)I$, which denote compounds with all H-atoms in the C-H bonds replaced by deuterium,

3.) d_8T_2(PyD)Br, the perdeuterated bromide, in which the H atoms in all N-H bonds are replaced by deuterium.

2. Experimental

The compounds were synthesized as described in [6]. Perdeuterated bromide d_8T_2(PyD)Br was obtained by a dissolution of stoichiometric quantities of perdeuterated thiourea $(ND_2)_2CS$ and the pyridinium bromide in partially deuterated ethanol C_5H_5OD. All crystals obtained were ground to powder, degassed and sealed off under vacuum in glass ampoules.

The second moment of the NMR line was measured as function of temperature by a continuous wave spectrometer working for protons at a frequency of 28 MHz. Its values, found by numerical integration of the absorption curve derivatives were corrected for the finite modulation field.

The spin-lattice relaxation time T_1 was measured – as function of temperature – by pulse spectrometry working at 58.9 MHz. The measurements were performed by using the saturation recovery method. Both spectrometers were constructed in the Radiospectroscopy Laboratory at the Institute of Physics, AMU.

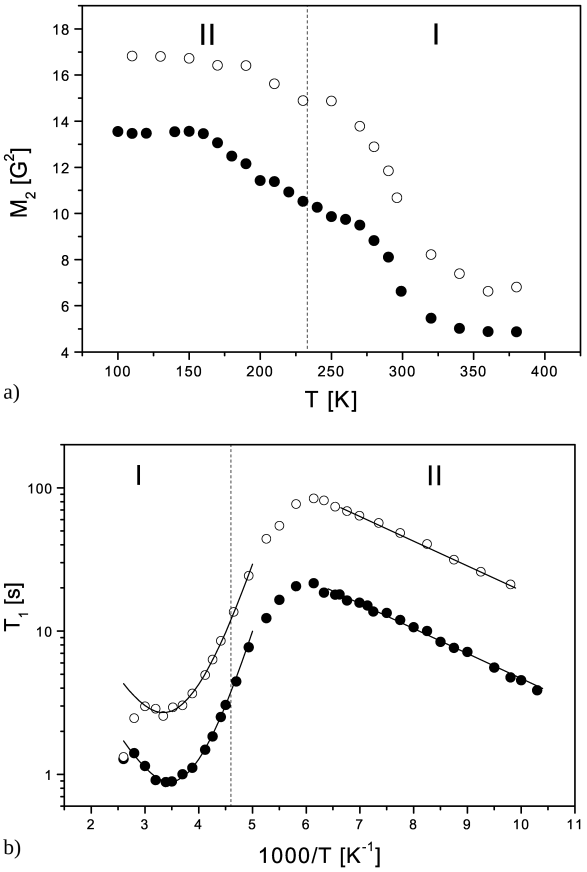

Fig. 1. The temperature dependence of the NMR second moment M_2 (Fig. 1a) and spin-lattice relaxation time T_1 (Fig. 1b) for protonated T_2(PyH)Cl (●) and perdeuterated $T_2(d_5PyH)Cl$ (○).

The temperature of the sample was controlled by means of a gas-flow cryostat and monitored with a Pt resistor to an accuracy of 1 K.

3. Results

The NMR results obtained for thiourea pyridinium chloride, bromide, iodide and their perdeuterated analogues are presented in Figs. 1, 2, and 3, respectively. In the figures dashed lines denote the temperatures of the phase transitions revealed in the dielectric studies.

3.1. Chloride

The second moment of 13.5 G^2 (note that 1 Gauss = 1 Millitesla/10) observed at the lowest temperatures studied starts – at about 165 K – to decrease slowly to 9.7 G^2 registered at 275 K, and then more rapidly to 4.5 G^2 obtained at the highest temperatures. For the $T_2(d_5PyH)Cl$ analogue the second moment decreases from 16.8 G^2 at 110 K to 6.7 G^2 observed above 360 K (Fig. 1a).

The temperature dependence of the spin-lattice relaxation time T_1 shows a minimum of 0.9 s at 295 K for the protonated sample, and of 2.6 s at 299 K for perdeuterated one. Above the minimum – for both samples – T_1 starts to decrease similarly as below 167 K, where a decreasing of T_1 is observed in a wide temperature range (Fig. 1b).

3.2. Bromide

For the protonated sample the second moment decreases from 14.8 G^2 at 100 K to a plateau value of ca 10 G^2, observed in the range of 225 – 275 K, to decrease further to a value of 5.0 achieved at 380 K.

For $T_2(d_5PyH)Br$, the second moment of 16 G^2 observed in phase III diminishes slowly up to 270 K, to decrease then more rapidly to a value of 6.2 G^2 at 380 K.

For $d_8T_2(PyD)Br$ a value of about 3 G^2, registered at our low temperature limit, diminishes monotonically in the whole temperature range to reach 0.9 G^2 at 380 K (Fig. 2a).

Measurements of the spin-lattice relaxation time performed for $T_2(PyH)Br$ and two perdeuterated samples ($T_2(d_5PyH)Br$ and $d_8T_2(PyD)Br$) have revealed very similar plots of the temperature dependence for all of the compounds. In the phase III, the T_1 values diminish, to increase slightly at the phase transition $T_{III\rightarrow II}$ and then decrease again to reach – in the vicinity of 256 K – minima of different depths: 0.9 s for $T_2(PyH)Br$, 3.0 s for $T_2(d_5PyH)Br$ and 2.0 s for $d_8T_2(PyD)Br$ (Fig. 2b).

3.3. Iodide

A reduction of the second moment from 11.2 G^2 found at 100 K, our low temperature limit, is stopped at the phase transition II→I to reveal a plateau of the mean value of 9.8 G^2 observed in the temperature range 165 – 270 K. Then the second moment decreases to 4.5 G^2 achieved at 375 K.

For $T_2(d_5PyH)I$ a plateau value of ca. 14 G^2 is observed up to 260 K, the temperature above which the second moment is reduced to 6.2 G^2 at 375 K, our high temperature limit (Fig. 3a).

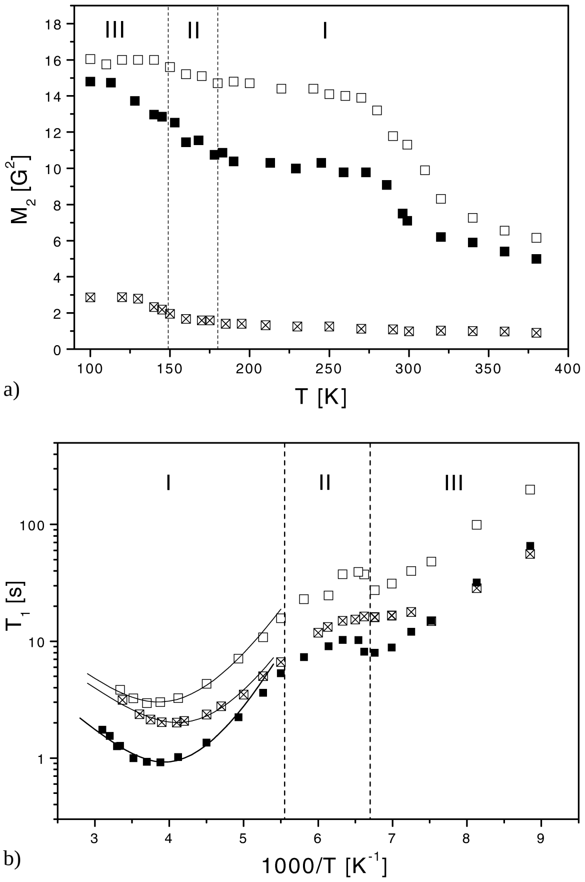

Fig. 2. The temperature dependence of the NMR second moment M_2 (Fig. 2a) and spin-lattice relaxation time T_1 (Fig. 2b) for protonated $T_2(PyH)Br$ (■) and perdeuterated: $T_2(d_5PyH)Br$ (□) and $d_8T_2(PyD)Br$ (☒).

The temperature dependence of the spin-lattice relaxation time obtained for $T_2(PyH)I$ and $T_2(d_5PyH)I$ is evidently different from those observed for the chloride and bromide, showing two T_1 minima separated by the phase transition at 165 K. In phase II minima of 0.9 s for $T_2(PyH)I$ and 2.9 s for $T_2(d_5PyH)I$ are observed at 138 K, while in phase I minima of similar depths as in phase II are observed at 222 K (Fig. 3b).

4. Calculation and Discussion

An evident reduction of the experimental second moment M_2 observed with increasing temperature must reflect an onset of a molecular reorientation in the crystal lattice. To describe the nature of the motion a calculation of the second moment for the rigid lattice

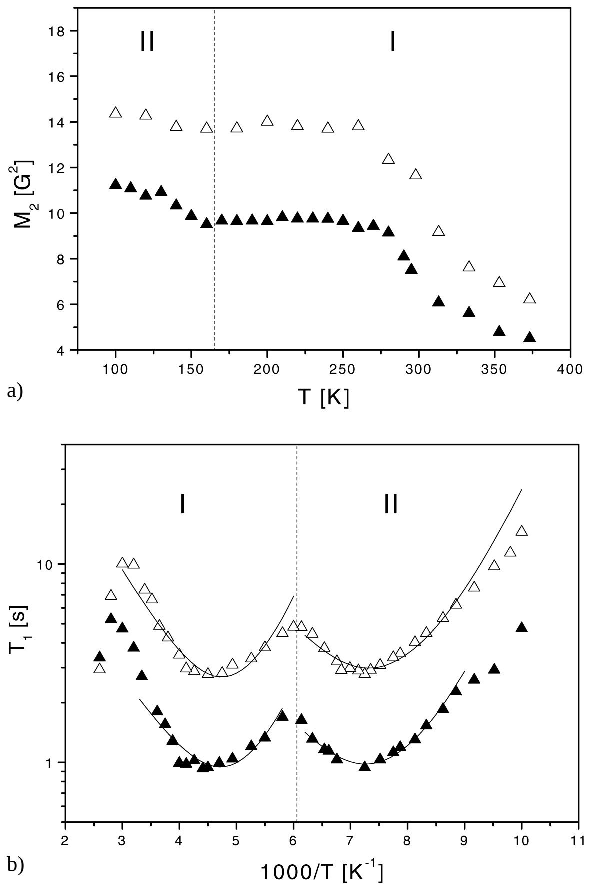

Fig. 3. The temperature dependence of the NMR second moment M_2 (Fig. 3a) and spin-lattice relaxation time T_1 (Fig. 3b) for protonated T_2(PyH)I (▲) and perdeuterated: T_2(d$_5$PyH)I (△).

Table 1. The fit activation parameters and ΔM_2 values obtained for the pyridinium cation C_6' reorientation over inequivalent potential barriers in T_2(PyH)Cl and T_2(d$_5$PyH)Cl.

	T_2(PyH)Cl	T_2(d$_5$PyH)Cl
E_A [kJ/mol]	23.1	21.2
E_B [kJ/mol]	15.3	13.9
K [1/s]	5.1×10^{11}	2.2×10^{11}
ΔM_2 [G^2]	3.8	0.9

and possible reorientations must be done and compared with the experimental values. For the considered thiourea pyridinium halide inclusion compounds such calculations have been performed by using the Van Vleck formula [8] and appropriate second moment reduction factors, as was done for many other compounds [9, 10]. However, the calculations could not be performed by using the hydrogen atom positions given in [6], since it is well known that X-ray analysis does not determine them precisely, giving the distances of the H atoms to the bonded heavier atoms evidently shorter than the internuclear distances. So the values obtained by the X-ray analysis have been corrected by extending the N-H and C-H vectors to the average neutron derived distances of 1.03 Å and 1.089 Å, respectively [11]. Such a corrected geometry leads to the intramolecular second moments obtained for the rigid structure of a thiourea molecule equal to 14.7 G^2 and of a pyridinium cation equal to 4.0 G^2. Taking weighted contributions of both values into account and estimating the intermolecular part of the second moment to be about 4 G^2 we found the total second moment for the rigid structure of the considered compounds (M_2^{rigid}) to be about 14 G^2. This is very close to the highest experimental values observed for the protonated chloride and bromide, proving the rigidity of their structures at the lowest temperatures studied. This is not observed for the iodide. However, since its further plot of the experimental second moment is similar to those observed for the chloride and bromide, one can expect a similar value for the rigid lattice of the iodide, as well. As this is not registered at the lowest temperatures, the value observed must be already motionally reduced.

The diminishing of the second moment at the higher temperatures reflects two motional processes: a first one – slowly reducing the second moment in a wide temperature range and a second one, observed above 280 K, manifested by a more rapid M_2 decreasing. The different slopes of the plots are separated by a more (for bromide and iodide) or less (for chloride) evident plateau value of about 9.8 G^2. Two motional processes can be ascribed to two dynamically different objects in the crystal lattice, which is suggested also by the resonance line shape, showing – in all the compounds studied – two components of different linewidths. It can be supposed that one comes from the thiourea molecule and the other one from the pyridinium cation.

The experimental facts observed at the low temperatures, like diminishing of the second moment in a very wide temperature range and a relatively high value of the T_1 minima can be easily attributed to reorientation of the pyridinium cation around the pseudohexagonal C_6' symmetry axis, taking place between inequivalent potential wells, as was found in other pyridinium salts [12 – 14]. The second moment calculated for such a model of pyridinium cation motion, assum-

Table 2. The fit activation parameters and ΔM_2 values obtained for the pyridinium cation C_6' reorientation over inequivalent potential barriers in T_2(PyH)Br, T_2(d_5PyH)Br, d_8T_2(PyD)Br.

	T_2(PyH)Br	T_2(d_5PyH)Br	d_8T_2(PyD)Br
E_A [kJ/mol]	21.2	18.3	19.6
E_B [kJ/mol]	14.1	11.9	12.6
K [1/s]	7.0×10^{11}	2.1×10^{11}	4.9×10^{11}
ΔM_2 [G^2]	4.1	0.9	2.1

ing a rigid thiourea sublattice, is equal to 10.4 G^2 ($M_2^{\text{rot.}}$), agreeing well with the plateau values observed in our experiment.

To describe the spin-lattice relaxation time T_1 for such a reorientation of the pyridinium cation, an asymmetric double-well potential, characterized by two activation energy values E_A, E_B and two different probabilities W_1 and W_2 has been assumed [14]. The spin-lattice relaxation rate T_1^{-1} is then given by

$$T_1^{-1} = \gamma^2 \Delta M_2 \left\{ \frac{3a}{(1+2a)^2} g(\tau_1) + \frac{a}{1+2a} g(\tau_2) \right\}, \quad (1)$$

where

$$g(\tau_i) = \frac{\tau_i}{1+\omega^2\tau_i^2} + \frac{4\tau_i}{1+4\omega^2\tau_i^2}. \quad (2)$$

The correlation times τ_1 and τ_2 are defined by

$$\tau_1^{-1} = 2W_1 + W_2, \; \tau_2^{-1} = 3W_2, \quad (3)$$

where

$$W_1 = K \exp(-E_A/RT), \; W_2 = K \exp(-E_B/RT), \quad (4)$$

and K is the temperature independent frequency factor.

The population parameter a is given by

$$a = \exp(-\Delta/RT) \quad (5)$$

where the value $\Delta = E_A - E_B$ is a measure of the asymmetry of the potential barriers. ΔM_2 is the change of the second moment due to the reorientation.

By fitting theoretical values of T_1 in (1) to the experimental points (solid lines in the figures) activation parameters of the cation motion have been extracted (Tables 1–3). In the fitting procedure, ΔM_2 for the protonated compounds was assumed to be 3.6 G^2, resulting from $M_2^{\text{rigid}} - M_2^{\text{rot.}} = (14 - 10.4)$ G^2.

The question arises why two T_1 minima are observed for the iodide. Very often such a case reflects two dynamically different cations [10, 15, 16], but this is not crystalographically justified in our compound. On the other hand, the similar depths and shapes of the two minima observed for the iodide and those for the chloride and bromide suggest the same mechanism of the relaxation in all the compounds. Thus we rather think that the two minima reflect the pyridinium cation reorientation in two different phases of the iodide. Theoretical fitting to both experimental plots yields activation parameters of the pyridinium cation reorientation in the two phases (Table 3). The increase in the activation energies obtained at the phase transition II→I must lead to a decrease in the frequency of the motion at this transition. Figure 4 shows a jump-wise change of the frequencies ν_1 and ν_2, calculated as reciprocals of the correlation times τ_1 and τ_2. One can see that the frequencies of the reorientation decrease at the temperature of the phase transition to the pre-minimum values which, increasing again after the transition, must lead to another T_1 minimum in high temperature phase, which is observed for the iodide in the experiment.

Table 3. The fit activation parameters and ΔM_2 values obtained for the pyridinium cation C_6' reorientation over inequivalent potential barriers in T_2(PyH)I and T_2(d_5PyH)I.

	T_2(PyH)I		T_2(d_5PyH)I	
	Phase I	Phase II	Phase I	Phase II
E_A [kJ/mol]	16.4	12.6	15.9	11.7
E_B [kJ/mol]	10.6	8.7	10.8	8.2
K [1/s]	3.7×10^{11}	16.3×10^{11}	3.7×10^{11}	10.1×10^{11}
ΔM_2 [G^2]	3.8	3.8	0.9	0.9

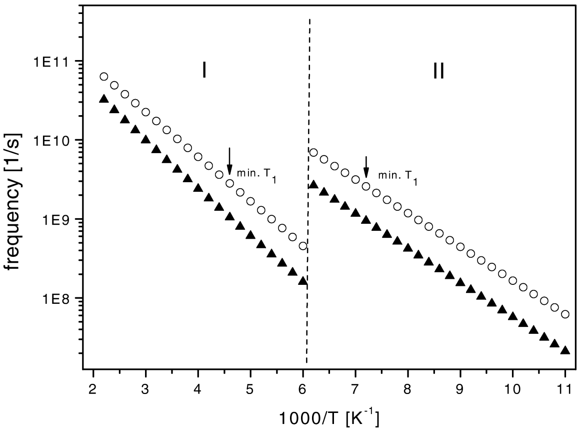

Fig. 4. The temperature dependence of the frequencies ν_1 (○) and ν_2 (▲) of the pyridinium cation reorientation in two phases of T_2(PyH)I.

The activation energies extracted from the relaxation experiment for all three halides have shown that the height of the potential barriers hindering the pyridinium cation reorientation depends on the type of the anion. The values obtained for the iodide, evidently lower than those for the chloride and bromide, confirm the greater motional freedom of the cation in this compound, revealed already by the motionally reduced second moment at the low temperatures.

The further decrease of the second moment from the plateau value of about 9.8 G^2 to ca. 4.8 G^2, observed in all three halides, can be possibly interpreted in terms of the thiourea molecule reorientation around the C=S bond, as found in other thiourea inclusion compounds [3, 17, 18]. The preliminary calculation of the potential barriers for the possible thiourea reorientations shows that it can not be – for a steric reason – a reorientation of the whole molecule around its two-fold axis but only a hindered rotation of 90°. The theoretical second moment value for such a motion was found to be 4.5 G^2, in good agreement with the experimental value. The precise activation parameters for the thiourea motion could not be extracted from the relaxation experiment because the corresponding T_1 minimum has not been reached before our high temperature limit. Hence the activation energy of the motion could only be derived from the second moment experiment by using the Waugh-Fiedin formula [19]. It was estimated to be about 40 kJ/mol in all the compounds, so evidently higher than the activation energy of 30 kJ/mol found in pure thiourea [20]. It can thus confirm the idea that the hydrogen bonds – which certainly play an essential role in the potential barrier hindering the reorientation – are stronger in the inclusion compounds than in pure thiourea [17, 21, 22]. It is worth noting that, although the potential barriers for the reorientation of the pyridinium cation are different in all the compounds studied, the barrier for the thiourea molecule is roughly the same regarding the halide.

A decrease of the spin-lattice relaxation time T_1 with decreasing temperature observed in the chloride would probably lead to a minimum governed by the proton motion in the hydrogen bond N-H$\cdots$S, as found in other compounds [23]. Activation energy 3.5 kJ/mol obtained from the slope of the T_1 plot well characterizes the potential barrier in such a hydrogen bridge [11].

The NMR study performed for the perdeuterated halides has revealed the same motional processes as in the protonated samples. The theoretical second moment for the rigid structure of the chloride was calculated similarly as for the protonated analogue and was found to be 16.9 G^2, which agrees well with the experimental values registered for the chloride and bromide at the lowest temperatures. This value is not observed for the iodide, revealing the motionally narrowed second moment already at the lowest temperatures studied.

At the high temperature limit the second moment observed for all d_5 halides is almost the same and equal to about 6.3 G^2. This value agrees very well with the theoretical one (6.4 G^2) calculated for the model assuming C_6' reorientation of the pyridinium cation over inequivalent potential barriers followed by the hindered rotation of the thiourea molecule around its C=S bond. Thus, it confirms the same dynamical behavior of the molecules as in the protonated samples. However, the experimental plots are apparently different. This results from very small dipolar interaction modulated by the perdeuterated cation reorientation. Such a motion, marked by only one hydrogen atom, reduces the second moment by only about 0.6 G^2, leading also to the high value of the T_1 minimum observed for all three halides.

The activation parameters obtained for the perdeuterated samples from the fitting of the theoretical T_1 values to the experimental plots (ΔM_2 was assumed to be 0.6 G^2) are presented in Tables 1 – 3. These parameters could be extracted only for the reorientation of the pyridinium cation. The activation energies for the thiourea motion extracted from the Waugh-Fiedin formula are – in the accuracy limit – very similar to those derived for the protonated analogues and equal to about 40 kJ/mol.

An additional ^{1}H NMR study of perdeuterated d_8TPyDBr could only reveal a pyridinium cation reorientation, since the thiourea molecule was totally obscured by its full perdeuteration. The decrease of the experimental second moment observed in the whole temperature range studied, and the lowest value obtained (0.9 G^2) well confirm the assumed model of the pyridinium cation reorientation, that is a reorientation around its C_6' symmetry axis over inequivalent potential barriers. The ΔM_2 value of 2.1 G^2, extracted from the second moment experiment, well fits to the T_1 plot and the height of the observed T_1 minimum.

5. Conclusions

Summarizing, we can say that in the considered thiourea pyridinium halide inclusion compounds and their perdeuterated analoques two dynamical processes have been revealed: the pyridinium cation reorientation around the pseudohexagonal C_6' symmetry axis over inequivalent potential barriers and the hindered rotation of the thiourea molecule around the C=S bond. The cation motion was found to be hindered by the energy barriers, the heights of which depend on the kind of the anion. The energy barrier for the thiourea molecule was found to be evidently higher than in pure thiourea, reflecting stronger hydrogen bonds in the inclusion compounds.

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