Molecular Motion in Tetraphenyltin Studied by NMR

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NMR second moment and spin-lattice relaxation times in the laboratory (60 and 25 MHz) and in the rotating frame (B_1 = 2.1 mT) were studied for polycrystalline tetraphenyltin $Sn(C_6H_5)_4$ in a wide temperature range. Two kinds of motions were detected: isotropic rotation of whole molecules and reorientations/oscillations of phenyl rings. A dependence of the potential energy of the molecule in the crystal on the angle of the phenyl ring rotation about the Sn–C bond was obtained on the basis of atom-atom calculations. The amplitude of the ring-oscillations at 133 K was estimated as ± 7°. Below room temperature the magnetisation recovery is significantly non-exponential, which may be interpreted as due to the correlated motion of phenyl rings.

Key words: NMR; Relaxation; Potential Energy.

Introduction

Tetraphenyltin belongs to a family of tetraaryl compounds built of four phenyl rings C_6H_5 bound to the central atom (X = C, Si, Ge, Sn or Pb). The compounds crystallise in the tetragonal system, space group $P\bar{4}2_1c$, $Z = 2$ [1–7]. The molecule symmetry in the crystal is $\bar{4}$. The length of the X–C bond depends on the central atom and varies from 1.50 to 2.29 Å for carbon and lead, respectively. The change of the central atom allows a modification of intramolecular interactions among the phenyl rings. Increased length of the X–C bond results in a decrease in the ratio of the molecule volume to the volume per molecule in the elementary cell, so to a decrease in the crystal packing coefficient [8], which testifies a change in the intermolecular interactions. Results of the structural studies are reported in [4–6]. The length of the Sn–C bond is 2.14 Å, and the elementary cell parameters at room temperature are $a = 12.058$ Å, $c = 6.568$ Å [6]. The shape of the molecule is shown in Figure 1. The possible conformations of both isolated and arranged in crystal molecules of the tetraaryl compounds (X = C, Si, Sn and Pb) were calculated [9]. Applying the atom-atom potential method, the potential energy of these compounds was calculated as a function of the phenyl ring rotation angle. Analysis of molecule conformation in the crystal was made on the basis of the molecular energy changes as a functions of the phenyl ring rotation angle about the tetragonal X–C axis, and the whole molecule rotation about the $\bar{4}$ symmetry axis. The differences between the conformations of isolated molecules and molecules in the crystal were found to be insignificant. The conformations found from the structural studies and implied by the calculations are in very good agreement. For tetraphenylmethane and tetraphenylsilicon the potential energy of molecules was calculated by the full relaxation empirical force field [10, 11]. The results have shown that the rotation of a phenyl ring about the C–C axis in the isolated tetraphenylmethane molecule is possible only when correlated with rotations of the other rings. The axis is six-fold and the energy barrier for such a motion is 62 kJ/mol.

Literature devoted to the experimental study of molecular reorientations in this group of compounds is rather scarce. In a recent work, a study of the molecular dynamics of tetraaryl compounds by the mionic resonance (μSR) was reported [12, 13]. The relaxation rate was mea-

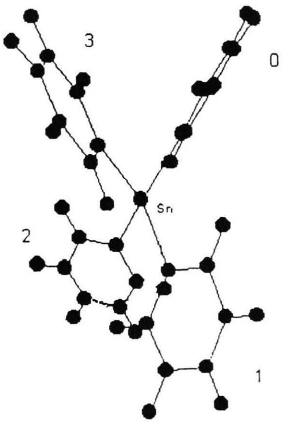

Fig. 1. The shape of a molecule of tetraphenyltin.

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sured for $X(C_6H_5)_4$ where X=Ge, Sn, Pb in the temperature range from 10 to 475 K, and for all compounds the presence of maxima in the dependencies was noted. The activation energies for the process were determined, and it was found that the activation energy decreases with increasing size of the central atom. For tetraphenyltin the activation energy is about 16 kJ/mol. The process was interpreted as rotation of phenyl groups about the X–C axis. The QNS study carried out for this group of compounds [14] was undertaken to verify this interpretation. If the molecules perform fast stochastic reorientations, the experimental spectrum should reveal a quasi-elastic component apart from the elastic one, which was not observed. Hence, the effect of relaxation could not be attributed to the rotation of phenyl groups but to torsional vibrations of these groups. The contradictory results obtained by the μSR and QNS methods prompted us to undertake an NMR study in order to identify the character of molecular reorientations in tetraphenyltin – one of the tetraaryl compounds.

Experimental

Tetraphenyltin, purchased at Aldrich-Chemie (96% purity, melting point 497–500 K), was subjected to further purification by a few times repeated crystallisation from pyridine. After purification the melting point increased to 511 K. The purified substance was powdered and placed in a glass ampoule, degassed and sealed.

The second moment of the NMR line was measured in a wide range of temperatures (100 to 480 K) by a continuous wave spectrometer working at a frequency of 28 MHz. Its values, found by numerical integration of the absorption curve derivative, were corrected for the finite modulation field. The spin-lattice relaxation times were measured in the laboratory (T_1) and rotating ($T_{1\rho}$) frames by pulse spectrometers working at 60 and 25 MHz.

Measurements of T_1 were performed using the saturation method, while $T_{1\rho}$ was measured by the spin-locking method in a rotating field of B_1=2.1 mT. The T_1 relaxation time was measured for temperatures from 102 to 480 K at 60 MHz and from 91 to 217 K at 25 MHz, whereas the $T_{1\rho}$ time was measured in the range from 480 to 400 K. All spectrometers used were constructed at the Radiospectroscopy Laboratory at the Institute of Physics, AMU. 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.

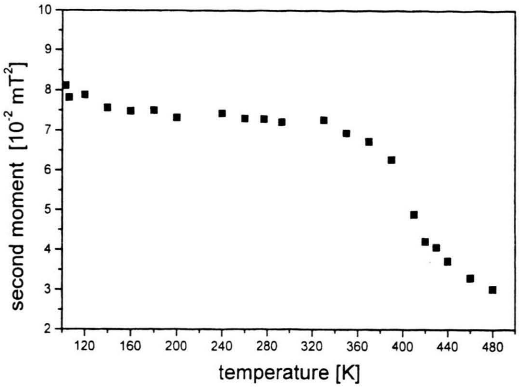

Fig. 2. The temperature dependence of the second moment.

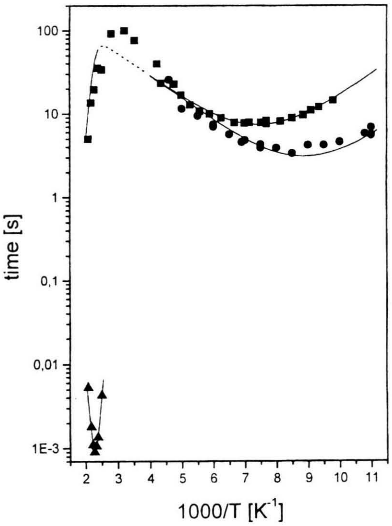

Fig. 3. The temperature dependence of the spin-lattice relaxation time T_1 for (■) 60 MHz and (●) for 25 MHz and the rotating frame relaxation time (▲) $T_{1\rho}$ (B_1=2.1 mT).

Results

Figure 2 presents the temperature dependence of the second moment. In the low-temperature range M_2 slightly decreases from $8 \cdot 10^{-2}$ mT^2 at 100 K to $7.4 \cdot 10^{-2}$ mT^2 at 200 K, then M_2 remains unchanged (plateau) up to 330 K and then starts to decrease to $3 \cdot 10^{-2}$ mT^2 at 480 K.

Figure 3 shows the dependence of the relaxation time T_1 (at 60 and 25 MHz) and $T_{1\rho}$ on the reciprocal of temperature. T_1 minima of 3.7 s and 8 s were observed at 125 K and 133 K at the frequencies 25 and

60 MHz, respectively. Moreover, a minimum of $T_{1\rho}$ of 0.9 ms was noted at 440 K. For temperatures below 293 K, the recovery of magnetisation M_z at both frequencies is two-exponential. Figure 3 presents only the T_1 components of significant contributions (greater than 60%), as the other ones are practically temperature independent.

Calculations and Discussions

Second Moment

On the basis of the structural data obtained for tetraphenyltin at room temperature [6], the theoretical value of the second moment of the NMR line, corresponding to the rigid lattice, was calculated from the Van Vleck formula [15]. As no information on the positions of protons has been given in the X-ray analysis [4–6], they were generated assuming the C–H bond length of 1.08 Å and the C–C–H angle of 120°. The intramolecular part of the second moment M_2 was $2.9 \cdot 10^{-2}$ mT^2, while the intermolecular part was $4.58 \cdot 10^{-2}$ mT^2, so the total second moment value was $7.48 \cdot 10^{-2}$ mT^2, which is in good agreement with the experimental value of $7.4 \cdot 10^{-2}$ mT^2. A slight increase in M_2 observed for temperatures below 200 K, can be caused by an increase in the intermolecular part due to a contraction of the crystal lattice.

As follows from the calculations, the shortest proton-proton distances of 2.817 Å in the tetraphenyltin molecule are between the protons at the ortho positions of different phenyl rings. The shortest distances between protons from different molecules are: in the para-para positions 2.418 Å, in the para-meta positions 2.589 Å and in the meta-meta positions 3.282 Å.

Relaxation Times

Analysis of the temperature dependence of the relaxation times points to the occurrence of two thermally activated processes in tetraphenyltin: a low- (L-TP) and high-temperature (H-TP) one. The rate of the relaxation can be expressed as

$$1/T_1 = (1/T_1)_{\mathrm{HTP}} + (1/T_1)_{\mathrm{LTP}}, \tag{1}$$

where the first and the second terms describe the relaxation rate of the high- and low-temperature processes, respectively. If the relaxation is caused by dipolar interaction, the relaxation rates T_1 and $T_{1\rho}$ are determined by the formulae [16, 17]

$$1/T_1 = C[\tau_c/(1 + \omega_0^2 \tau_c^2) + 4\,\tau_c/(1 + 4\,\omega_0^2 \tau_c^2)], \tag{2}$$

$$1/T_{1\rho} = C[3\,\tau_c/2(1 + 4\,\omega_1^2 \tau_c^2) + 5\,\tau_c/2(1 + \omega_0^2 \tau_c^2) + \tau_c/(1 + 4\,\omega_0^2 \tau_c^2)], \tag{3}$$

where $\omega_1 = \gamma B_1$, $\tau_c = \tau_0 \exp(E_a/\mathrm{RT})$, $C = 2\gamma^2 \Delta M_2/3$, and τ_c is the correlation time, E_a the activation energy, γ the gyromagnetic ratio, ω_0 the Larmor frequency, B_1 the induction of high frequency field, ΔM_2 the reduction of the second moment value due due to the reorientation, and C the relaxation constant.

Table 1. The activation parameters.

Process	C, s^{-2}	ΔM_2, mT^2	E_a, kJ/mol	τ_0, s
H-TP ($T_{1\rho}$)	$1.5 \cdot 10^9$	$3.1 \cdot 10^{-2}$	82.4	$1.3 \cdot 10^{-16}$
L-TP (T_1)	$3.6 \cdot 10^7$	$0.08 \cdot 10^{-2}$	5.1	$1.7 \cdot 10^{-11}$

The activation parameters of the two processes were obtained from the best fit of (2) and (3) to the experimental values of T_1 and $T_{1\rho}$. The results of the fit are shown in Fig. 3 (solid line), while the activation parameters are collected in Table 1. The high-temperature process of high activation energy (82.4 kJ/mol) and the corresponding reduction of the second moment $3.12 \cdot 10^{-2}$ mT^2 can be attributed to the isotropic reorientation of the tetraphenyltin molecules. In case of istotropic reorientation, the intramolecular part of the second moment is reduced to zero, whereas it is very difficult to the estimate the reduction of the intermolecular part. Nevertheless, for isotropic reorientation the value of M_2 must be smaller than $4.58 \cdot 10^{-2}$ mT^2, which is consistent with the experimental results.

The low-temperature process of a low activation energy is related to a very small change in M_2, which is indicative of a small amplitude of the reorientations. Let us consider two possible kinds of motion:

1) simple harmonic oscillations of phenyl rings about the Sn–C bond by the angle described by the formula

   $\phi = \alpha \sin \omega t + \phi_0$, where α is the amplitude,

2) reorientational jumps of phenyl ring between two positions at a distance of $2\,\alpha$ angle about the axis of the Sn–C bond.

The reduction factor ρ of the intraphenyl part of the second moment is

$$\rho = \frac{\overline{M_2}}{M_2^{\mathrm{R}}} = 1 - \frac{\Delta M_2}{M_2^{\mathrm{R}}}, \tag{4}$$

where M_2^R is the M_2 corresponding to the rigid lattice and $\bar{M}_2$ the value averaged by of the motion considered.

In the case of oscillation, the factor ρ can be expressed as [18]

$$\rho = 1 - \frac{3}{4}[(1 - J_0^2(\alpha)) \cdot \sin^2(2\psi) + (1 - J_0^2(2\alpha)) \cdot \sin^4(\psi)], \quad (5)$$

where α is the oscillation amplitude, ψ the angle between the interproton vector and the axis of reorientation, and J_0 the zero order Bessel function. For small α, (5) takes the form

$$\rho = 1 - \frac{3}{2}\alpha^2 \sin^2 \psi. \quad (6)$$

In the case of reorientation, the factor ρ takes the form

$$\rho = 1 - 3 \cdot (\sin\alpha \cdot \sin\psi)^2 \cdot (1 - \sin^2\alpha \cdot \sin^2\psi), \quad (7)$$

where α is a amplitude of reorientations and ψ the angle between the interproton vector and the axis of reorientation. When the interproton vector makes an angle of 90° ($\psi = 90°$) with the axis of reorientation, (7) takes the form given in [19].

For small α, (7) becomes

$$\rho = 1 - 3\,\alpha^2 \cdot \sin^2\psi\,(1 - \alpha^2 \sin^2\psi). \quad (8)$$

In the phenyl ring undergoing reorientations/oscillations about the Sn–C bond, the angle ψ takes the values 30°, 60°, and 90°. As follows from (7) and (8), for small angles the dependence of factor ρ on the angle α is similar for oscillations and reorientations. The value of ΔM_2 determined for the low-temperature (Table 1) process is only $0.08 \cdot 10^{-2}$ mT^2, so the reduction factor is $\rho = 0.99$. According to (5) and (7), this value of the reduction factor will be obtained at $\psi = 30°$ for $\alpha = \pm 7°$ and $\alpha = \pm 10°$, for reorientations and oscillations, respectively; at $\psi = 60°$ for $\alpha = \pm 4°$ and $\alpha = \pm 6°$, and at $\psi = 90°$ for $\alpha = \pm 3.5°$ and $\alpha = \pm 5°$.

Of course, (5) and (7) concern the reduction of the intraphenyl part of the second moment, while the factor ρ refers to the total value of M_2. As follows from the above considerations, reorientations or oscillations of very small amplitude of an order of a few degrees are possible. On the basis of the studies performed a distinction between these two models of motion is not possible.

To obtain a more detail description of molecular dynamics of tetraphenyltin, the atom-atom potential method proposed by Kitajgorodski [8] was applied. This method allows a calculation of the energy curve corresponding to an arbitrary reorientational rotation of the molecule or its fragments, and provides information on the shape and height of the energy barrier, and the multiplicity of the reorientation axis. In the case of thermally activated motion the calculated value of the barrier height can be compared with that resulting from experiment.

Table 2. The constants *A*, *B*, *C* given by Kitajgorodski [9].

Interactions	*A* [kJ/mol Å^6]	*B* [kJ/mol]	*C* [Å^{-1}]
H–H	238.49	175728	4.86
C–C	1497.87	175728	3.58
C–H	644.34	175728	4.12

Assuming the structural data from [6], the potential energy of an isolated molecule was calculated versus the angle of rotation ϕ of the phenyl ring about the Sn–C bond, and similar calculations were performed for the molecule in the crystal. The potential energy U is a sum

$$U = \sum_{i,j} f(r_{i,j}), \quad (9)$$

where f is the potential between the non-bonded atoms i, j, and r_{ij} is the distance between them.

The potential of interaction between non-bonded atoms separated by r is

$$f(r) = \frac{A}{r^6} + B \cdot \exp(-C \cdot r), \quad (10)$$

where *A*, *B*, and *C* are constants.

We have assumed the *A*, *B*, and *C* constants given by Kitajgorodski [9] for the interactions C–C, and H–H and C–H, included in Table 2. The interactions Sn–C, and Sn–H have not been taken into account because they do not depend on the angle of rotation ϕ. Similar calculations have been performed for the constants *A*, *B*, and *C* given by Williams [20] and the obtained dependence of the potential energy on the angle ϕ was of the same character as for the rotations described below.

Isolated Molecule

The potential energy of an isolated molecule was calculated for the rotation of one of the phenyl rings in the ϕ range from 0° to 360°, at every 1°; with the other phenyl rings assumed to remain in the initial position implied by structural data. Figure 4 presents the $U(\phi)$ dependence obtained for the first ring; analogous dependencies were calculated for the other rings.

In the initial structure, all the rings are in the same energetic situation:

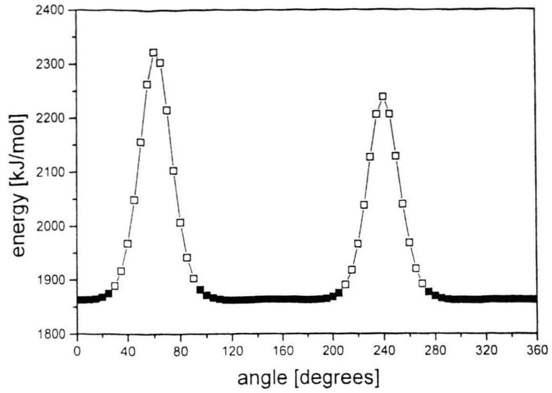

Fig. 4. The potential energy $U(\phi)$ of an isolated molecule for the rotation of the phenyl ring (see text).

- Free rotation of a single phenyl ring about the Sn–C bond is not possible for steric reasons. During rotation of one of the rings the distances among the atoms of the ring and those of the other rings change, and the distance between hydrogen atoms from neighbouring rings is shorter than the extreme 1.9 Å (empty markers on Figure 4)
- Each of the rings has a double-well potential. The depths of the minima are about 0.6 and 1.3 kJ/mol, relative to the height of the maximum between them, so that the energy difference between them is 0.7 kJ/mol (full markers on Figure 4). Each of the rings is at one shallower minimum. The rings can oscillate in the minimum or jump by 60° over the energetic barrier of a height of 1 kJ/mol. Table 3 presents the positions and the corresponding energies at the potential energy minima for the phenyl rings. The ranges of angles for zero and the second rings for which its rotation is impossible are 30°–90° and 210°–270°, and for the first and the third rings are 90°–150° and 270°–330°.

The situation when one of the rings jumped to the second minimum was also considered. Owing to the symmetry of the problem an arbitrary ring could be considered, and we chose the zero ring. As could expected, the energy dependence on the rotation angle for the other rings changed.

- Analysis of a further rotation of the first ring gave the ranges of angles for which its rotation is impossible 90°–150° and 270°–330°, so the same as before. The potential in the ranges of possible rotations has become flat and without clearly marked minimum.
- The rotation of the second ring is even more restricted – only in the ranges 330°–30° and 150°–210°, the ring is at the minimum of a single-well potential.
- The situation of the third ring is completely different; its potential has 6 minima separated by the barriers of ~ 1 kJ/mol, separated by about 60°. The result, indicating the possibility of the phenyl ring reorientation about the six-fold axis, is in qualitative agreement with the findings for tetraphenylmethane reported in [11]. The calculations of the potential energy of a tetraphenyltin molecule as a function of the rotation angle of the phenyl rings about the axis of the Sn–C bond have shown that the motion of a single ring strongly depends on the positions of the other rings; so it is a correlated motion, as suggested by [10, 11]. Table 4 gives the positions and the corresponding energies of the minima of the phenyl rings potential assuming the zero ring at the second minimum.

The Molecule in the Crystal

The $U(\phi)$ dependence for a tetraphenyltin molecule in the crystal is shown in Figure 5. Similarly as in the case of the isolated molecule, one of the rings was rotated in the range for 0° to 360°, while the other rings were motionless. For each of the four rings the same dependence of the potential energy on the rotations angle was obtained. In the crystal the energetic situation of the molecule drastically changes. The possibility of a motion of an individual ring is much restricted, mainly due to the

Table 3. The positions and the corresponding energies at the potential energy minima for the phenyl ring of tetraphenyltin molecule.

Ring	0		1		2		3	
Position of the minimum	–55°	* 0°	* 2°	56°	–60°	* 10°	* 2°	56°
Potential energy minima [kJ/mol]	1861.99	1862.69	1862.69	1862.03	1862.81	1863.29	1862.57	1861.92

An asterisk (*) means the ring position at the minimum as follows from structural studies.

Table 4. The positions and the corresponding energies at the potential energy minima for the phenyl ring of tetraphenyltin molecule.

Ring	0			1		2
Position of the minimum	* −55°	0°		0°–60°		0°
Potential energy minima [kJ/mol]	1861.99	1862.69		1862.62–1863.30		1862.18
	3					
	0°	59°	119°	185°	237°	302°
	1862.98	1862.96	1862.64	1863.14	1862.76	1862.77

An asterisk (*) means the ring position at the minimum.

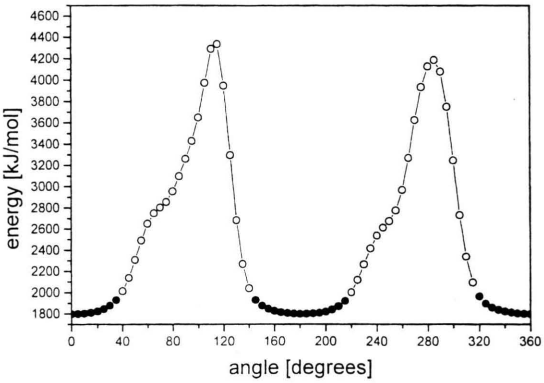

Fig. 5. The potential energy $U(\phi)$ of a molecule in the crystal for the rotation of the phenyl ring (see text).

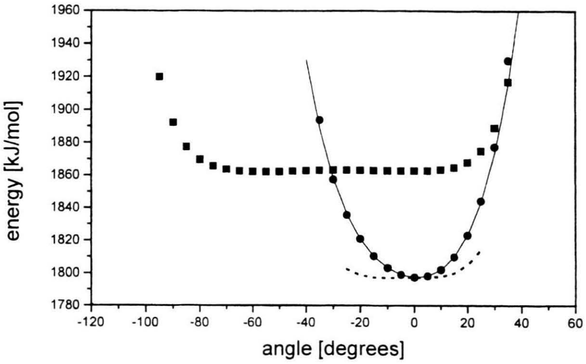

Fig. 6. The potential for a molecule of tetraphenyltin: isolated and in the crystal. Solid line (——) fit based on (11), broken line (------) anharmonic part of (11).

interaction between the hydrogens from neighbouring molecules. The phenyl ring potential has become single-well and the amplitude of motion of a given ring has been substantially restricted.

Figure 6 presents the potentials obtained for an isolated molecule and a molecule in the crystal. The effect of the surrounding environment on the molecule of tetraphenyltin is evident.

As follows from the calculations of the potential energy for molecules in the crystal as a function of the angle of rotation of phenyl rings about the Sn–C axis, their motion should be strongly correlated. This supposition is confirmed by the non-exponential recovery of magnetisation. With increasing temperature the inter-and intramolecular interactions are averaged and the non-exponential character of the magnetisation recovery weakens.

The non-exponential recovery of magnetisation can take place when [21]:

- there are a few, at least two, kinds of resonance spins or subsystems, which undergo relaxation at different rates,
- when the sample is not powdered enough,
- when the system undergoes a correlated motion.

For the compound considered the first two situations are irrelevant, and the third one seems to be most probable. In the literature only a system of three proton-proton vectors is well elaborated experimentally and theoretically for a methyl group [22–24]. In the compound the reorientations/oscillations of one phenyl ring is correlated with the motion of neighbouring rings from the same and different molecules. This kind of molecular motions changes not only the orientation of the internuclear vectors but also their length.

The potential energy of the phenyl ring in a tetraphenyltin molecule as a function of the rotation angle was approximated as in [25], by the function

$$V(\phi) = a + b\phi + c\phi^2 + d\phi^3 + e\phi^4. \quad (11)$$

From the best fit by the least squares method of this function to the results obtained for the range from $-20°$ to $20°$, the following values of the parameters were found

$$a = 1797.2 \text{ kJ/mol}, \; b = -5.56 \text{ kJ/mol rad},$$
$$c = -165.74 \text{ kJ/mol rad}^2, \; d = 72.33 \text{ kJ/mol rad}^3,$$
$$e = 308 \text{ kJ/mol rad}^4.$$

The result of the fit is marked with the solid line in Fig. 6, while the broken line represents the anharmonic part of the potential energy (the sum of the fourth and fifth as well as first in (11)). The contribution of the anharmonic terms to the potential energy is insignificant for the angles from $-20°$ to $+10°$. The mean square of the amplitude of the phenyl ring oscillations can be found from the equation [25]

$$\langle \phi^2 \rangle = \frac{RT}{2c}. \tag{12}$$

The root of this expression $\langle \phi^2 \rangle^{1/2}$ corresponds to half of the width of the potential energy curve cut off above $RT/2$ from its minimum.

The maximum value of the oscillation amplitude can be found from the expression

$$\Delta\phi_{1/2} = \sqrt{\frac{RT}{c}}, \tag{13}$$

and it corresponds to half of the width of the potential energy curve cut off above RT from its minimum.

For 133 K, at which the T_1 relaxation time takes its minimum value, $\langle \phi^2 \rangle^{1/2}$ and $\Delta\phi_{1/2}$ are 3.3° and 4.7°, respectively. If RT in (12) and (13) is replaced by E_a determined from the measurements of T_1 as a function of temperature, the corresponding values of $\langle \phi^2 \rangle^{1/2}$ and $\Delta\phi_{1/2}$ are 7° and 9.9°. The oscillation amplitudes obtained in this way are similar to those estimated from T_1 measurements.

Conclusions

The experimental and calculated results presented above point to occurrence of the following kinds of motions in tetraphenyltin:

- reorientations/oscillations of phenyl rings, of a small amplitude, ±7° at 133 K,
- isotropic reorientations of the whole molecules about their centres of gravity.

The observed non-exponential recovery of magnetisation can be attributed to the correlated motion of the phenyl rings. This conclusion is supported by the results of the calculations of potential energy of the rings as a function of the angle of rotation about the Sn–C axis.

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