Structure and Molecular Motions in Rubidium Tetraphenylborate

A. Pajzderska, H. Małuszyńska, and J. Wąsicki
Faculty of Physics, A. Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland
Reprint requests to A. P.; E-mail: apajzder@main.amu.edu.pl

Z. Naturforsch. **57 a,** 847–853 (2002); received June 12, 2002

By X-ray diffraction it was found that at 293 K the crystals of rubidium tetraphenylborate are tetragonal, space group $I\bar{4}2m$, $a = b = 11.212(2)$ Å, $c = 8.098(2)$ Å, with 2 molecules of $Rb^+[C_{24}H_{20}B]^-$ in the unit cell. The molecular reorientations as functions of temperature were studied by ^{1}H NMR. Two types of motions were detected: an anisotropic reorientation of the tetraphenylborate anions about their mass centres, and small-angle reorientations / oscillations of the phenyl rings. The dependence of the potential energy of the anion in the crystal on the angle of the phenyl ring rotation about the B-Ph bond was obtained on the basis of atom-atom calculations. The dynamics of this compound was compared to that of tetraphenyltin.

Key words: NMR; Ralaxation; Potential Energy; X-ray; Crystal Structure.

1. Introduction

Rubidium tetraphenylborate is an ion-molecular crystal belonging to the family of tetraphenylborate salts. The compounds crystallize in the $I\bar{4}2m$ space group [1], and the positions of heavy atoms (Rb, B, C) have been determined [2]. The tetraphenylborate-anion is composed of four phenyl rings bonded to the central boron atom. The structure of such an anion is similar to that of the phenyl derivatives $X(C_6H_5)_4$, where X = C, Si, Ge, Sn, Pb, being molecular crystals. In our earlier papers the dynamics of tetraphenyltin compounds has been studied by Raman scattering [3], neutron diffraction [4] and nuclear magnetic resonance (NMR) [5]. In this compound results of NMR measurements and atom-atom potential energy calculations have proved the presence of two types of thermally activated motions: isotropic reorientation of the whole molecule about its centre of gravity and small-angle oscillations of the phenyl rings.

The aim of the present study on rubidium tetraphenylborate was to determine the detailed crystal and molecular structure of the compound as well as the type of molecular reorientations and their activation parameters.

2. Experiments

Rubidium tetraphenylborate was purchased from Aldrich-Chemie (96% purity). For the X-ray measurements we prepared single crystals grown by slow evaporation of an acetone solution. For the NMR measurements, polycrystalline samples were used.

A transparent crystal of the dimensions 0.25 × 0.15 × 0.60 mm was put on a KM-4-KUMA diffractometer, with graphite monochromator, MoK_α radiation, using the ω-2θ scan mode. Two control reflections measured after each of 100 reflections showed no significant intensity changes. Lattice parameters were refined from setting angles of 30 reflections in the 19 to 30° 2θ range.

The second moment of the NMR line was measured in temperature at 100 to 500 K by a continuous wave spectrometer working at 28 MHz. The values obtained by numerical integration of the absorption curve derivative were corrected for the finite modulation field. The spin-lattice relaxation times T_1 were measured by pulse spectrometers working at 60 MHz. Measurements of T_1 were performed using the saturation method for temperatures from 100 to 500 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.

3. Results

3.1. X-ray Results

The structure of rubidium tetraphenylborate was solved by direct methods SHELXS-97 [6] and refined

0932–0784 / 02 / 1100–0847 $ 06.00 © Verlag der Zeitschrift für Naturforschung, Tübingen · www.znaturforsch.com

Table 1. Crystal data and structure refinement of rubidium tetraphenylborate.

Empirical formula	$C_{24}H_{20}BRb$
Formula weight	404.68
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	tetragonal, $I\bar{4}2m$
Unit cell dimensions	$a = b = 11.212(2)$ Å $c = 8.098$ (2) Å
Volume	1018.0(4) Å^3
Z, calculated density	2, 1.320 g/cm^3
Absorption coefficient	2.435 mm^{-1}
$F(000)$	412
Crystal size	0.25 × 0.15 × 0.60 mm
θ Range for data collection	2.57 to 30.08 °
Limiting indices	$-15 \leq h \leq 15, 0 \leq k \leq 15, 0 \leq l \leq 11$
Reflections collected / unique	1674 / 807 [R(int) = 0.0542]
Completeness to $\theta = 30.08$	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	807 / 0 / 35
Goodness-of-fit on F^2	0.939
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0389$, $wR2 = 0.0958$
R indices (all data)	$R1 = 0.0512$, $wR2 = 0.1023$
Absolute structure parameter	0.007(15)
Largest diff. peak and hole	0.475 and –0.411 e· Å^{-3}

Table 2. Atomic coordinates ($\cdot 10^4$) and equivalent isotropic displacement parameters (Å$^2 \cdot 10^3$) for rubidium tetraphenylborate. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Rb	10000	10000	10000	40(1)
B	10000	10000	15000	27(1)
C(1)	10814(2)	10814(2)	13756(4)	30(1)
C(2)	11895(2)	10399(2)	13095(3)	38(1)
C(3)	12513(3)	11015(3)	11872(4)	50(1)
C(4)	12073(3)	12073(3)	11245(6)	55(1)
H(2)	12283	9596	13600	30
H(3)	13317	10636	11358	30
H(4)	12566	12572	10325	30

by SHELXL-97 [7]. The H atom positions, calculated assuming C-H = 1.08 Å and refined as riding model, are given in Table 1, atomic coordinates in Table 2, bond lengths and angles in Table 3 and anisotropic displacement parameters in Table 4. The Ortep drawing at 50% probability of rubidium tetraphenylborate is given in Fig. 1 and the unit cell contents in Figure 2.

Table 3. Bond lengths (Å) and angles (°) for rubidium tetraphenylborate.

B-C(1)	1.638(3)	C(1)-C(2)	1.404(3)
C(2)-C(3)	1.392(4)	C(3)-C(4)	1.381(4)
C(4)-C(3)$^{\#1}$	1.382(4)		
C(1)$^{\#2}$-B-C(1)$^{\#3}$	112.22(12)	C(1)$^{\#2}$-B-C(1)$^{\#4}$	112.22(12)
C(1)$^{\#3}$-B-C(1)$^{\#4}$	104.1(2)	C(1)$^{\#2}$-B-C(1)	104.1(2)
C(1)$^{\#3}$-B-C(1)	112.22(12)	C(1)$^{\#4}$-B-C(1)	112.22(12)
C(2)$^{\#1}$-C(1)-C(2)	115.3(3)	C(2)$^{\#1}$-C(1)-B	122.06(16)
C(2)-C(1)-B	122.06(16)	C(3)-C(2)-C(1)	122.4(3)
C(4)-C(3)-C(2)	120.6(3)	C(3)$^{\#1}$-C(4)-C(3)	118.6(4)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ y, x, z; $^{\#2}$ –x + 2, –y + 2, z; $^{\#3}$ –y + 2, x, –z + 3; $^{\#4}$ y, –x + 2, –z + 3.

Table 4. Anisotropic displacement parameters (Å$^2 \cdot 10^3$) for rubidium tetraphenylborate. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rb	46(1)	46(1)	27(1)	0	0	0
B	27(1)	27(1)	27(2)	0	0	0
C(1)	31(1)	31(1)	28(1)	–1(1)	–1(1)	–5(1)
C(2)	34(1)	45(1)	34(1)	0(1)	3(1)	–2(1)
C(3)	41(1)	67(2)	43(1)	–1(1)	11(1)	–13(1)
C(4)	60(2)	60(2)	43(2)	8(1)	8(1)	–27(2)

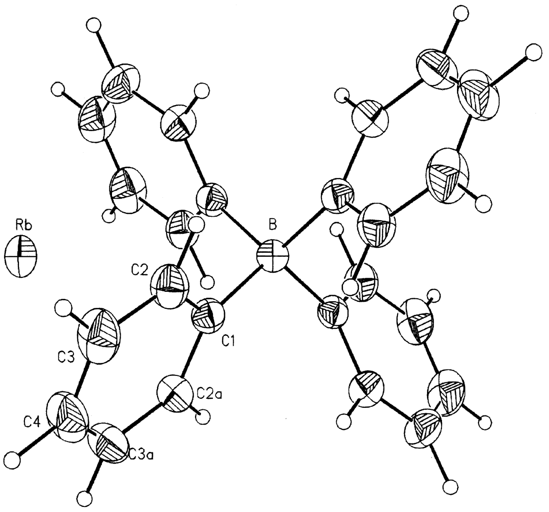

Fig. 1. Ortep drawing at 50% probability of rubidium tetraphenylborate.

The X-ray structure analysis confirmed the unit cell constants and space group reported in [1] and [2]. There are two rubidium tetraphenylborate molecules in the unit cell. Both B and Rb atoms are at $\bar{4}2m$ site symmetry with the tetraphenyl boron anion well ordered, having $\bar{4}2m$ symmetry. Four phenyl rings surround each Rb atom with a distance between the Rb atom and the center of the phenyl ring of 2.155 Å.

Table 5. Elementary cell volume V_{kom}, distance $R_{\mathrm{X\text{-}H}}$ between the central atom and hydrogen atom in *para* position, and $R_{(\mathrm{X-X})/2}$, half of the distance between the central atoms of neighbouring molecules in rubidium tetraphenyl borate and tetraphenyl tin.

	Unit-cell lengths		V_{kom}	$R_{\mathrm{X\text{-}H}}$	$R_{(\mathrm{X\text{-}X})/2}$
	a [Å]	c [Å]	[Å^3]	[Å]	[Å]
$(C_6H_5)_4BRb$	11.212	8.098	1018.173	5.50	4.45
$Sn(C_6H_5)_4$	12.058	6.568	954.957	6.00	4.57

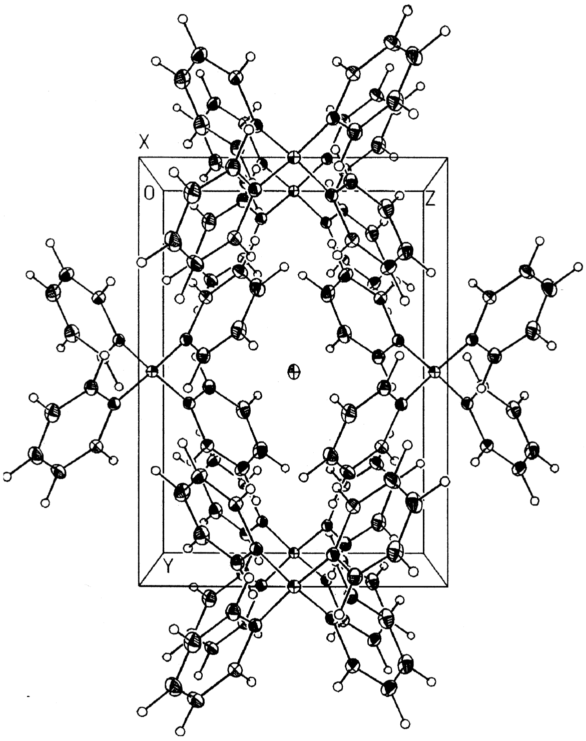

Fig. 2. The unit cell contents.

Only these $Rb^+ \ldots \pi$ and Van der Waals interactions are observed in this crystal structure.

Having determined the crystal structure of rubidium tetraphenylborate, we could compare its geometrical data with that obtained for tetraphenyltin.

Table 5 gives the elementary cell parameters and cell volume of rubidium tetraphenylborate and tetraphyenyltin. The structure of the molecule enables its approximation by a sphere of a radius equal to the distance from the central atom X (= B, Sn) to the hydrogen atom of the phenyl ring in the para position. This radius is denoted as $R_{\mathrm{X\text{-}H}}$. Its values are given in Table 5, together with the values of half of the distance between the centres of neighbouring anions of tetraphenylborate and neighbouring molecules of tetraphenyltin ($R_{\mathrm{X\text{-}X}}$). It should be emphasised that for the molecules the distance $R_{\mathrm{X\text{-}X}}$ is shorter than $R_{\mathrm{X\text{-}H}}$, which means that the anions or molecules cannot be treated as separate balls but are mutually geared. This conclusion is supported also by the fact that in both the tetraphenylborate and tetraphenyltin [5] anions, certain distances between the hydrogen atoms belonging to different molecules are shorter than the distances between the hydrogen atoms of different rings but in the same molecule. For tetraphenyltin the distances are of the order of 2.5 Å, which means that they are comparable with the shortest distances between hydrogen atoms in the same ring.

3.2. NMR Results

Figure 3 presents the temperature dependence of the NMR second moment of rubidium tetraphenylborate at 100 to 480 K.

In the low-temperature range value of second moment is 7.9 G^2 and does not change up to 180 K. Above this temperature the second moment decreases, reaching 6.2 G^2 at 300 K.

Figure 4 presents the spin-lattice relaxation time T_1 versus inverse temperature. T_1 reaches a minimum of 12 s at 295 K (1000/T = 3.4 K^{-1}).

4. Calculations

4.1. The Activation Parameters

On the basis of the structural data for rubidium tetraphenylborate obtained at room temperature, [Sect. 3.1] and the van Vleck formula [8], the theoretical value of the second moment for the rigid lattice was calculated to be 7.65 G^2, where the intramolecular component was 3.82 G^2, and the intermolecular component 3.83 G^2. The total value of the second moment agrees well with the plateau observed at the lowest temperatures (7.9 G^2).

For rubidium tetraphenylborate the inter- and intramolecular contributions to the second moment are comparable, whereas for tetraphenyltin the intermolecular part (4.6 G^2) is greater than the intramolecular contribution (2.9 G^2) [5]. Usually in molecular crystals the situation is opposite – the contribution of the intermolecular part is much smaller than that

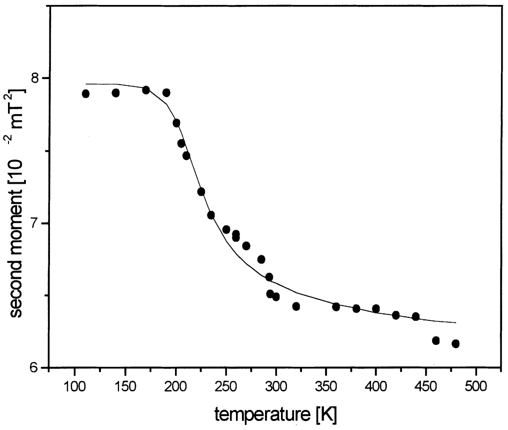

Fig. 3. Temperature dependence of the second moment of NMR line for rubidium tetraphenylborate, the solid line presents the fit to (2).

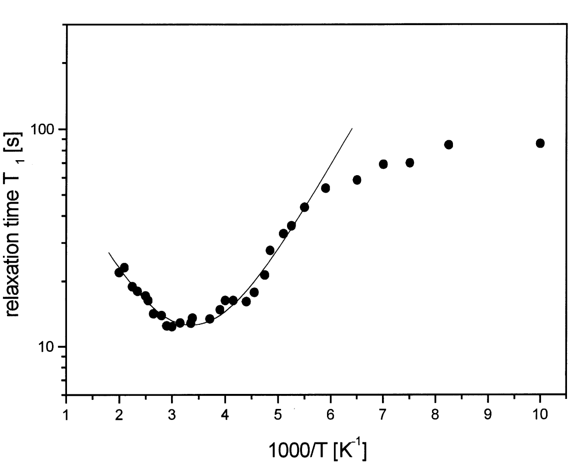

Fig. 4. log T_1 versus inverse temperature for rubidium tetraphenylborate; solid line presents the fit to (1).

of the intramolecular component, due to the fact that the distances between the molecules are 2 - 3 times greater than those in the molecules. However, in the compounds studied these distances are comparable, and in tetraphenyltin some intermolecular distances are smaller than intramolecular ones.

If the relaxation is caused by the dipolar interactions modulated by molecular reorientations, the relaxation time T_1 [9] and the temperature dependence of the second moment M_2 [10] are given by

$$1/T_1 = C[\tau_c/(1+\omega_0^2\tau_c^2)+4\tau_c/(1+4\omega_0^2\tau_c^2)]. \quad (1)$$

$$M_2 = M_2^{\text{rigid}}\left[\frac{1}{4}+\frac{3}{2\pi}\text{arctg}\left(\gamma\sqrt{M_2}\tau_c\right)\right], \quad (2)$$

Table 6. Activation parameters for $(C_6H_5)_4BRb$ and $Sn(C_6H_5)_4$ [3].

	Det. from the temp. dependence of T_1		Det. from the temp. dependence of M_2	
	$(C_6H_5)_4BRb$	$Sn(C_6H_5)_4$	$(C_6H_5)_4BRb$	$Sn(C_6H_5)_4$
τ_0 [s]	$6.7\cdot10^{-11}$	$1.7\cdot10^{-11}$	$3.3\cdot10^{-9}$	$1.3\cdot10^{-16}$
E_a [kJ/mol]	7.9	5.1	19.1	82.4
ΔM_2 [G^2]	0.04	0.08	1.8	3.1

$$\tau_c = \tau_0 \exp(E_a/RT),$$

$$C = 2\gamma^2\Delta M_2/3,$$

where τ_c is the correlation time, E_a the activation energy, γ the gyromagnetic coefficient, ω_0 the Larmor frequency, M_2^{rigid} the second moment for rigid structure, M_2 the motionally averaged second moment, $\Delta M_2 = M_2^{\text{rigid}} - M_2$ the reduction of the second moment caused by reorientation, and C the relaxation constant.

From the best fit of the functions (1) and (2) to the experimental data of T_1 and M_2, we obtained the activation parameters for the molecular reorientations. The results of the fit are presented in Figs. 3 and 4 as solid lines, and the activation parameters, compared with the activation parameters obtained for tetraphenyltin [5], are given in Table 6.

As follows from the temperature dependences of the relaxation time and second moment, there are two thermally activated processes in rubidium tetraphenylborate. One of them is related to the large reduction of the second moment by about 2 G^2, and high activation energy ~ 19 kJ/mol, and the second one is related to a small reduction of the second moment by less than 0.1 G^2 and low activation energy ~7 kJ/mol. The former process, manifested by the second moment reduction of 2 G^2, does not affect the relaxation time in the temperature range studied. The activation parameters obtained for this motional process suggest that the the corresponding T_1 minimum would occur at a higher temperature than the melting point of the compound.

Let us analyze first the high activation energy process. In the temperature range from 350 to 480 K the second moment is greater than the calculated intermolecular part. This means that the intramolecular part is not completely averaged, which indicates an anisotropic reorientation of anions about their centres of gravity. If the reorientation were isotropic, the intramolecular part of the second moment would be reduced to zero and the observed value of M_2 would be equal or smaller than the intermolecular part, as observed for tetraphenyltin.

The above interpretation of the process is consistent with our earlier results obtained for tetraphenyltin. The reduction of the second moment of tetraphenylborate begins at 180 K, while for tetraphenyltin at 310 K. In rubidium tetraphenylborate the anions are separated by rubidium cations, so they have greater freedom of movement than the tetraphenyltin molecules. Thus their reorientation can start at a lower temperature and they need less energy for the reorientation (19 kJ/mol). In the tetraphenyltin crystal the molecules are geared in (see 3.1) so their reorientation starts at higher temperatures and needs greater activation energy (∼ 82 kJ/mol).

The second process, characterised by a low activation energy and corresponding to a small change in the second moment of less than 0.1 G^2 is more difficult to interpret. Small changes in the second moment may suggest oscillations or reorientations by a small angle [11, 12]. In [5] an analysis of the reduction factor $\rho = M_2/M_2^{\text{rigid}}$ versus the oscillation and the reorientation angle ϕ was made for different interproton vectors in the phenyl rings. For small angles ϕ the reduction factor ρ shows a similar behaviour for the two kinds of movements. Significant differences between the ρ value for oscillations and reorientations appear for $\phi > 20°$. The very small change in the second moment observed in the experiment (∼ 0.1 G^2) corresponds to a reduction factor $\rho = 0.99$. Such a value of ρ was obtained for an angle of oscillations or rotations not greater than $\phi = \pm 10°$. The calculations have been performed for the intramolecular part of the second moment, while the experimentally obtained ρ has been obtained for the total M_2. According to the calculations, a movement corresponding to the minimum in T_1, a small activation energy and a small change in M_2, are equally probable for reorientations or oscillations of a very small amplitude (of a few degrees). However, the calculations performed do not allow to differentiate between these two types of motion. To gain better insight into the process, further calculations are necessary.

4.2. Atom-Atom Calculations

To perform a more comprehensive interpretation of our results, the atom-atom potential method, proposed by Kitajgorodski [13], was applied. The potential energy U of an isolated anion was calculated as a function of the rotation angle ϕ of the phenyl ring about the B-Ph bond. Analogous calculations were performed for the anion in the crystal lattice using the structural data obtained from the X-ray analysis and assuming the 6-exp potential and the constants A, B, and C of Kitajgorodski [14], describing the interactions C-C, H-H, C-H. The interactions B-C, B-H, were disregarded as they do not depend on the rotation angle ϕ, and not the absolute value of the intramolecular interactions but its angular dependence is important.

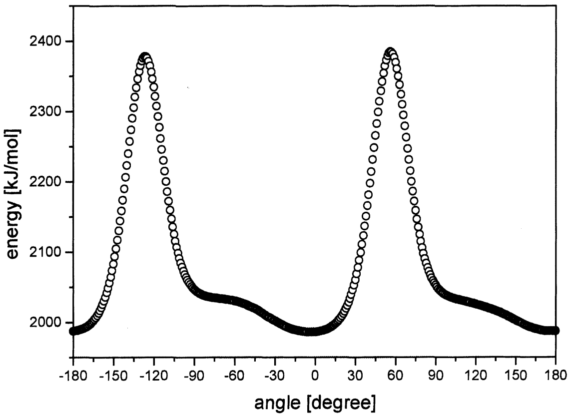

Fig. 5. The potential energy of an isolated anion as a function of the angle of rotation of one of its phenyl rings, $U(\phi)$.

In the calculations for the isolated anion and the anion set in the crystal lattice the potential energy was calculated for the rotations of one of the phenyl rings from $\phi = 0°$ to $\phi = 360°$, by steps of 1°; assuming the other rings fixed in the positions following from the crystallographic data. This assumption corresponds to the model in which the time the ring stays in the equilibrium position is much longer than the time of a jump to a neighbouring equilibrium position. The $U(\phi)$ dependence for the isolated anion and the anion set in the crystal are shown in Figs. 5 and 6, respectively.

Because of the high symmetry of the anion it is irrelevant which ring rotates and which doesn't. The calculations confirm that all the rings are in the same energy states, and the positions 0° and 180° are equivalent.

During a rotation of one of the rings the distances between its atoms and the atoms of the other rings change. There are such positions of the phenyl ring

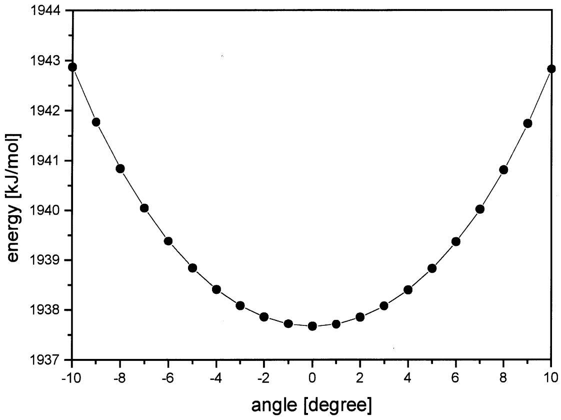

Fig. 6. The potential energy of an anion set in the crystal, as a function of the rotation angle of one of its phenyl rings.

for which the distance between the hydrogen atoms of the neighbouring rings is smaller than the extreme of 1.9 Å (empty markers in Fig. 5). The results of the calculations have led to the important conclusion that the phenyl ring of the tetraphenylborate anion cannot – for steric reason – undergo hindered reorientations about the axis of the bond between the central atom and the phenyl ring (B-Ph). As the anion has only one minimum of the potential energy, it cannot perform reorientation jumps.

4.3. Calculations of the Vibrations Frequency of the Phenyl Ring and the Force Constant

On the basis of the known dependence of the potential energy on the phenyl ring angle of rotation in the crystal, we can calculate the average and maximum amplitude of oscillations. The potential energy was approximated by the following function, after [15]:

$$U(\phi) = a + b\phi + c\phi^2 + d\phi^3. \tag{3}$$

The terms $c\phi^2$ and $d\phi^3$ describe the harmonic and non-harmonic contributions to the potential energy, respectively.

This function was fitted by the least squares method to the results obtained for the angle ϕ varying from –15° do 15°, leading to the values a = 1936,0 kJ/mol, b = –0,4596 kJ/mol·rad, c = 191,16 kJ/mol·rad^2. In this range of the angle ϕ the potential energy function is well described by a square function. A term with the angle in the third power is necessary to describe the potential for $\phi \gg \pm 20°$.

The mean square of the amplitude of the phenyl ring oscillation amplitude can be determined from the formula [15]

$$\langle \phi^2 \rangle = \frac{RT}{2c}. \tag{4}$$

The root of this expression, $\langle \phi^2 \rangle^{1/2}$, stands for the half width of the potential energy curve cut off at $RT/2$ from the minimum and is the mean amplitude of oscillations. The maximum value of the oscillation amplitude can be found from the formula:

$$\Delta\phi_{1/2} = \sqrt{\frac{RT}{c}}, \tag{5}$$

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

For 295 K, at which the relaxation time T_1 reaches a minimum, the values $\langle \phi^2 \rangle^{1/2}$ and $\Delta\phi_{1/2}$ are 4,6° and 6,5°, respectively. If we take RT from (4) and (5) and determe E_a from the temperature dependence of T_1, we get $\langle \phi^2 \rangle^{1/2}$ = 8,2° and $\Delta\phi_{1/2}$ = 11,7°. The oscillation amplitudes estimated in this way are similar to those obtained on the basis of the second moment change.

5. Discussion

In rubidium tetraphenylborate, similarly to tetraphenyltin, two activation processes, characterised by different activation energies, have been observed. One process, characterised by a high activation energy and manifested by a second moment reduction, can be interpreted as anisotropic reorientation of tetraphenylborate anions and isotropic reorientation of the tetraphenyltin about its centre of gravity. The second process, corresponding to low activation energy, manifested by a small change in the second moment and a considerable change in T_1 minimum, has been interpreted as small-angle oscillations / reorientations of the phenyl rings. The results of the atom-atom calculations have shown that the phenyl ring of the tetraphenyl borate anion cannot – for steric reasons – perform hindered reorientations about the bond between the central atom and the phenyl ring (B-Ph). Moreover, the phenyl ring cannot perform reorientational jumps, as it has only one minimum of potential energy. The amplitude of the phenyl ring movement at the potential energy minimum has been estimated to be a few degrees. The motion of the

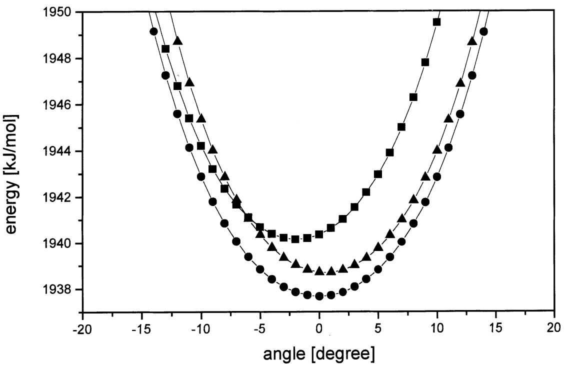

Fig. 7. The angular dependence of the potential energy for a rotation of one phenyl ring, assuming different arrangements of neighbouring rings: a) (●) all other rings at their equilibrium positions, b) (■) other rings of the same anion deviated by a few degrees from the equilibrium positions, c) (▲) all other rings in the crystal deviated randomly by a few degrees from their equilibrium positions.

phenyl ring significantly depends on the neighbouring molecules, because of their dense packing in the crystal and the gear in of neighbouring rings. As the X-Ph bond is shorter in rubidium tetraphenylborate (1.6 Å) than in tetraphenyltin (2.14 Å), the process of small-angle oscillations / reorientations of phenyl rings in the former compounds requires greater activation energy.

The interpretation of the activation energy for the motion at the single minimum of the potential energy requires further considerations. Usually, the activation energy is interpreted as that needed to pass the energy barrier, equal to the difference between the minimum and maximum of the potential energy. In the compound studied each phenyl ring is at the potential energy minimum, and the activation energy can be treated as that needed for the ring to get out of the minimum. For a more detailed interpretation of this activation energy we have calculated the angular dependence of one phenyl ring in a given anion assuming different arrangements of neighbouring rings:

a) all other rings remain in their equilibrium positions,

b) three other rings in the same anion deviate slightly (by a few degrees) from their equilibrium positions,

c) all other rings in the crystal deviate randomly by a few degrees from their equilibrium positions.

The results of the angular dependence of the potential energies calculated for these initial conditions are presented in Figure 7. If all phenyl rings occupy their equilibrium positions, the potential energy minimum of the rotating ring takes the lowest value. If the neighbouring rings in the same anion deviate by a few degrees from the equilibrium positions, the potential energy minimum of the rotating ring takes a higher value. If the phenyl rings of all neighbouring molecules in the crystal deviate from their equilibrium positions, the potential energy minimum of the rotating ring shifts by a few degrees and takes a value by a few kJ/mol higher than in the previous cases.

One can see that the change in the arrangement of the neighbouring rings changes the position and increases the value of the potential energy minimum for a rotation of the ring in a given anion. Since, the rotating ring is forced to take a new, higher minimum, it means that it must overtake a certain small energy barier. Thus we can conclude that it is the barier, the value of which has been found in the NMR experiment, as a low activation energy of about ∼7kJ/mol. That value can be treated as the mean energy needed for small-angle oscillations / reorientations of the phenyl rings.

[1] S. Arnott and S. C. Abrahams, Acta Crystallographica **11**, 449 (1958).
[2] Y. Ozol, S. Vimba, and A. Ienins, Kristalogafija **7**, 362 (1962).
[3] A. Pajzderska, C. Ecolive, A. Girard, T. Wasiutyński, J. Wąsicki, and J. Sciesinski, J. Raman Spectr. **33**, 618 (2002).
[4] A. Pajzderska, J. Wąsicki, L. Bobrowicz-Sarga, I. Natkaniec, and T. Wasiutyński, Mol. Physics Report **31**, 103 (2001).
[5] A. Pajzderska, J. Wąsicki, and S. Lewicki, Z. Naturforsch. **54a**, 488 (1999).
[6] G. M. Sheldrick, SHELXS-97, Program for Solution of Crystal Structures, University of Göttingen (1997).
[7] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen (1997).
[8] J. H. van Vleck, Phys. Rev. **74**, 1168 (1948).
[9] N. Blombergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).
[10] A. Abragam, Priciples of Nuclear Magnetism, Oxford University Press (1985).
[11] E. R. Andrew, J. Chem. Phys. **18**, 607 (1950).
[12] K. Van Putte, J. Mag. Res. **2**, 23 (1970).
[13] A. I. Kitajgorodski, Kryształy molekularne, PWN, Warszawa 1976.
[14] N. A. Ahmed, A. I. Kitajgorodsky, and K. V. Mirskaya, Acta Cryst. **B27**, 867 (1971).
[15] U. Shmueli and P. A. Kroon, Acta Cryst. A30, 768 (1974).