

# An NMR solid-echo Study of Guanidinium Cation Reorientation in $[\text{C}(\text{NH}_2)_3]_3\text{Sb}_2\text{Cl}_9$

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The NMR solid-echo polycrystalline tris-guanidinium nonachlorodiantimonate (III) has been studied in a wide temperature range. The temperature dependences of a time position and an amplitude of solid-echo are characterized by minima at ca. 143 K and 273 K, which are assigned to the reorientation of two dynamically inequivalent guanidinium cations  $[\text{C}(\text{NH}_2)_3]^+$ . The motional parameters of the two types of guanidinium cations have been determined. — PACS: 64.70K; 76.60E

*Key words:* Organic Crystals; Nuclear Magnetic Resonance.

## 1. Introduction

Guanidinium crystals have interesting physical properties (see [1] and references therein). In guanidinium salts the cation  $[\text{C}(\text{NH}_2)_3]^+$  is planar or nearly planar and undergoes a reorientational motion around its  $C_3$  symmetry axis. In tris-guanidinium nonachlorodiantimonate,  $[\text{C}(\text{NH}_2)_3]_3\text{Sb}_2\text{Cl}_9$  there are two types of guanidinium cations  $[\text{C}(\text{NH}_2)_3]^+$ : the first is situated between polyanionic  $(\text{Sb}_2\text{Cl}_9^{3-})_n$  layers, and the second inside cavities formed by polyanions [1, 2]. According to an NMR study [1], the second type is the more mobile one. The present paper deals with a study of the molecular dynamics of guanidinium cations in  $[\text{C}(\text{NH}_2)_3]_3\text{Sb}_2\text{Cl}_9$  by using a new NMR technique described in [3–5].

## 2. Experimental Results

The  $^1\text{H}$  NMR study has been performed at 110–373 K by using a spectrometer of 60 MHz. The amplitude of the magic echo and the time of its maximum have been measured applying a sequence of two-pulse magic echos  $630^\circ_\gamma - \tau - 90^\circ_\chi - \text{Acq}(t)$  [4]. The results are shown in Figs. 1 and 2. The time of the magic echo maximum does not change in the temperature ranges 166–219 K and 315–373 K, while the minima are observed at 143 K and 273 K. A similar dependence is observed for the amplitude of the two-pulse magic echo. The solid lines in the figures are the theoret-

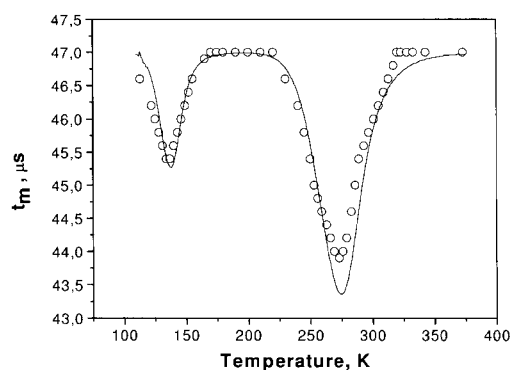


Fig. 1. The temperature dependence of the time position of the dipolar echo maximum in  $[\text{C}(\text{NH}_2)_3]_3\text{Sb}_2\text{Cl}_9$  for the pulse sequence  $630^\circ_\gamma - \tau - 90^\circ_\chi - \text{Acq}(t)$ .  $t_2 = 3.6 \mu\text{s}$ ;  $\tau - t_1 = 3.6 \mu\text{s}$ . The solid line is the theoretical curve.

cal fits, which allowed to extract activation parameters for the two dynamically different guanidinium cations. The fitted parameters are presented in Table 1.

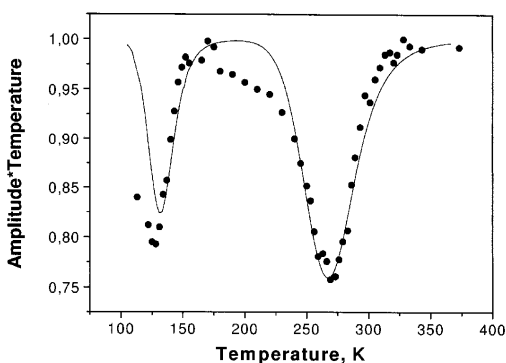
## 3. Discussion of Experimental Results

The temperature dependence of the time position and amplitude of the echo are determined by the dipolar correlation function [3–5]

$$h(t'', t') = W \sum_{i,j} \overline{a_{ij}(t'') a_{ij}(t')}, \quad (1)$$

Table 1. Motional parameters for reorientation of two different guanidinium cations  $[\text{C}(\text{NH}_2)_3]^+$ .

	$E_a$ (kJ/mol)		$\tau_{c0}$ (s)		$M_{21}^{\text{intra}}$ ( $\text{G}^2$ )	$\overline{M_{21}^{\text{intra}}}$ ( $\text{G}^2$ )
First type of cations	20.5	23.5	$1.6 \cdot 10^{-14}$	$1.6 \cdot 10^{-14}$	$i = 1:5$	$i = 1:2$
	[1]	[1]				
Two other types of cations	54.5	47.5	$1.3 \cdot 10^{-16}$	$10^{-14}$	$i = 2:9.5$	$i = 2:5$
	[1]	[1]				

Fig. 2. The temperature dependence of the amplitude of the echo (X) temperature (in arbitrary units) in  $[\text{C}(\text{NH}_2)_3]_3\text{Sb}_2\text{Cl}_9$  for the pulse sequence  $630_X^0 - \tau - 90_X^0 - \text{Acq}(t)$ .  $t_2 = 3.6 \mu\text{s}$ ;  $\tau - t_1 = 3.6 \mu\text{s}$ . The solid line is the theoretical curve.

where

$$W = \frac{3}{4} \gamma^4 \hbar^2 I(I+1) \frac{1}{N}, \quad (2)$$

and

$$a_{ij}(t') = R_{ij}^{-3}(t') [1 - 3 \cos^2 \theta_{ij}(t')]. \quad (3)$$

In (1) the upper bar denotes the average of the values  $a_{ij}(t'')a_{ij}(t')$  during the random motions of the spin-pair  $i-j$ . In (2)  $\gamma$  and  $I$  are the gyromagnetic ratio and nuclear spin, respectively. In (3)  $R_{ij}$  and  $\theta_{ij}$  are the spherical coordinates of vector  $\mathbf{R}_{ij}$  (of the pair of spins  $i, j$ ) in the laboratory frame where the vector of the external magnetic field is parallel to  $z$ -axis.

The correlation function  $h(t'', t')$  may be separated into intra- and inter-molecular contributions

$$h(t', t'') = h^{\text{intra}}(t', t'') + h^{\text{inter}}(t', t''). \quad (4)$$

where  $h^{\text{intra}}(t', t'')$  is the intramolecular contribution to the correlation function  $h(t'', t')$ , and  $h^{\text{inter}}(t', t'')$  is the intermolecular contribution to the correlation function  $h(t'', t')$ .

The intermolecular dipolar interactions in  $[\text{C}(\text{NH}_2)_3]_3\text{Sb}_2\text{Cl}_9$  are much smaller than the intramolecular dipolar interactions [1], so for simplicity we omit them in our consideration of the correlation function  $h(t'', t')$ .

For nuclei of a given cation (the first or the second type) the correlation functions  $h_{ij}(|t'' - t'|) = \overline{a_{ij}(t'')a_{ij}(t')}$  and  $h_{\alpha\beta}(|t'' - t'|) = \overline{a_{\alpha\beta}(t'')a_{\alpha\beta}(t')}$  have the form [5, 6]

$$h_{ij}(t) = (\overline{a_{ij}})^2 + [a_{ij}^2 - (\overline{a_{ij}})^2] \exp\left(-\frac{t}{\tau_{c1}}\right), \quad (5a)$$

$$h_{\alpha\beta}(t) = (\overline{a_{\alpha\beta}})^2 + [a_{\alpha\beta}^2 - (\overline{a_{\alpha\beta}})^2] \exp\left(-\frac{t}{\tau_{c2}}\right), \quad (5b)$$

where  $t = |t'' - t'|$ ; the indexes  $i$  and  $j$  denote the nuclei of the first type of cations, while  $\alpha$  and  $\beta$  denote nuclei of the second type of cations. The upper bar denotes the average of the random motions of the nuclei:

$$\overline{a_{ij}} = \frac{1}{n} \sum_{l=1}^n a_{ij}(\Omega_l), \quad (6a)$$

$$\overline{a_{\alpha\beta}} = \frac{1}{\gamma} \sum_{m=1}^{\gamma} a_{\alpha\beta}(\Omega_m). \quad (6b)$$

Here  $\Omega_l$  ( $l = 1, \dots, n$ ;  $n = 3$ ) denotes the  $l$ -orientation of vectors  $\mathbf{r}_{ij}$  in the reorienting first cation and  $\Omega_m$  ( $m = 1, \dots, \gamma$ ;  $\gamma = 3$ ) denotes the  $m$ -orientation of vectors  $\mathbf{r}_{\alpha\beta}$  in the reorienting second cations. In (5)  $\tau_{c1}$  and  $\tau_{c2}$  are the correlation times for the reorientation of the first and second type of the cations.

Inserting (5) into (1), and using (2) and (3) and the formula of van Vleck for  $M_2$ , we obtain

$$h^{\text{intra}}(t) = \overline{M_{21}^{\text{intra}}} + (M_{21}^{\text{intra}} - \overline{M_{21}^{\text{intra}}}) \exp\left(-\frac{t}{\tau_{c1}}\right) + \overline{M_{22}^{\text{intra}}} + (M_{22}^{\text{intra}} - \overline{M_{22}^{\text{intra}}}) \exp\left(-\frac{t}{\tau_{c2}}\right). \quad (7)$$

Here  $M_{21}^{\text{intra}}$  is the intramolecular part of the second moment of the NMR line obtained for the rigid structure of the first type of the cations;  $\overline{M_{21}^{\text{intra}}}$  is the intramolecular second moment averaged by the reorientation of that first cation. Similarly,  $M_{22}^{\text{intra}}$  and  $\overline{M_{22}^{\text{intra}}}$  in (7) concern the second type of cations and denote the rigid second moment, reduced by the reorientation of that cation, respectively.

The echo signal (the pulse sequence  $(2n+1) \cdot 90_X^0 - \tau - 90_X^0 - \text{Acq}(t)$ ) in solids is determined by the equation [3–5]

$$\begin{aligned}
V(t, t_2, \tau, t_1) = (-1)^n \beta & \left[ 1 - \frac{1}{4} \int_0^{t_1} (t_1 - z) h(z) dz - \frac{1}{2} \int_0^{t_1} z \cdot h(z) dz - \frac{t_1}{2} \int_{t_1}^{\tau-t_1} h(z) dz - \frac{1}{2} \int_{\tau-t_1}^{\tau} (\tau - z) h(z) dz \right. \\
& - \int_0^{\tau-t_1} [(\tau - t_1) - z] h(z) dz - \frac{1}{2} \int_{\tau+t_2-t_1}^{\tau+t_2} [(\tau + t_2 - t_1) - z] h(z) dz + \frac{t_1}{2} \int_{\tau+t_2}^{t-t_1} h(z) dz \\
& + \frac{1}{2} \int_{t-t_1}^t (t - z) h(z) dz - \int_{t_2}^{\tau+t_2-t_1} (t_2 - z) h(z) dz + (\tau - t_1) \int_{\tau+t_2-t_1}^{t-\tau} h(z) dz \\
& \left. + \int_{t-\tau}^{t-t_1} [(t - t_1) - z] h(z) dz - \int_0^{t-\tau-t_2} [(t - \tau - t_2) - z] h(z) dz + \dots \right]. \quad (8)
\end{aligned}$$

Inserting (7) into (8), we obtain

$$V(t, t_2, \tau, t_1) = (-1)^n \beta \exp \left\{ -\frac{1}{2} K_0 \left[ t - \left( 2\tau + t_2 - \frac{t_1}{2} \right) \right]^2 - \sum_{i=1,2} K_i \tau_{ci}^2 R_i(t, t_2, \tau, t_1, \tau_{ci}) \right\}, \quad (9)$$

where  $\beta = \hbar \omega_0 / kT$  and

$$\begin{aligned}
R_i(t, t_2, \tau, t_1, \tau_{ci}) = & -\frac{7}{4} + \frac{t}{\tau_{ci}} - \frac{3t_1}{4\tau_{ci}} - \frac{t_2}{\tau_{ci}} - \frac{1}{4} \exp\left(-\frac{t_1}{\tau_{ci}}\right) - \exp\left(-\frac{t_2}{\tau_{ci}}\right) - \frac{1}{2} \exp\left(-\frac{t}{\tau_{ci}}\right) \\
& + \frac{1}{2} \exp\left(-\frac{\tau - t_1}{\tau_{ci}}\right) - \frac{1}{2} \exp\left(-\frac{t - t_1}{\tau_{ci}}\right) + \frac{1}{2} \exp\left(-\frac{\tau + t_2}{\tau_{ci}}\right) + \exp\left(-\frac{t - \tau}{\tau_{ci}}\right) \\
& + \exp\left(-\frac{t - \tau - t_2}{\tau_{ci}}\right) + \frac{1}{2} \exp\left(-\frac{\tau}{\tau_{ci}}\right) + \frac{1}{2} \exp\left(-\frac{\tau + t_2 - t_1}{\tau_{ci}}\right). \quad (10)
\end{aligned}$$

In (9)

$$\begin{aligned}
K_0 &= \overline{M_{21}^{\text{intra}}} + \overline{M_{22}^{\text{intra}}}, \\
K_1 &= \left( \overline{M_{21}^{\text{intra}}} - \overline{M_{21}^{\text{intra}}} \right), \\
K_2 &= \left( \overline{M_{22}^{\text{intra}}} - \overline{M_{22}^{\text{intra}}} \right). \quad (11)
\end{aligned}$$

The experimental and theoretical temperature dependences of the time position and the amplitude of the echo signal (pulse sequence  $(2n+1) \cdot 90_Y^0 - \tau - 90_X^0 - \text{Acq}(t)$ ) obtained for the polycrystalline sample of the tris-guanidinium nonachlorodiantimonate,  $[\text{C}(\text{NH}_2)_3]_3\text{Sb}_2\text{Cl}_9$  are shown in Figs. 1 and 2. The motional parameters obtained are presented in Table 1. The correlation time  $\tau_{ci}$  ( $i = 1, 2$ ) is assumed to be related to the activation energies  $E_{ai}$  through the Arrhenius relations

$$\tau_c = \tau_{c0} \exp(E_a/RT).$$

For rigid guanidinium cations the theoretical value of the second moment is  $M_2^{\text{intra}} \cong 15 \text{ G}^2$  ( $1 \text{ G}^2 = 0.01 (mT)^2$ ) [1, 7]. This value agrees – in the accuracy limit – with the experimental value  $M_2^{\text{intra}} = M_{21}^{\text{intra}} + M_{22}^{\text{intra}} = 14.5 \text{ G}^2$ . The reorientation of the guanidinium cation about the  $C_3$  symmetry axis reduces the second moment to about  $3.9 \text{ G}^2$ , so the theoretical values for  $M_{2i}^{\text{inter}}$  ( $i = 1, 2$ ) must be  $M_{21}^{\text{inter}} = 1.3 \text{ G}^2$  and  $M_{22}^{\text{inter}} = 2.6 \text{ G}^2$ . The experimental values  $\overline{M_{21}^{\text{inter}}} = 2 \text{ G}^2$  and  $\overline{M_{22}^{\text{inter}}} = 5 \text{ G}^2$  do not agree with the theoretical ones. It is possible that this discrepancy results from the fact that the axes of reorientation of the guanidinium cations are not exactly perpendicular to the plane of the guanidinium cation  $[\text{C}(\text{NH}_2)_3]^+$ .

It is important to note that the value  $\tau_{c0} = 10^{-14} \text{ s}$  obtained in our experiment for the motion of the second type of the cations is more reasonable than the value  $\tau_{c0} = 1.3 \cdot 10^{-16}$  obtained in [1].

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