

THE LATTICE DYNAMICS OF ADAMANTANE. III. THE TETRAGONAL PHASE<sup>1</sup>

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Dispersion curves are calculated for high-symmetry directions in the crystal of the tetragonal phase of adamantane with the use of "6-exp" function. The computed frequency distribution function is compatible with the spectrum obtained experimentally by Stockmeyer and Stiller.

*1. Introduction*

In the first paper of this series on the lattice dynamics of adamantane [1] calculations are presented for the high-temperature phase. The agreement with experiment (as regards the frequency distribution function) implied that the applied model, consisting in the description of intermolecular interactions by means of the "6-exp" function, is correct.

With lower temperatures of the crystal the anharmonic effects (*e.g.*, thermal expansion) become smaller, and the potential of the "atom-atom" interaction gives a better agreement with experiment as regards, for example, the heat of sublimation [2]. Therefore it seems it is purposeful and interesting to perform calculations of the lattice dynamics for the low-temperature form of adamantane and to compare the obtained results with experimental data and results obtained for the cubic phase.

In the successive sections this paper presents a description of the structure of the tetragonal phase (Sec. 2), a discussion on the symmetry of force constant tensors (Sec. 3), and the calculated dispersion curves, frequency distribution functions and conclusions arrived at from the comparison between calculations and experiment (Secs 4 and 5).

*2. Crystalline structure of tetragonal phase*

At a temperature of  $-65^{\circ}\text{C}$  the adamantane crystal transforms from the high-temperature (cubic phase) to the low-temperature one (tetragonal phase) [11]. The structure of the tetragonal phase has been examined roentgenographically at a temperature of  $-110^{\circ}\text{C}$  [4,5].

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The crystal's symmetry is described by the space group  $P4_2c$  ( $D_{2d}^4$ ). The face-centered cubic cell becomes transformed into a body-centered tetragonal one with two molecules in the cell. This is presented diagrammatically in Fig. 1. The dimensions of the tetragonal cell can be expressed by means of the cubic lattice constant,

$$a_T = \frac{a_C}{2}; \quad c_T = a_C.$$

The values of the lattice constants of the tetragonal lattice were calculated from these relations with the use of the known values of cubic lattice constant at room temperature and the

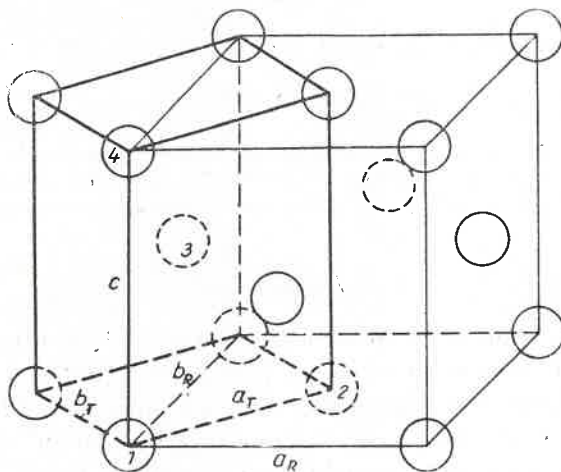


Fig. 1. A diagram of the formation of the tetragonal elementary cell of adamantane from the cubic cell

expansion coefficient [6]. The obtained values, 6.45 and 9.07 Å, differ somewhat from parameters obtained roentgenographically [4] at 163°K, *viz.*, 6.60 and 8.81 Å.

During the lowering of temperature of the crystal the adamantane molecules rotate about an axis parallel to the  $c$ -axis of the crystal by an angle of  $9^\circ$  at the phase transition point (208.6°K). The molecules lying in the (001) plane rotate in the same direction, while all others in the opposite direction. Therefore in the tetragonal phase there are two translationally nonequivalent sets of molecules. After rotation of the molecules the crystal passes on to a configuration more advantageous in terms of energy, what in Ref. [7] was proved by the finding of a minimum in the function of potential energy.

### 3. Tensors of force constants and the dynamical matrix

The function of crystal potential energy assumed for our calculations and the procedure of force constant calculations have been described in a preceding paper [1]. The force constants were calculated<sup>2</sup> in the reference frame of the axes of the cubic phase crystal, the only change

<sup>2</sup> Computations were performed on the ODRA-1204 computer at the Computation Center of the Institute of Physics of the Jagellonian University in Cracow.

being in the matrix of direction cosines describing the orientation of the molecule axes. Calculations take account of interactions with nearest neighbours and molecules distant by the lattice constants.

The symmetry of the tensor of force constants in the cubic phase system stems from the following relationships:  
for pairs of molecules 1-3:

$$\sigma^{(cb)} \cdot \Phi(1-3) \cdot \tilde{\sigma}^{(cb)} = \Phi(1-3)$$

$$C_2^{(a)} \cdot \Phi(1-3) \cdot \tilde{C}_2^{(a)} = \Phi(1-3)$$

and for pairs of molecules 1-2:

$$\sigma^{(ab)} \cdot \Phi(1-2) \cdot \tilde{\sigma}^{(ab)} = \Phi(1-2)$$

$$C_2^{(c)} \cdot \Phi(1-2) \cdot \tilde{C}_2^{(c)} = \Phi(1-2)$$

$$C_2^{(ab)} \cdot \Phi(1-2) \cdot \tilde{C}_2^{(ab)} = \Phi(1-2).$$

Carrying out the symmetry operations listed above leads to the tensors presented in Table I. This table also gives the tensors for the same pairs of molecules in the reference frame of the tetragonal crystal axes, obtained through the transformation

$$\Phi^T = T \cdot \Phi^C \cdot \tilde{T}$$

TABLE I

Symmetry of tensors of force constants

in reference frame of cubic crystal axes						
$\Phi(1-3)$				$\Phi(1-2)$		
$\begin{bmatrix} A' & 0 & 0 & 0 & a' & b' \\ 0 & B' & D' & c' & 0 & 0 \\ 0 & D' & C' & d' & 0 & 0 \\ 0 & -c' & -d' & \alpha' & 0 & 0 \\ -a' & 0 & 0 & 0 & \beta' & \delta' \\ -b' & 0 & 0 & 0 & \delta' & \gamma' \end{bmatrix}$	$\begin{bmatrix} A'_1 & E'_1 & 0 & 0 & 0 & b'_1 \\ E'_1 & A'_1 & 0 & 0 & 0 & -b'_1 \\ 0 & 0 & B'_1 & -d'_1 & d'_1 & 0 \\ 0 & 0 & -d'_1 & \alpha'_1 & \varepsilon'_1 & 0 \\ 0 & 0 & d'_1 & \varepsilon'_1 & \alpha'_1 & 0 \\ -b'_1 & b'_1 & 0 & 0 & 0 & \gamma'_1 \end{bmatrix}$					
in reference frame of tetragonal crystals axes						
$\Phi(1-1)$			$\Phi(1-3)$			$\Phi(1-2)$
$\begin{bmatrix} A_0 & 0 & 0 & 0 & 0 & 0 \\ 0 & A_0 & 0 & 0 & 0 & 0 \\ 0 & 0 & B_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \alpha_0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \alpha_0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \beta_0 \end{bmatrix}$	$\begin{bmatrix} A & C & D & a & b & e \\ C & A & D & -b & -a & -e \\ D & D & B & f & -f & 0 \\ -a & b & -f & \alpha & \gamma & \delta \\ -b & a & f & \gamma & \alpha & \delta \\ -e & e & 0 & \delta & \delta & \beta \end{bmatrix}$			$\begin{bmatrix} A_2 & 0 & 0 & 0 & 0 & 0 \\ 0 & B_2 & 0 & 0 & 0 & a_2 \\ 0 & 0 & C_2 & 0 & b_2 & 0 \\ 0 & 0 & 0 & \alpha_2 & 0 & 0 \\ 0 & 0 & -b_2 & 0 & \beta_2 & 0 \\ 0 & -a_2 & 0 & 0 & 0 & \gamma_2 \end{bmatrix}$		

where

$$T = \begin{bmatrix} S & 0 \\ 0 & S \end{bmatrix}; \quad S = \begin{bmatrix} \frac{\sqrt{2}}{2} & \frac{\sqrt{2}}{2} & 0 \\ -\frac{\sqrt{2}}{2} & \frac{\sqrt{2}}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

The tensors of force constants for the other pairs of molecules may be obtained from tensors  $\Phi(1-3)$  and  $\Phi(1-2)$  by acting on them with appropriate symmetry elements of the  $D_{2d}^4$  group. These elements have been given in the second paper of this series [3]. The components of the  $\Phi(1-1)$  tensor were calculated from the invariance conditions of the potential energy of the crystal with respect to translations and rotations of the crystal as a whole [8, 9]: for translation-translation force constants ( $\Phi^{TT}$ ):

$$\sum_{l'k'} \Phi_{ij}^{TT}(lk, l'k') = 0$$

and for libration-libration couplings ( $\Phi^{LT}$ ):

$$\sum_{l'k'} \Phi_{ij}^{LL}(lk, l'k') = \sum_{\substack{ps \\ l'k'}} \delta_{jps} \cdot \Phi_{ip}^{LT}(lk, l'k') \cdot X_s(lk, l'k')$$

where  $\Phi^{LT}$  are the libration-translation force constants,  $X_s$  is the component of the vector of the distance between the molecules  $lk$  and  $l'k'$ , and  $\delta_{jps}$  is the antisymmetric Levi-Civita tensor.

The calculated values of the  $\Phi(1-1)$  tensor components are as follows:

$$A_0 = -8A - 2A_2 - 2B_2$$

$$B_0 = -8B - 4C_2$$

$$\alpha_0 = -8\alpha - 2\alpha_2 - 2\beta_2 + a_T(4f - 2b) + 4b \cdot c_T$$

$$\beta_0 = 8\beta - 4\gamma_2 + a_T(4a_2 - 8e).$$

Since the system of principal axes of the molecule's moment of inertia does not coincide with the system of crystal axes, the tensors of force constants were transformed additionally to the system of the molecule's axes according to the relations:

$$\Phi^M(1-3) = A_1 \cdot \Phi^T(1-3) \cdot \tilde{A}_3$$

$$\Phi^M(1-2) = A_1 \cdot \Phi^T(1-2) \cdot \tilde{A}_1$$

The superscript  $M$  indicates that the tensor is expressed in the system of axes of the molecule, the superscript  $T$  likewise in the system of axes of the tetragonal crystal, and  $A_1$  and  $A_3$  are the respective matrices of direction cosines of the molecules 1 and 3.

The elements of the twelfth-order dynamical matrix were computed according to the formula given in Ref. [1]. In solving the secular equation use was made of the results of lattice vibration analysis by group-theoretical methods, diagonalizing the dynamical matrix blockwise by means of the matrix obtained from the polarization vectors [3].

#### 4. Dispersion curves and frequency distribution function

Calculations of the dispersion curves for the tetragonal phase of adamantane were performed for the following directions: [100], [001], [110], and [011]. The results of computations are shown in Figs 2 to 5. The diagrams have the vibrational modes obtained from the group-theoretical analysis indicated [3].

Attention is focused to the fact that most of the dispersion curves are flat *i.e.*, the

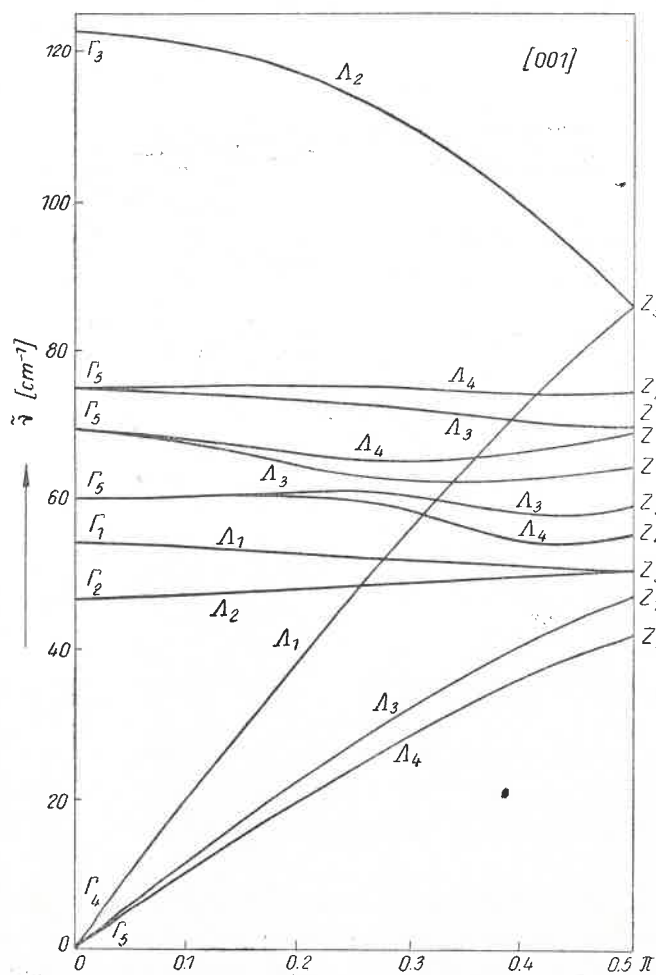


Fig. 2. Dispersion branches for the [001] direction

frequency of librational vibrations depends very weakly on the value of the wave vector. Strong dispersion is displayed only by the translational modes with polarization parallel to the  $c$ -axis of the crystal. The large value of the frequency of this vibration of symmetry  $\Gamma_3$  at point  $\vec{q} = 0$  implies strong intermolecular interactions along the  $c$ -axis of the crystal.

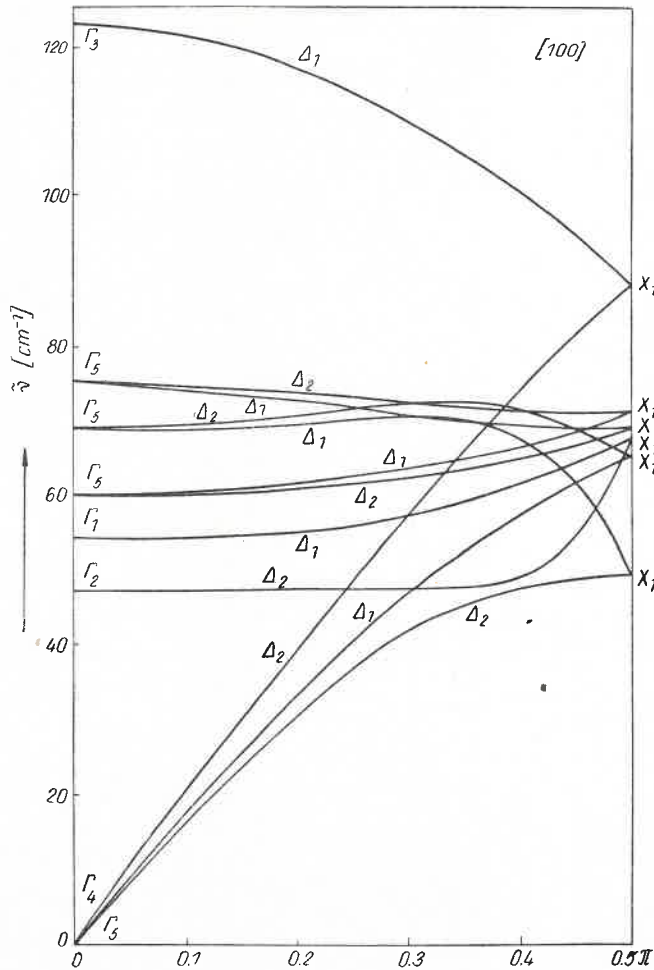


Fig. 3. Dispersion branches for the [100] direction

A similar conclusion is arrived at by the authors of Ref. [4] in their study on the tetragonal phase structure.

The lack of optical measurements of lattice vibrations at the point  $\vec{q} = 0$  by optical spectroscopic techniques makes impossible any comparison of computations with experiment. No data is available in the literature on the values of amplitudes of thermal vibrations of the adamantane molecule in the tetragonal phase.

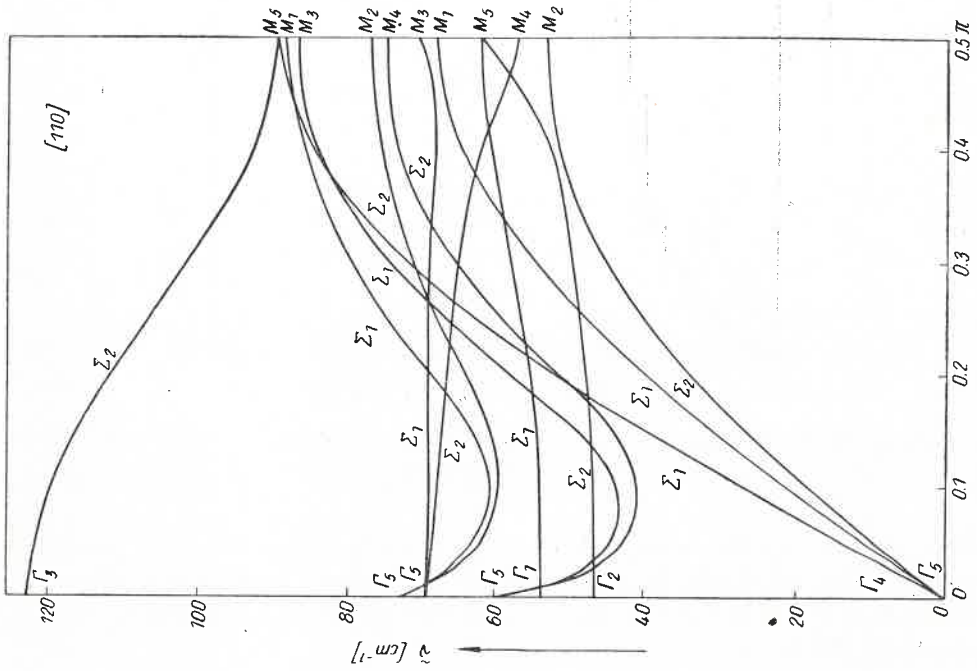


Fig. 4. Dispersion branches for the [110] direction

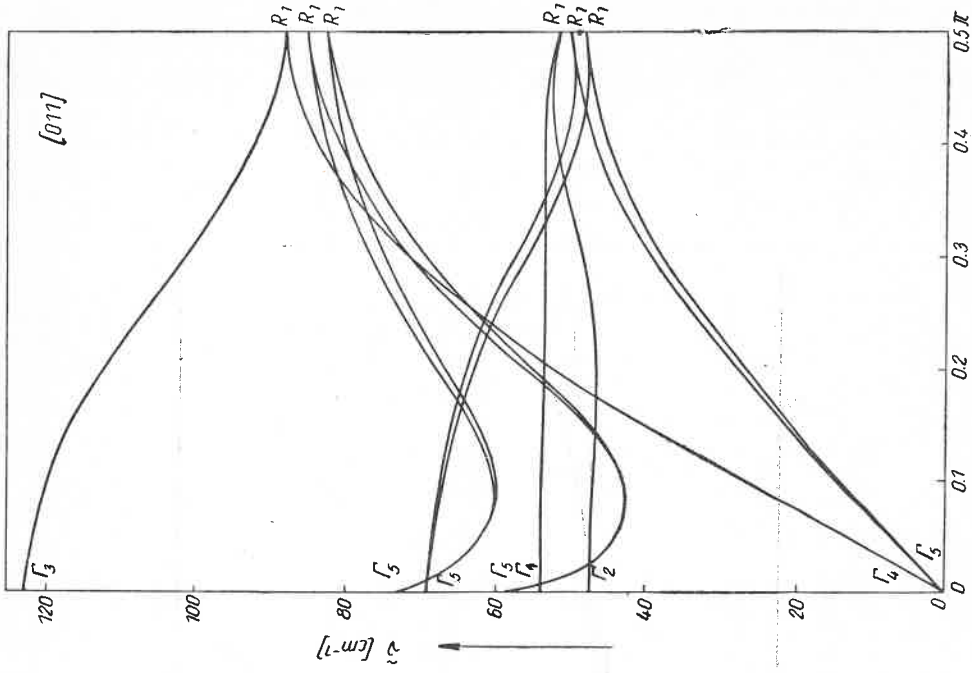


Fig. 5. Dispersion branches for the [011] direction

The increased packing of molecules of adamantane in the tetragonal structure causes that the mean frequency of librational vibrations about the  $c$ -axis (in phase  $\Gamma_1$ ,  $46.5 \text{ cm}^{-1}$  and out of phase  $\Gamma_2$ ,  $54 \text{ cm}^{-1}$ ) is much higher than that for the cubic phase at the same temperature,  $29.5 \text{ cm}^{-1}$ .

It is rather strange that the splitting of degenerate vibrations is so extremely weak for all considered directions of the Brillouin zone.

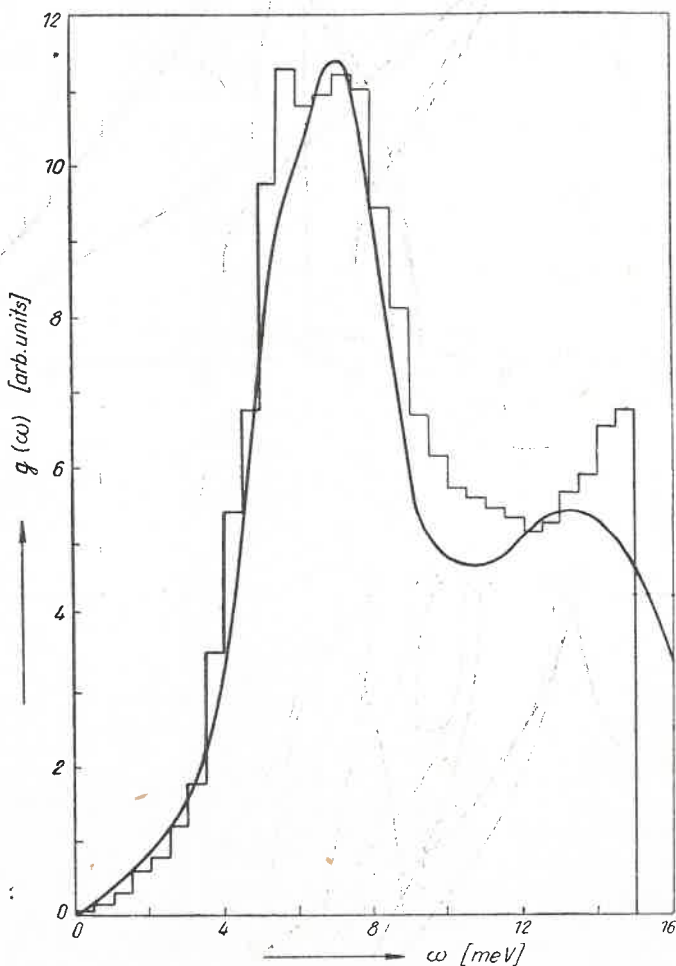


Fig. 6. Frequency distribution function for tetragonal phase of adamantane; histogram — calculations, continuous line — experiment [10]

On the basis of the known dispersion curves calculations of the frequency distribution function were performed. Fig. 6 compares computations (in the form of a histogram) for the temperature of  $208^\circ\text{K}$  with the results of the measurement made by Stockmeyer and Stiller [10] at  $198^\circ\text{K}$ .



### 5. Conclusions

Fig. 6 shows there is good agreement between the calculated frequency distribution function and the experimental one. The high intensity of the central band in the  $g(\omega)$  spectrum is primarily due to the weak dispersion of librational modes. This band, however, does not arise exclusively due to librational vibrations; there is also a certain contribution from translational vibrations (optical and acoustic), except for the translation along the  $c$ -axis of the crystal. The other band observed at about 13 meV has its origin in the optical translational vibration of polarization parallel to the  $c$ -axis.

The assumption of no coupling between internal vibrations and lattice vibrations appears to be quite true. Such coupling would bring about a decrease in the frequency of the highest external vibrations. Hence, in the case of the tetragonal phase of adamantane this would concern the translation vibration of frequency  $122.5 \text{ cm}^{-1}$  at  $\vec{q} = 0$ . As the 13-meV band in the  $g(\omega)$  spectrum is due entirely to this vibration, the effect of such coupling would have to be evident right from the frequency distribution function.

In conclusion it must be stated that the assumed force model of the adamantane crystal gives good results in the problem of lattice dynamics, and there is compatibility with experiment. This provides us with hope that good results will be achieved in the determination of some physical and thermodynamical quantities which characterize both polymorphic states of adamantane. This problem will be dealt with in a subsequent paper.

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