

EO dehydration on increasing temperature. The only embarrassment remaining with this is that the H_1 phase with a larger micelle curvature occurs at a higher concentration than L_α^H , even if only by a few degrees. It results in H_1 melting above T_c , the first example of this. A possible explanation is that the H_1 phase provides a lower intermicellar interaction energy contribution.

At even higher concentrations, the H_1/L_α transition appears to occur without any other intermediate phases intervening. Caution should be exercised in regarding this as a firm result because intermediate phases can have textures resembling H_1 (as with the deformed hexagonal phase). Moreover, the phase formation could involve slow kinetics as is demonstrated by the metastability in $C_{16}EO_6$.^{17,30} We were unable to examine this transition in detail because of the limited availability of $C_{22}EO_6$. The remaining rich variety of phases formed by $C_{22}EO_6$ is really unremarkable, resembling other previously published systems.^{11-13,15-17}

The L_α^H phase clearly owes its stability to the intramicellar curvature forces, which exclude the existence of circular rod micelles above the cloud temperature. This is likely to arise from the dislike of the C_{22} chains for an all-trans conformation. (Note that even in the H_1 phase the rod micelle radius is significantly less than the extended C_{22} chain length of 2.8 nm.) This is the reason why the H_1 phase melts well below the temperature observed with the C_{10} - C_{16} derivatives ($36 \pm 1^\circ\text{C}$). This supports the idea of an important role for chain length/conformation energies stabilizing intermediate phases.

Finally, it should be noted that there are many ways in which defects can be included in a lamellar structure; some of these have been considered theoretically by Bagdassarian et al.³¹ There may well be a number of possible intermediate phase structures of which the one considered here is but a single example. It will be interesting to investigate the structure of intermediate phases both stable and metastable in even longer chain surfactants in order to explore the range of mechanisms and structures by which systems move from L_α to H_1 phases.

Acknowledgment. S.S.F. thanks CAPES, Brazil, for a research studentship. We also thank Lancashire Polytechnic for supporting this project.

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Intermolecular Interaction of Antimony Trichloride in the Crystal of the Bimolecular Menshutkin Complex with Diphenylamine

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(Received: March 27, 1992; In Final Form: August 31, 1992)

The relationship between the change in the constants of intra- and intermolecular force fields of the molecules at the gas-crystal transition is discussed. Raman spectra of the crystal of bimolecular complex $(C_6H_5)_2NH \cdot 2SbCl_3$ at 293 and 77 K are obtained. Theoretical group and normal coordinate analysis of vibrations in the complex are performed. The intermolecular force constants are calculated without the application of model potentials, and the low frequency spectrum of the complex crystal is interpreted. It is quantitatively found that the intermolecular interaction between $SbCl_3$ molecules is stronger than that between $SbCl_3$ and hydrocarbon.

Introduction

The intermolecular interaction of molecular systems is of interest for many fields of science. The direct observation of intermolecular interaction is possible using low frequency IR and Raman spectroscopies. However, when the intermolecular interaction is studied

by these methods, the problem of interpreting the intermolecular spectrum arises. Use of model potential for calculating intermolecular force constants and lattice mode^{1,2} meet with difficulty because it is necessary to vary a large number of parameters, which results in uncertainty of the solution, increasing with the increase

of atoms in a molecule.³ Thus these methods are unsuitable for interpreting the information on the temperature dependence of spectral bands, phase-structure transitions, and other small factors of the change in the intermolecular interaction.⁴ Use of other methods^{5,6} requires the knowledge of the nature of intermolecular interaction, which is not always possible a priori. In normal coordinate analysis, the force constants from the calculation of model compounds are often transferred.⁷ At the same time, it is known that the change of the intermolecular interaction at the gas-condensed phase transition, during the variation of temperature, pressure, and other factors, influences the intramolecular force field.⁸⁻¹⁰ Especially problematic is the transference of force constants in the normal coordinate analysis of inorganic molecules. In this case the additional information on intermolecular interaction and interpretation of lattice mode spectrum is of interest.

One of such methods for the estimation of intermolecular interaction is based on the relationship between changes in the intramolecular and intermolecular force fields occurring during the gas-phase (free molecule) to condensed-phase (excited molecule) transition. The occurrence of such a relationship was not called in question by many researchers.^{1,2} However, this method was first employed for calculating the intermolecular interaction in pyramidal XY_3 molecules in the works of refs 10 and 11. However, the theoretical base of this method is not developed sufficiently. This left some doubts when the method was used for calculating the intermolecular interaction of various molecules.

The crystals of Menshutkin complexes are of interest as the objects of investigation with intermolecular interaction of a different nature.¹²⁻¹⁴ Some complexes were studied using nuclear quadrupole resonance (NQR),^{15,16} Raman,^{17,18} and IR¹⁹ spectroscopies. The appearance of X-ray diffraction data of the crystals of Menshutkin complexes^{13,14,20,22} allowed fuller use of spectral results. In refs 18 and 23, the lattice mode spectra of the crystals of some complexes were calculated and interpreted, but the nature of intermolecular interaction defining the structure of the complexes was studied unsufficiently. It is known that the formation of crystal structure is affected by the donor-acceptor interaction of antimony trichloride with an aromatic ring,¹² the coordination Sb-Hal (Hal = halogen) interaction,^{14,20} and the dipole interaction of $SbHal_3$ molecules.⁶

In this work we attempt to discuss this method of intermolecular interaction calculation in a more general theoretical way and to study the intermolecular interaction of antimony trichloride in the Menshutkin complex crystal with diphenylamine using Raman spectra.

Experimental Section

The distilled antimony trichloride was used to obtain the complex. The distillation was performed in the presence of annealed $CaCl_2$. The complex was prepared immediately after distillation. If required, the distilled antimony trichloride was stored in a desiccator with dry $CaCl_2$.

After being weighed, the components were sealed in ampules under vacuum, heated in an oil bath to melting, and violently stirred. The obtained complexes were purified in a sealed ampule by zone melting.²⁴ The formation of the complexes was verified by color and by melting temperature using the literature data,^{12,20} as well as by NQR spectroscopy.

Raman spectra were recorded using a double monochromator DFS-24 (LOMO, Russia) with excitation by He-Cd LG-62 and LG-70 lasers (Ukraine; exciting line 441.6 nm, irradiation power 100 and 40 mW, respectively). The spectral width of the monochromator slit was 1–2 cm^{-1} . A standard 90° geometry was used for illumination. The spectra were recorded at temperatures of 293 and 77 K. For recording the spectra at 77 K, an ampule with the sample was placed in a Dewar with liquid nitrogen.

Theory

The method is based on the superposition of the energies of intramolecular and intermolecular interaction during the condensed-phase formation.¹ For a molecule in a free state (gas) and in the condensed phase, the following expression is thus valid:¹

$$F(Q) = F^0(q) + V(\xi) \quad (1)$$

where $F^0(q)$ and $F(Q)$ are the potential energies of the free molecule and of the molecule in the condensed phase, q and Q are the corresponding vibrational coordinates ($q = r - r^0$, $Q = r - r_c$) which are combined together by the relation

$$Q = q - \Delta q \quad (2)$$

where $\Delta q = r_c - r^0$ is the change in the equilibrium value of the bond lengths and valence angles during the transition of a molecule from the free to condensed phase. $V(\xi)$ is the potential energy, and ξ is the coordinate of intermolecular interaction.

We expand the terms of expression 1 into a Taylor series near the point $Q_0 = 0$, the equilibrium position of a molecule in the condensed phase:

$$F_0|_{Q_0} + \sum_i \frac{\partial F}{\partial Q_i} Q_i|_{Q_0} + \frac{1}{2} \sum_{ij} \frac{\partial^2 F}{\partial Q_i \partial Q_j} Q_i Q_j|_{Q_0} + \dots = F^0_0|_{Q_0} + \sum_i \frac{\partial F^0}{\partial Q_i} Q_i|_{Q_0} + \frac{1}{2} \sum_{ij} \frac{\partial^2 F^0}{\partial Q_i \partial Q_j} Q_i Q_j|_{Q_0} + \dots + V_0|_{Q_0} + \sum_i \frac{\partial V}{\partial Q_i} Q_i|_{Q_0} + \frac{1}{2} \sum_{ij} \frac{\partial^2 V}{\partial Q_i \partial Q_j} Q_i Q_j|_{Q_0} + \dots \quad (3)$$

While the left hand terms of expression 3 may be interpreted according to the known physical quantities (bonding energy, harmonic and anharmonic force constants), the interpretation of the right hand terms of the expression would require the smallness of the change in the geometry of the equilibrium position of a molecule during the phase transition to be assumed. Then, expanding the potential energy derivatives of a free molecule in the power of Δq , it is likewise possible to obtain the terms with a physical meaning of harmonic and anharmonic force constants of a free molecule. After some transformations, expression 3 may give rise to the equation that relates the force constants of a free molecule and the molecule in the condensed phase to the force constants of intermolecular interaction:

$$f_{ij} = f^0_{ij} + \sum_m \alpha^0_{ijm} \Delta q_m + \sum_{m,l} \beta^0_{ijml} \Delta q_m \Delta q_l + \dots + \sum_{x,y} B^{xy}_{ij} v_{xy} \quad (4)$$

where α^0_{ijm} and β^0_{ijml} are the constants of the anharmonicity of a free molecule, v_{xy} are the intermolecular force constants, and the elements of the fourth-order tensor B^{xy}_{ij} are determined from the geometrical properties of inter- and intramolecular coordinates:

$$B^{xy}_{ij} = \frac{\partial^2 \xi_x}{\partial Q_j} \frac{\partial \xi_y}{\partial Q_i} \quad (5)$$

If the change in geometry of the equilibrium position of a molecule during the gas-phase-condensed-phase transition is small

$$f_{ij} - f^0_{ij} \gg \sum_m \alpha^0_{ijm} \Delta q_m + \sum_{m,l} \beta^0_{ijml} \Delta q_m \Delta q_l + \dots \quad (6)$$

expression 4 corresponds to the simple relationship between the force constants of intra- and intermolecular interaction:^{10,11}

$$f_{ij} = f^0_{ij} + \Delta f_{ij} \quad (7)$$

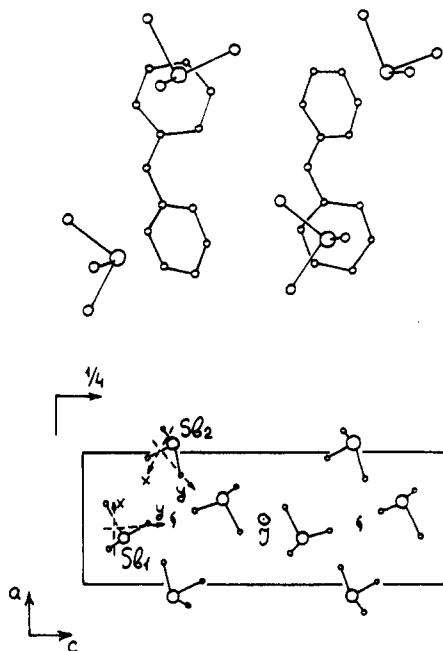
where Δf_{ij} are the phenomenological coefficients of the intermolecular interaction. On the basis of expressions 5 and 7, the normal coordinate analysis of molecule vibrations by spectra of gas and condensed phases allows the determination of the force constants of intermolecular interaction.

However, for calculation the intermolecular interaction, the normal coordinate analysis of intramolecular vibrations and the determination of intramolecular force constants must be performed with the accuracy of no less than the values of the force constants of intermolecular interaction. In this case the transference of intramolecular force constants found earlier for similar compounds is not applicable, and the use of iteration methods is in question.

For pyramidal XY_3 molecules, it was shown^{10,11} that the diagonal force constants of the potential energy matrix are mainly sensitive to the appearance of intermolecular interaction. Thus the approximation of four force constants f_r , f_α , $f_{rr'}$, and $f_{\alpha\alpha'}$ was

TABLE I: Geometry and Interpretation of Intermolecular Vibrations of SbCl_3 in Complexes

complex	type of SbCl_3 molecule	temperature, K	geometry of SbCl_3						intramolecular frequencies, cm^{-1}					
			bond lengths, Å			bond angles, deg								
			r_1	r_2	r_3	α_1	α_2	α_3	A_s	E_s	E_s	A_d	E_d	E_d
SbCl_3 (pure)	gas	496	2.33	2.33	2.33	99.5	99.5	99.5	380	352	352	153	122	122
diphenylamine	1	293	2.377	2.356	2.357	92.4	95.2	93.2	352	321	316	165	142	129
		77							350	320	314	166	147	132
2SbCl_3	2	293	2.380	2.382	2.366	92.2	94.3	91.7	341	321	304	165	147	142
		77							339	318	302	171	161	147

Figure 1. Lattice cell of the crystal of the $(\text{C}_6\text{H}_5)_2\text{NH} \cdot 2\text{SbCl}_3$ complex.

used for calculating the intermolecular interaction, and the intramolecular force constants may be found analytically.

Results and Discussion

According to X-ray data,²⁰ the lattice cell of the complex $(\text{C}_6\text{H}_5)_2\text{NH} \cdot 2\text{SbCl}_3$ belongs to the $P2_1/c$ space group with four molecules in the complex ($z = 2$) (Figure 1), and the crystal cell has two SbCl_3 molecules with different positions with respect to the symmetry elements and hydrocarbon, as well as with different bond lengths and valence angles. This difference was taken into consideration in spectrum interpretation and normal coordinate analysis of SbCl_3 vibrations. The geometrical parameters of the molecules are presented in the Table I.

The arrangement of SbCl_3 molecules in the lattice cell of the complex with diphenylamine and other hydrocarbons has a certain regularity. In all the crystals,^{13-15,20-22} there is a sublattice of SbCl_3 molecules having the same arrangement with respect to each other, and the molecules are located parallel to each other in mutually inverse directions along the z axis in site-symmetry coordinates. This arrangement is also observed in the crystal of pure antimony trichloride. Such an arrangement is characteristic for the weak dipole-dipole and coordination $\text{Sb}-\text{Cl}'$ interactions forming just that structure of the sublattice of antimony trichloride. For the bimolecular complexes,^{14,20} two sublattices of SbCl_3 are characteristic, whose molecules are not linked by symmetry elements, have different geometrical parameters, and are located in mutually perpendicular directions. The presence of the hydrocarbon changes relatively little the arrangement of SbCl_3 molecules with respect to each other. So it may be assumed that the intermolecular interaction between SbCl_3 molecules is stronger than the donor-acceptor interaction with the aromatic system of the hydrocarbon.

The theoretical group analysis using site symmetry gives the correlation diagram which implies the distribution of the SbCl_3 vibrations among symmetry classes shown in Chart I.

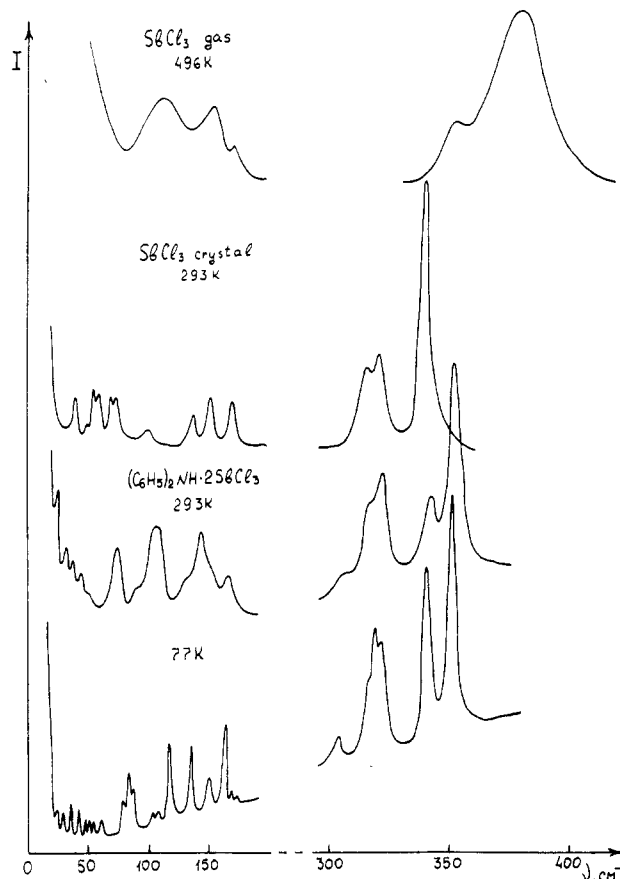


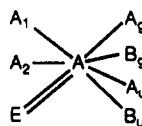
Figure 2. Raman spectra of the complex crystals and pure antimony trichloride.

CHART I

$$G_m \quad G_s \quad G_l \quad \Gamma_{\text{intern}} = 12A_g + 12A_u + 12B_g + 12B_u$$

$$C_{3v} \quad C_1 \quad C_i \quad \Gamma_{\text{transl}} = 6A_g + 6A_u + 6B_g + 6B_u$$

$$A_1 \quad A_2 \quad E \quad \Gamma_{\text{libr}} = 6A_g + 6A_u + 6B_g + 6B_u$$



According to the selection rules, the Raman spectra of the complexes are expected to have A_g and B_g vibrations. Figure 2 shows the Raman spectra of the complex crystal at temperatures of 293 and 77 K and the SbCl_3 spectra in gas and crystal phases. According to theoretical group analysis, the polarization spectra of the crystal of this complex are unsuitable due to the low symmetry of the crystal and also difficult due to the hygroscopicity of antimony trichloride. So the assignment of the bands of intramolecular spectra are based on some empirical assumptions concerning the regularities on the transformation of the SbCl_3 intramolecular spectrum during the gas-crystal transition.¹⁸ The most probable band assignment of intramolecular spectra is given in Table I. For convenience, the symbols of vibration types are conserved for the symmetry-free C_{3v} molecule. The interpretation of vibrational frequencies for SbCl_3 spectra in gas and crystal

TABLE II: Intra- and Intermolecular Force Constants of SbCl₃ in Complexes

complex	type of SbCl ₃ molecule	temperature, K	intramolecular constants				intermolecular constants					
			f_r	f_a	$f_{rr'}$	$f_{aa'}$	ν_{Rx}	ν_{Ry}	ν_{Rz}	ν_{Tx}	ν_{Ty}	ν_{Tz}
SbCl ₃ (pure)	gas	496	1.941	0.620	0.177	0.106						
SbCl ₃ (pure)	crystal	293	1.558	0.881	0.106	0.059	0.413	0.552	0.130	1.086	1.103	0.602
diphenylamine	1	293	1.605	0.785	0.124	0.059	0.328	0.426	0.083	0.820	0.850	0.543
		77	1.587	0.814	0.124	0.053	0.356	0.467	0.098	0.909	0.932	0.572
2SbCl ₃	2	293	1.487	0.861	0.094	0.024	0.420	0.555	0.121	1.080	1.110	0.679
		77	1.499	0.962	0.100	0.012	0.491	0.666	0.171	1.333	1.328	0.732

TABLE III: Calculated and Experimental Frequencies of Lattice Vibrations of SbCl₃ in Complexes

complex	type of SbCl ₃ molecule	temperature, K	lattice vibrations of SbCl ₃ , cm ⁻¹											
			ν_{Lx}		ν_{Ly}		ν_{Lz}		ν_{Tx}		ν_{Ty}		ν_{Tz}	
			calc	expt	calc	expt	calc	expt	calc	expt	calc	expt	calc	expt
diphenylamine	1	293	49	47	56	47	36	20	116	105	118	105	94	89
		77	51	50	58	54	39	21, 26	122	115	123	115	97	101
								34						
2SbCl ₃	2	293	55	47	63	71	44	33	133	129	134	129	105	89
		77	60	59	69	77, 81	52	41, 45	147	147	147	147	109	106
						84								

phases is taken from refs 10 and 11.

Using the obtained interpretation of intramolecular vibrations, from four solutions of a secular equation

$$\det (GF - \lambda E) = 0 \quad (8)$$

a physical appropriate one was chosen (Table II).

The anharmonic data of SbCl₃ was not found. So, the overtones of AsCl₃ were used.²⁵ The anharmonic constant α is 1.36 mdyn/Å. The maximal geometry change of SbCl₃ in the complex is 0.05 Å, and the $\alpha\Delta r$ value is 0.068 mdyn/Å; that is lower the values of Δf (Table II).

For pyramidal XY₃ molecules, some geometrical coefficients B_{ij}^{γ} were earlier obtained.^{10,11}

for librational vibrations in site-symmetry coordinates

$$\begin{aligned} \nu_{Lx} &= \Delta f_r \sin(\alpha/2) + 0.5\Delta f_a \\ \nu_{Ly} &= 1.155\Delta f_r \sin(\alpha/2) + 0.866\Delta f_a \end{aligned} \quad (9)$$

$$\nu_{Lz} = 0.5\Delta f_a$$

for translational vibrations

$$\nu_{Tx} = 3\Delta f_r [1 - \frac{1}{3} \sin^2(\alpha/2)]^{1/2} \quad (10)$$

The intermolecular motions of molecule were defined along the main axes of inertia and were defined in Figure 1. The projection of the directions of changing bonds of the molecule to the motion of each atom during the motion of a molecule as an entity was used in the next equations for translation along x and y axes.

$$\begin{aligned} \nu_{Tx} &= 2\Delta f_r \sin(\alpha/2) + 2\Delta f_a \\ \nu_{Ty} &= (4/3^{1/2})\Delta f_r \sin(\alpha/2) + 3^{1/2}\Delta f_a \end{aligned} \quad (11)$$

where α is a valency angle of the molecule and Δf_r and Δf_a is the change of diagonal force constants of the molecule at the gas-crystal transition.

The calculations of the intermolecular constants ν_{Tx} , ν_{Ty} , and ν_{Tz} has shown that the intermolecular interaction of antimony trichloride in the direction of x and y axes of the site symmetry is stronger than that in the z direction through the Sb atom to hydrocarbon. This confirms quantitatively the assumption that the interaction between SbCl₃ molecules in the complex crystal is stronger than the interaction of SbCl₃ with π -electrons of the aromatic ring of diphenylamine. Accordingly, the coordination interaction between SbCl₃ molecules and the dipole-dipole interaction between SbCl₃ molecules is a more important factor for

the structure formation of the lattice cell of the complex than the donor-acceptor interaction.

Using expressions 9 and 10, only the diagonal force constants of intermolecular interaction were calculated, which determined the characteristic approximation of the frequencies of SbCl₃ lattice modes. The obtained values of the translational and librational frequencies of SbCl₃ in the complex crystal are given in Table III. On the basis of the calculation of lattice modes, the assignment of low frequency Raman bands of the complex crystal was performed. Decreasing temperature from 293 to 77 K leads to increasing force constants of intermolecular interaction and frequencies of lattice modes, which corresponds to the high frequency shift of the observed low frequencies in the spectrum. In some cases (at 77 K) there was still an uncertainty in the spectrum interpretation. This is explained both by the possibility of a distortion in the crystal symmetry with decreasing temperature and the corresponding disturbance of the selection rules and by the simplicity of the model used for the calculation of characteristic intermolecular vibrations.

Conclusions

Raman spectra of the crystal of the (C₆H₅)₂NH·2SbCl₃ complex are obtained at 293 and 77 K. Theoretical group and normal coordinate analysis of SbCl₃ vibrations in the complex were performed. The change in the intramolecular force field at the gas-crystal transition is discussed. The considered method for calculation of intermolecular force constants makes it possible to interpret the lattice mode spectrum of the complex crystal without the application of model potentials and assumptions on the nature of the intermolecular interaction. On the basis of this calculation, it was concluded that the Sb-Cl' coordination and dipole-dipole interactions between SbCl₃ molecules prevail over the donor-acceptor Sb-hydrocarbon interaction.

Acknowledgment. The author gratefully acknowledges the help of Irena Kondyurin in the preparation of complexes.

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Stable and Metastable Solid Phases of Dicyclopropylacetylene

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In Final Form: August 10, 1992)

Different solid phases of dicyclopropylacetylene are studied for the first time using low-temperature Raman spectroscopy. Dicyclopropylacetylene (C_8H_{10}) appears in three solid phases and one mesomorphic phase. Besides three independent well-defined crystalline phases (I_1 , I_2 , II), on certain conditions a mixture of phases whose composition is not quite clear also exists. Between crystalline phases I_1 and I_2 a phase transition around 115 K is observed. The mesomorphic phase (I) which exists in the narrow temperature interval below the melting point (214 K) is assumed to be a glassy one.

1. Introduction

Because of various inter- and intramolecular interactions, organic molecules display a wide repertory of possible structures, especially on transition from liquid to the crystalline state.¹ The nature of these mesomorphic phases (or mesophases) was the subject of many studies, particularly those concerning liquid and plastic crystals.^{2,3} Recently, attention is paid to glass transitions exhibited by different substances on cooling of either liquid, liquid crystal, or the crystal itself.⁴

Dicyclopropylacetylene (DCPA), C_8H_{10} , represents such an example of an organic molecule with some of the mentioned properties. The number and nature of its phases below room temperature as far as the authors know have not been reported in the literature. No X-ray data and only the infrared spectrum of DCPA at the temperature of liquid nitrogen have been published so far.⁵

Vibrational spectroscopy and calorimetric methods are often used for the phase identification.⁶⁻⁸ Simpler experimental conditions and the possibility of measuring low-frequency bands make Raman spectroscopy preferable to an infrared technique in this type of investigation. We undertook therefore Raman measurements in the wide temperature interval—from room temperature down to ≈ 25 K.

In the present paper all observed phase sequences together with the description of conditions in which phases were obtained will be presented. Frequencies of all observed Raman bands are listed in Table I.

Observed and calculated vibrational frequencies of the DCPA molecule in liquid, which were the subject of our previous work,⁹ were a good basis for identification of bands in the solid.

Our attention has been focused on two spectral regions: that below 160 cm^{-1} which we shall call the low-frequency (LF) region and the interval between 350 and 550 cm^{-1} which will be called the middle-frequency (MF) region. The main difficulty during assignment stemmed from the large bandwidth and asymmetry

of overlapping bands in the MF interval, where on the basis of the normal-coordinate calculation the appearance of skeletal modes was expected. The assignment in Table I is based on calculated values for the cis conformation and includes the Raman bands of liquid at 518 , 460 , and 390 cm^{-1} . The apparent asymmetry of 518 - and 390-cm^{-1} bands could be caused by two additional low-intensity bands at ~ 480 and $\sim 420\text{ cm}^{-1}$, which would indicate that the number of conformers in liquid is at least two (see Figure 3 in ref 9).

Excitations in MF and LF regions thus presented themselves as the most sensitive to changes in conformation and lattice structure, respectively.

2. Experimental Section

DCPA was prepared according to the procedure of Köbrich et al.¹⁰ by the reaction of 1-chloro-2,2-dichloropropylethylene (CDCE) with *n*-butyllithium. CDCE was obtained from the chlorination of dicyclopropyl ketone. DCPA was purified by vacuum distillation, using a spinning band column, and the purity was checked by mass spectrometry and infrared spectroscopy.

Low-temperature Raman spectra were recorded by a DILOR Z-24 Raman spectrometer with a triple monochromator using a CTI CRYOGENICS (HELIX, CRYODINE) Model 21 cryostat with closed cycle helium refrigerator (Lake Shore Cryotronics Model DRC-70C controller). Attached to the cold finger was a specially constructed mount for capillary tube containing sample sealed under vacuum (see Figure 1). To provide better thermal contact, indium foil was used.

On comparing the temperature of melting given by calorimetric measurements and that read on our cryostat display we observed a discrepancy. The difference between two temperature scales (Raman and calorimetric) is approximately 15°C and originates from local heating in the focus of the laser beam. Namely, the temperature sensor within the cryostat head does not measure the true, higher temperature of the sample since it is attached to the