VIBRATIONAL SPECTRUM OF *p*-AMYLOXYBENZYLIDENE-*p*-TOLUIDINE IN THE CRYSTALLINE PHASE

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PACS 33.20.Fb; 31.15.eg

The Raman spectrum of *p*-amyloxybenzylidene-*p*-toluidine (ABT) liquid crystal in the crystalline phase has been analyzed. The spectrum was recorded in a spectral range of 0–1650 cm^{-1} and at room temperature ($T = 293$ K). The quantum-chemical computer simulation of a molecular geometry has been carried out, and the vibrational frequencies of ABT molecules have been calculated by applying the B3LYP/6-31G(*d,p*) method. The results of quantum-chemical computer simulation were used to interpret the experimental Raman spectrum. The conformational parameters of ABT molecules in the crystalline phase have been determined.

1. Introduction

Liquid crystals find a rather wide application in modern industry. First of all, they are used for manufacturing the monitors of personal computers, TV sets, and other facilities to display information. That is why new liquid crystal substances are searched for and synthesized, and, respectively, the molecular mechanisms governing the macroscopic properties of mesogenes and their modifications are studied. Knowing the intramolecular processes and understanding their nature would allow the synthesis of liquid crystal substances with prespecified properties to be thoroughly dealt with. A considerable number of liquid crystal substances have been synthesized during the last time. The most studied of them are substances with a benzylidene-aniline core. Benzylidene-anilines belong to a wide class of objects, which are capable to form the liquid crystal phase. The most widespread representatives of this group of chemical substances are benzylidene-aniline (BA), *p*-amyloxybenzylidene-*p*-toluidine (ABT), benzylidene-toluidine (BT), N-(*n*-methoxybenzylidene)-*n*-butylaniline (MBBA), and N-(*p*-ethloxybenzylidene)-*p*-butylaniline (EBBA). The basic component of corresponding molecules is a benzylidene-aniline (BA) core, $-C_6H_4-CH=N-C_6H_4-$, the geometrical structure of which is illustrated in Fig. 1. The indicated molecules differ from one another by only radicals attached on both sides of the core. The chemical structures of some benzylidene-anilines are shown in Table 1.

Table 1. Chemical structure of some benzylidene-anilines

Substance Name	Chemical structure
BA	$H-C_6H_4-CH=N-C_6H_4-H$
ABT	$NH_2-O-C_6H_4-CH=N-C_6H_4-CH_3$
BT	$H-C_6C_4-CH=N-C_6H_4-CH_3$
MBBA	$CH_3-O-C_6H_4\text{-}CH=N-C_6H_4-C_4H_9$
EBBA	$C_2H_5-O-C_6H_4-CH=N-C_6H_4-C_4H_9$

It should be noted that almost exhaustive experimental data concerning the structure, phase polymorphism, and spectral properties have been accumulated in the literature for such representatives of the mentioned series as MBBA and EBBA [1–5]. At the same time, the corresponding data are almost absent or at least they are very scarce for other substances, e.g., ABT. In particular, there are no data for ABT concerning its molecular conformations in various phase states; an unambiguous interpretation of the vibrational spectrum of ABT molecule is also absent.

One of the most informative techniques to study both the intramolecular structure and the properties of a molecular environment is the vibrational spectroscopy, in particular, Raman spectroscopy. A spectrum versus structure interrelation, as well as the correlation between structural variations in the course of phase transformations and the corresponding changes in vibrational

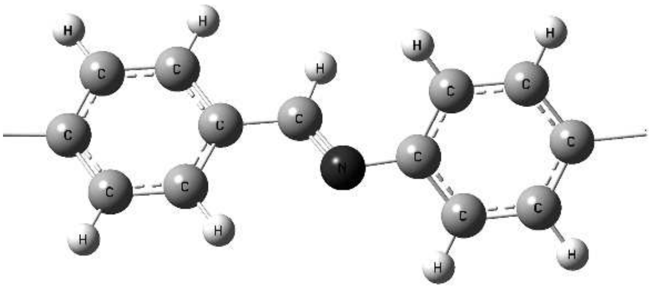

Fig. 1. Geometrical structure of benzylidene-aniline core

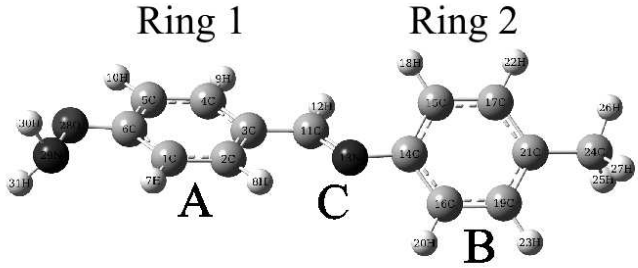

Fig. 2. Optimized geometry of ABT molecule obtained by computer simulation using the B3LYP/6-31G(d,p) method of DFT

spectra, was widely discussed in the literature for last years for many types of liquid crystal compounds (5CB, MBBA) [6–9]. Vibrational spectroscopy can be useful, when determining molecular conformations in various phase states and order parameters, or to obtain some information on features of the intermolecular interaction and the dynamics [10–12]. Therefore, in this work, an attempt was made to analyze the vibrational Raman spectrum of ABT, by taking advantage of computer simulation, to interpret the vibrational frequencies, and to determine the conformational parameters of the geometry of ABT molecule in the crystalline phase.

2. Experimental Part

We used an automated and computerized complex for spectral measurements developed on the basis of a DFS-24 double monochromator. An argon laser with a lasing wavelength of 514.5 nm was used as a source for Raman scattering excitation. The power of exciting radiation was 50–100 mW, which did not result in a substantial heating of the specimen during the registration of Raman spectra and in changes of its physical properties. Scattered light was monitored at an angle of 90° with respect to the direction of the incident laser beam. The vibrational spectrum was registered, provided that the widths of the input and output slits did not exceed 100 μm, so that the width of the monochromator instrument function did not exceed 2 cm^{-1}. The ABT vibrational spectrum was registered at a temperature of 293 K, when ABT was in the crystalline state. The crystal–nematic transition in ABT is observed at a temperature of 333 K.

3. Computer Simulation

Computer-assisted simulation was carried out, by using the Gaussian-03 software package [13]. We simulated an isolated molecule; therefore, the environmental effects were not taken into account. At the first stage, the geometry of ABT molecule was optimized. In other words, we found a stable minimum on the potential energy surface. The geometry was optimized by applying the method of density functional theory (DFT) and using the B3LYP exchange-correlation functional and the 6-31G(d,p) basis set. The latter uses an extra diffuse d-function to describe heavy atoms and an extra polarization p-function for the hydrogen atom H. The application of d-functions allows the interaction between atoms, systems with a rather large negative charge, and atoms with free electron pairs to be described better. The optimized geometry of ABT molecule is depicted in Fig. 2.

For the optimized geometry, the corresponding characteristic vibrational frequencies, normal vibrational modes, and model vibrational Raman spectrum were calculated. The frequency analysis was carried out at the same level of the theory and with the same set of basis functions as when optimizing the molecule geometry. Only positive values were obtained for vibrational frequencies; this confirms that the real minimum on the molecular potential energy surface was found [13]. As a rule, the model vibrational frequencies obtained in the harmonic approximation are overestimated in comparison with experimental ones. Therefore, for the coincidence of the frequencies of experimental and model spectra to be more exact, the latter was scaled by a certain scale factor. In the literature, there exists a specific scale factor for every method with a definite basis set. According to work [13], in the case of B3LYP/6-31G(d,p) set, the obtained ABT spectrum was scaled by a factor of 0.9613. The vibrational frequencies were interpreted with the help of the Gauss View 4.01 software package [14]. It allows the molecular vibrations that correspond to every vibrational frequency to be visualized and, respectively, helps in determining the type of those vibrations.

4. Analysis of the Vibrational Spectrum of ABT

The experimental spectrum and the model one obtained for the optimized geometry of ABT molecule using the B3LYP/6-31g(d,p) method are shown in Fig. 3. A detailed matching between the vibrational frequencies in the Raman spectrum of ABT and the corresponding vibrational modes in the range of 0–1650 cm^{-1} and a comparison with the obtained model frequencies in the Raman spectrum are carried out in Table 2. The following notations are used: ν, δ, and ω denote, respectively, valence, torsional, and deformation vibrations. The out-of-plane deformation δ-vibrations stand for such a type

Table 2. Interpretation of vibrational frequencies of ABT molecule in the crystalline state

Experiment cm^{-1}	Model, cm^{-1}	Interpretation
820	804.6	Out-of plane δ-vibrations of rings 1 and 2
961.2	980	Out-of plane $\delta(C_3–C_{11}–N_{13})+\omega(H_{12},H_8,H_9)$
1065	1080.5	Breathing mode of rings 1 and 2 $+\omega(H_9,H_{10},H_7,H_8)$
1126.3	1145	ν(C–C) vibration of ring 2 + breathing mode of rings 1
1154	1174.9	δ(C–H) vibrations of rings 1 and 2$+\nu(C_{14}{=}N)+\nu(C_3–C_{14})$
1211.4	1238	In-plane deformation vibration of ring 2$+\nu(C_6–O_{28})+\omega(H_{30},H_{31})$
1243.2	1275	ν(C–C) vibration of ring 1 $+\omega(H_{23},H_{20},H_{22},H_{18}, H_8,H_7,H_9,H_{10})$
1280.5	1304.5	Nonsymmetric ν(C–C) vibration of ring 2 $+\nu(C_3–C_{11})+\nu(C_5–O_{28})+\omega(H_{12})$
1348	1362	$\nu(C_{24}–C_{21})+\omega(H_{25},H_{26}, H_{27})$
1404.5	1401.8	$\nu(C_{14}{=}N_{13})$ + nonsymmetric δ(C–H) vibration of ring 2
1491	1476	Nonsymmetric ν(C–C)vibration of ring 1 and 2
1566.7	1554.1	$\nu(C_{14}{=}N_{13})$ +nonsymmetric ν(C–C) vibration of ring 2$+\delta(H–N_{29}–H)$
1591.7	1575.6	ν(C–C) vibrations of rings 1 and 2 $+\nu(C_{14}{=}N_{13})+\nu(C_{11}+C_3)+\delta(H–N_{29}–H)$
1605.6	1589.3	ν(C–C) vibrations of rings 1 and 2$+\nu(C_{14}{=}N_{13})+\nu(N_{13}+C_{11})+\delta(H–N_{29}–H)$
1620.7	1629.4	$\nu(C_{14}{=}N_{13})$ $+\nu$(C–C) vibrations of rings 1 and 2

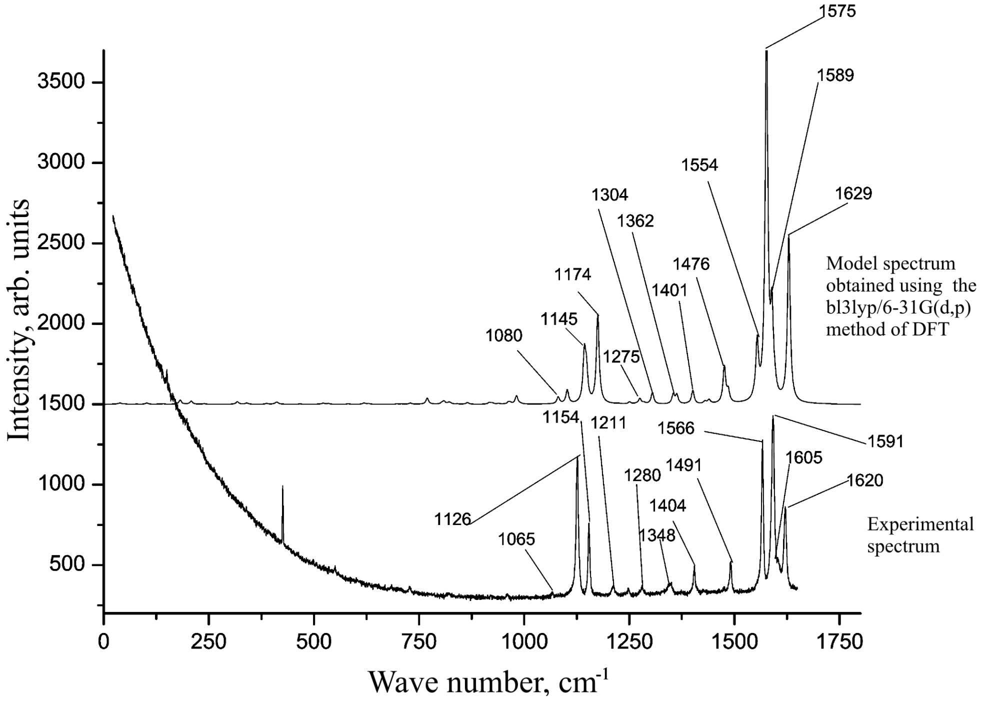

Fig. 3. Experimental and model spectra of ABT in the range of 0–1650 cm^{-1}

of vibrations, at which both the valence angle and the bond plane change.

It should be noted that the model and experimental spectra are in fine mutual correlation, both quantitative and qualitative. First of all, the attention should be paid to four intensive bands that arise in a spectral interval of 1500–1650 cm^{-1}. These are the vibrational bands with frequencies at 1620.7, 1605.6, 1591.7, and 1566.7 cm^{-1}. In the model spectrum, those bands appear at frequencies of 1629.4, 1589.3, 1575.6, and 1554.2 cm^{-1}, respectively. The vibrational band at 1620.7 cm^{-1} corresponds to valence vibrations of $\nu(C_{14}{=}N_{13})$ bond mixed with deformation-valence vibrations ν(C–C) in benzene rings 1 and 2. This band is typical, being observed for all mesogenes that contain a benzylidene-aniline core.

In particular, according to the results of work [10], this vibration was registered at frequencies of 1627 and 1628 cm^{-1} for liquid crystal substances 5O.5 and 5O.6, respectively. Liquid crystal 5O.7 was studied in work

[15]. The authors showed that an intensive band in the Raman spectrum at a frequency of 1624 cm^{-1} was observed in this case as well. They associated this vibration with the valence vibration of C=N bond mixed with the torsional vibration of C–N bond in the –C(H)=N– bridge. The substances mentioned above belong to the nO.m homologous series. Liquid crystals from this series consist of a benzylidene-aniline core and attached C_mH_{2m-2} and C_nH_{2n-2}–O– lateral groups. The integers n and m specify the number of carbon atoms C in those lateral groups. In work [16] dealing with substances 7.O4O.7 and 7.O5O.7, this vibration was observed at frequencies of 1627 and 1622 cm^{-1}, respectively. Substances 7.O4O.7 and 7.O5O.7 belong to the m.OnO.m homologous series. The substances in this series consist of two benzylidene-aniline cores with attached C_mH_{2m+1} alkyl groups and connected with each other by the –O–$(CH_2)_n$–O– bridge. Whence, a conclusion can be drawn that the frequency of this vibration weakly depends on the nature of lateral links of the benzylidene-aniline core, being exclusively governed by its internal structure. According to the results of work [15], two other vibrational frequencies, 1591.7 and 1566.7 cm^{-1}, are associated with degenerate vibrational modes of ν(C–C) vibrations in the benzene rings; these are 8**b** and 8**a** in Wilson's notations. The vibration at a frequency of 1605.6 cm^{-1}, the intensity of which is much lower than those of vibrations at 1591.7 and 1566.7 cm^{-1}, is also connected with deformation-valence ν(C–C) vibrations of benzene rings.

The next two intensive bands were observed in the experimental spectrum at frequencies of 1404.5 and 1491 cm^{-1}. The frequencies of 1401.8 and 1476 cm^{-1} in the model spectrum correspond to them. The vibration at 1491 cm^{-1} corresponds to the deformation-valence vibration of phenyl rings 1 and 2. The shape of ring 2 remains fixed at that, whereas the shape of ring 1 changes. The frequency of 1404.5 cm^{-1} corresponds to the deformation vibration of phenyl ring 2 mixed with the valence vibration $\nu(C_{14}{=}N_{13})$. Similar frequencies–1422 and 1499 cm^{-1}, respectively–were also observed in work [15] for liquid crystal 5O.7. On the basis of computer simulation results, the authors of work [15] related them to deformation vibrations of phenyl rings mixed with the vibration of the –C(H)=N– bridge.

The next intensive spectral bands in the experimental spectrum were observed at frequencies of 1126.3 and 1154 cm^{-1}. In the model spectrum, they correspond to the frequencies of 1145 and 1174.9 cm^{-1}, respectively. The vibrational mode at 1154 cm^{-1} corresponds to the deformation vibrations δ(C–H) of C–H bonds in both phenyl rings mixed with valence vibrations $\nu(C_{14}{=}N_{13})$ and $\nu(C_3{-}C_{14})$. The vibrational mode at a frequency of 1126.3 cm^{-1} was associated with valence vibrations ν(C–C) of bonds in benzene ring 2 mixed with the "breathing" vibrational mode of ring 1. In work [15], where liquid crystal 5O.7 was considered, the frequency of 1163 cm^{-1} was also associated with deformation vibrations of C–N bonds in phenyl rings mixed with valence vibrations of C=N bonds. This vibrational mode was identified by the authors of work [15] as that coinciding with degenerate mode 9**a** (in Wilson's notations) of benzene. Taking into account that the frequency of the band at 1154 cm^{-1} slightly differs from that of the band at 1163 cm^{-1} and that almost identical interpretations were given to both bands, we may suppose that, in our case, the 1154-cm^{-1} band can be identified with degenerate vibrational mode 9**a** of benzene.

5. Molecular Geometry

Taking advantage of the fact that the model and experimental Raman spectra of ABT are very similar to each other qualitatively, we may admit that the optimized geometry is qualitatively adequate to the structure of ABT molecule in the crystalline state. The theoretically calculated conformational parameters are listed in Table 3, where the following notations are used: plane **A** contains atoms C_1, C_2, C_3, C_4, and C_5 of ring 1; plane **B** atoms C_{14}, C_{15}, C_{17}, C_{21}, C_{16}, and C_{19}; and plane **C** atoms C_{11},H_{12}, and N_{13}; $\phi(\mathbf{A},\mathbf{B})$ and $\phi(\mathbf{B},\mathbf{C})$ are the dihedral angles between planes **A**, **C** and **B**, **C**, respectively; and R1 and R2 are the average lengths of C–C bonds in rings 1 and 2, respectively. Our calculations showed that planes **A** and **C** of benzene ring 1 almost coincide: the angle between them is only 1.2°. Plane **B** in benzene ring 2 is rotated by an angle of 37.9° with respect to the corresponding plane **C**. It is also worth noting that

Table 3. Conformational parameters of ABT molecule in the crystalline state

Parameters	Values
R1(C–C)	1.4 Å
R2(C–C)	1.4 Å
C=N	1.28 Å
O–N	1.44 Å
C–O	1.37 Å
ϕ(A,C)	1.2°
ϕ(B,C)	37.9°
$\phi(C_{11},N_{13},C_{14})$	120.3°
$\phi(C_3,C_{11},N_{13})$	123°
$\phi(C_6,O_{28},N_{29})$	113.7°

the N–O bond lies in plane **A** of benzene ring 1. The measured values of dihedral angles between benzene ring planes are in fine agreement with the corresponding values theoretically calculated in work [15] for dihedral angles in liquid crystals belonging to the nO.m series. The obtained theoretical values for dihedral angles between benzene ring planes in liquid crystals 5O.7, 4O.6, 3O.5, and 2O.4 were found to fall within the interval of 38–40°. In the case of liquid crystal 5O.7, the authors compared the calculated conformational parameters with the corresponding experimental data obtained in work [17] for the crystalline 5O.7. The theoretical parameters were found to agree well enough with the experimental ones, but the dihedral angle between the benzene ring planes; namely, the calculation using the B3LYP/6-31G(d,p1) method gives 37.5°, whereas the experimental value is 47°. The authors explained this discrepancy as a result of the neglect of the intermolecular interaction in their model calculations, although this interaction is especially considerable in the crystalline phase. A similar situation must take place in the ABT case, i.e. the calculated value of the dihedral angle between benzene rings is a little underestimated.

6. Conclusions

The vibrational spectrum of ABT liquid crystal has been analyzed and interpreted. While comparing the ABT vibrational spectrum with Raman spectra of other liquid crystals containing a BA core, the vibrational band at 1620 cm^{-1} was found to be characteristic, with its frequency weakly depending on the structure of lateral groups attached to the BA core. With the help of a computer-assisted quantum chemical simulation, the geometrical parameters of ABT molecule in the crystalline phase have been determined.

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Received 11.04.11.
Translated from Ukrainian by O.I. Voitenko

КОЛИВАЛЬНИЙ СПЕКТР p-АМІЛОКСІБЕНЗИЛІДЕН-p-ТОЛУЇДІНУ В КРИСТАЛІЧНІЙ ФАЗІ

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Резюме

У роботі виконано аналіз коливального раманівського спектра рідкого кристала p-амілоксібензиліден-p-толуїдіну (АБТ).

Спектр КРС було зареєстровано в інтервалі 0–1650 см$^{-1}$ за кімнатної температури $T = 293$ K, коли АБТ перебуває у кристалічній фазі. Проведено квантово-хімічне комп'ютерне моделювання геометрії та розрахунок теоретичних коливальних частот молекули АБТ методом B3LYP/6-31G(d,p). На основі результатів комп'ютерного моделювання виконано інтерпретацію експериментального спектра КРС, отримано конформаційні параметри молекули для кристалічного стану.