

Determination of the average orientation of 4-phenylpyridine in nematic solvent by means of infrared linear dichroism: Study of its conformational dependence on the dihedral angle between aromatic rings

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Abstract

A method using IR linear dichroic measurements for determination of the average orientation of the twisted 4-phenylpyridine in a nematic solvent is proposed. By means of this approach the relationship between orientational characteristics of solute molecule and its conformational state in nematic phase has been studied. This method combines an interactive subtraction procedure of IR polarized spectra of 4-phenylpyridine for determination of its vibrational transition moment orientation and DFT quantum chemical calculations as additional source of information of mutual orientation of aromatic subunits of the guest molecule.

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1. Introduction

A study of conformation of 4-phenylpyridine (4-PhPy) is of interest not only for the purpose of structural analysis of its organometallic complexes [1,2] but also can be useful for the elucidation of its orientational behavior in nematic liquid crystal.

As the molecule consists of phenyl and pyridine rings connected by a central bond its conformational state may simply be defined by the dihedral (or twist) angle between these aromatic subunits (see Fig. 1). Similarly to the biphenyl in solid state the molecule of 4-PhPy is planar with C_{2v} symmetry [3], while in liquids or in liquid crystals the twisting of the aromatic rings leads to the lowering of the symmetry to C_2 . Depending on solvent characteristics the

dihedral angle is expected to vary in certain limits likewise biphenyl and 4,4'-bipyridine [4].

The IR polarized measurements of embedded molecules such as biphenyl and its derivatives oriented partially in stretch polyethylene show that their conformations play an important role in their average orientation [5]. Murthy and Michl interpreted this fact by means of the established empirical correlation between molecular shape and the magnitudes of the so-called molecular orientational factors defining the average orientation of solute molecules in the anisotropic solvent [6].

In the present work orientational factors of 4-PhPy in a nematic solution have been studied as a function of the twist angle by the use of a similar approach as those described in [5]. As it is shown in theoretical section orientational parameters of solute molecules depend directly on the twist angle which turns out to be freely variable in the derived relations. Therefore estimation of its value demands extra experimental information. Since such is not available for nematic solution we propose in current

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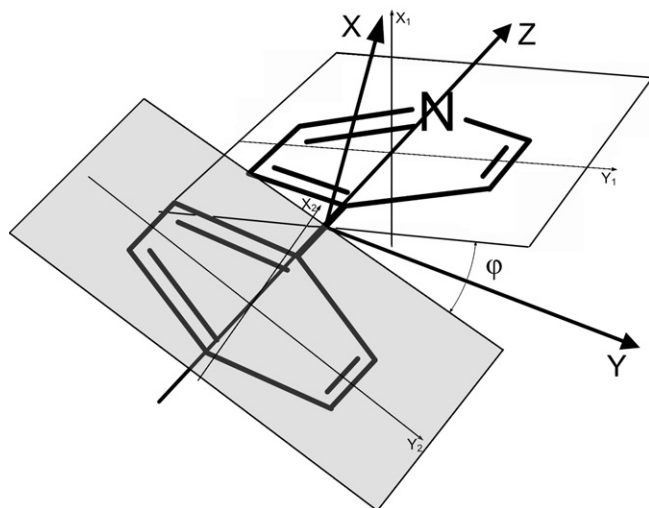


Fig. 1. The geometry of a twisted 4-phenylpyridine in nematic solution; X , Y and Z are principle molecular axes, where x_i , y_i and z_i ($i = 1, 2$) are local coordinate axes attached to both aromatic rings. ϕ is the dihedral (or twist) angle between two aromatic subunits.

study a qualitative approach for rough estimation of this angle. This method is based on the comparison of the experimental frequencies of out-of-plane C–H deformation vibrations with those predicted by DFT quantum chemical calculations at different values of the dihedral angle. This approach may be subjected to some criticism since presented theoretical data concerning calculated frequencies are related to the gas phase. However, it provides a reasonable estimation of possible dihedral angle in nematic liquid crystal. Analysis of out-of-plane C–H deformation vibrations turns out to be very useful since they are sensitive enough to change in the mutual orientation of aromatic rings [7]. Orientational factors of the twisted 4-PhPy in nematic solution were calculated using the estimated angle value. In order to characterize polarization of different vibrational modes of the guest molecule a symmetry band assignment of its IR polarized spectra was performed in addition.

2. Experimental

4-Phenylpyridine is a commercial product (Merck) which was used after sublimation. For spectral measurements 10 wt% solution of compound was prepared in isotropic solvent CCl_4 , as well as in nematic liquid crystalline solvent ZLI 1695 (Merck). The IR spectra of the isotropic and anisotropic solutions were recorded on a Bruker IFS 113v and IFS 55 Equinox FTIR spectrometer in the $4000\text{--}400\text{ cm}^{-1}$ spectral region with resolution of 2 cm^{-1} using a $25\text{ }\mu\text{m}$ path length KBr liquid cell. The parallel $A_{\parallel}(\nu)$ and perpendicular $A_{\perp}(\nu)$ polarized spectra of nematic solution and solvent were measured using Al/KRS5 wire-grid polarizer. The whole procedure is described in details elsewhere [6,8]. The FAR IR spectrum of 4-PhPy was measured by the following polyethylene

(PE) technique: a pellet of the mixture of substance and PE was prepared by soaking PE powder in solution of 4-PhPy in chloroform next then the solvent was evaporated.

3. Computational details

The geometry of 4-PhPy was completely optimized for gas phase using density functional (B3LYP, 6-31G** level of theory [9,10]) method implemented in the Gaussian 98 program suite [11]. The potential energy minimum was predicted at a twist angle of 36.7° between the phenyl and pyridine rings. This value is lower than those obtained by RHF method 43.5° [12], but both methods of calculation give reliable predictions of the equilibrium geometries in gas phase. Additionally, the twisting effect on some vibrational frequencies was studied stepwise in the range $0\text{--}90^\circ$ keeping the angle constant and optimizing the rest of the molecule at each step.

4. IR polarized spectra and frequency assignment

Valuable information about the average orientation of partially oriented molecules in nematic solution can be obtained by IR linear dichroic measurements using the so-called Thulstrup–Eggers reduction procedure [6]. It is based on an interactive subtraction $\Delta A(\nu) = A_{\parallel}(\nu) - m A_{\perp}(\nu)$, where $A_{\parallel}(\nu)$ and $A_{\perp}(\nu)$ are polarized absorbancies measured parallel and perpendicular with respect to the uniaxial orientation of nematic solvent (see Figs. 2 and 3a). During the procedure all bands of one and the same polarization can be simultaneously eliminated when the free varying parameter m becomes equal to the dichroic ratio $R = A_{\parallel}/A_{\perp}$, where A_{\parallel} and A_{\perp} are the corresponding integrated intensities. The spectra $\Delta A(\nu)$ thus prepared are known in the literature as reduced infrared linear dichroic (IR-LD) spectra [6,8,13] (see also Fig. 3b).

Since the measured R directly depends on the orientational characteristics of solute and those of the corresponding vibrational transition moment, this simple technique can be used not only to determine the average orientation

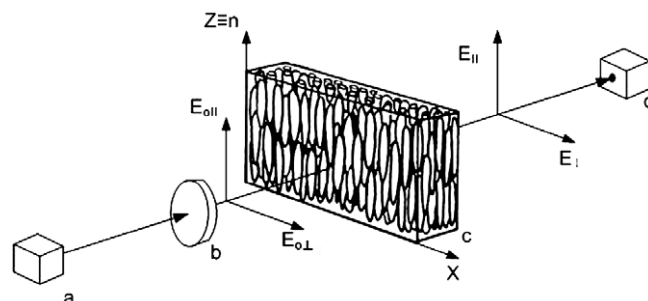


Fig. 2. A principal optical scheme for measurements of polarized absorption spectra of the liquid crystalline solution; (a) light source of IR radiation, (b) linear polarizer, (c) oriented sample (d) represents the light intensity detector. E_{\parallel} and E_{\perp} are parallel and perpendicular components of the light electric vector \mathbf{E} with respect to the nematic director \mathbf{n} .

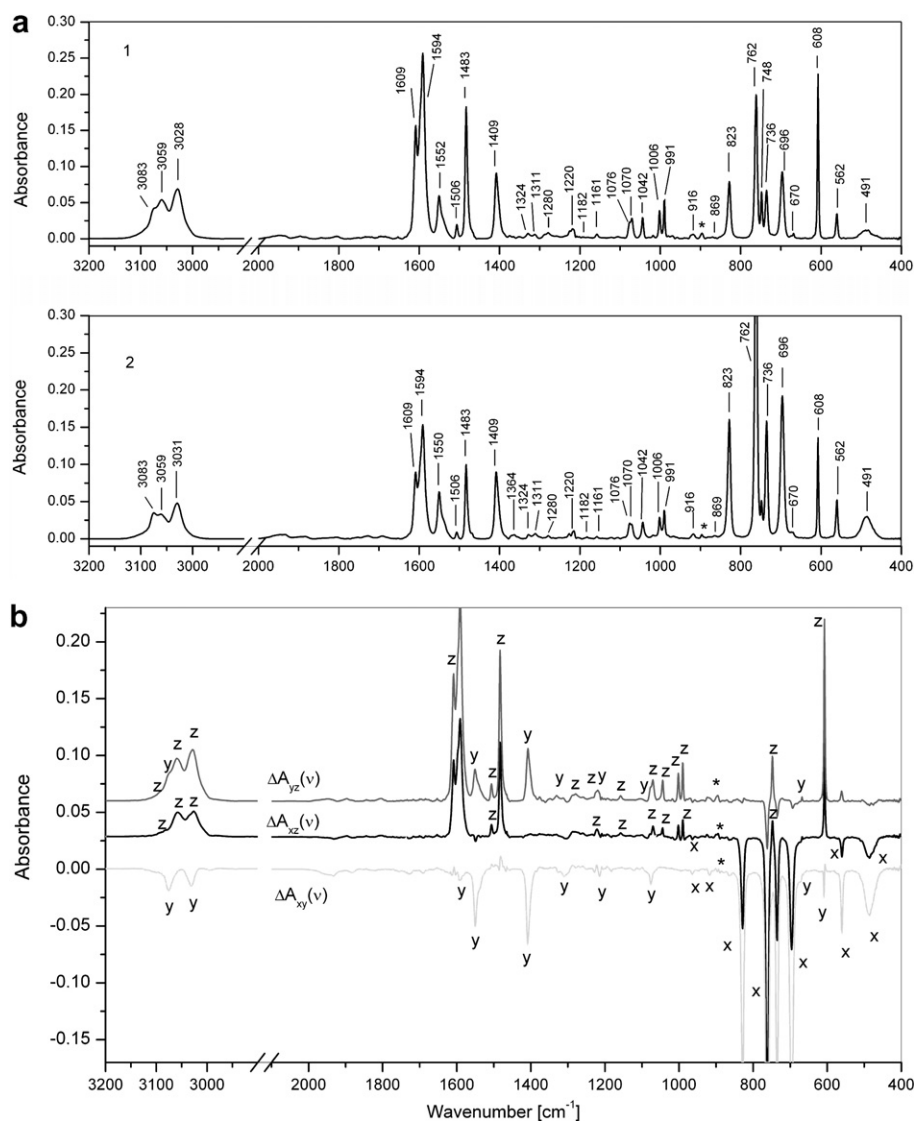


Fig. 3. (a) Polarized IR spectra of 4-PhPy: (1) and (2) are polarized absorbancies measured parallel and perpendicular with respect to nematic **n** director (see Fig. 2). (b) Reduced IR LD spectra $\Delta A_{yz}(v)$, $\Delta A_{xz}(v)$ and $\Delta A_{xy}(v)$ of 10 wt% nematic solution of 4-PhPy in nematic solvent ZLI-1695 obtained after consecutive elimination of *x*, *y* and *z* polarized bands. These spectral curves correspond to the orientational parameters $K_z = 0.465$, $K_y = 0.360$, $K_x = 0.183$. The indices of each reduced spectrum indicate the bands which remain after removal of all bands of the desired polarization (*x*, *y* and *z*). Asterisks point out non-compensated liquid crystal absorption (ruins).

of guest molecules but as a valuable tool for symmetry band assignment of their IR polarized spectra as well [6,8,13]. This procedure is very helpful for separation of in-plane from out-of-plane modes, since some of the corresponding bands are very close in position while their transition moments have different polarization (see Fig. 3b).

Isotropic and anisotropic IR spectra were recorded and compared in order to assign different frequency modes of 4-PhPy. The isotropic spectra of 4-PhPy in CCl₄ and KBr tablet are presented in Fig. 4, while the polarized and reduced IR-LD spectra in nematic solution are given by Fig. 3. The respective spectral data are listed in Table 1 along with the assignments of bands to different normal modes.

4-PhPy has 57 normal modes. In a solid state the molecule is planar and belongs to C_{2v} symmetry as its funda-

mental vibrations are divided into the following symmetry classes:

$$\Gamma(C_{2v}) = 20A_1 + 11B_1 + 7A_2 + 19B_2.$$

The IR active vibrations belong to the following symmetry species: A_1 , B_1 and B_2 and their distribution is presented in Table 1. All fundamentals are both infrared and Raman active except the A_2 modes. If we use a similar orientation of molecular axes *x*, *y* and *z* as this one shown on Fig. 1 at angle $\varphi = 0$, then the bands belonging to A_1 class should have *z* polarization while those corresponding to B_1 and B_2 should have *x* and *y* polarization, respectively.

In contrast to crystalline state 4-PhPy molecule is not planar in CCl₄ as well as in liquid crystal solution where φ differs from zero. In this case the symmetry of solute mol-

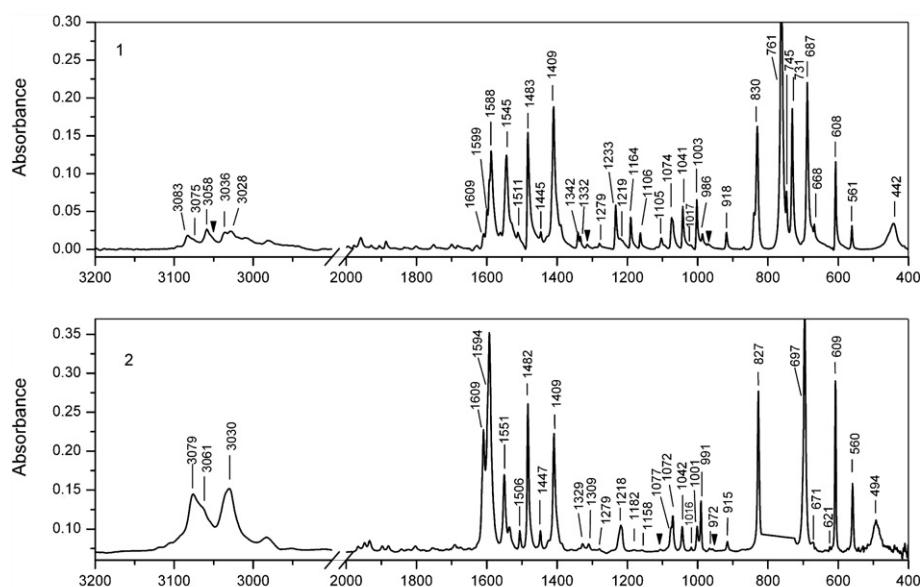


Fig. 4. Isotropic IR spectra of 4-PhPy in KBr tablet (1) and CCl_4 (2). Black triangles indicate additionally listed in Table 1 frequencies.

ecule is lowered down to C_2 and the fundamental vibrations are distributed among new symmetry classes:

$$\Gamma(C_2) = 27A + 30B,$$

where all normal modes are infrared and Raman active (see Table 1).

In accordance with the chosen molecular coordinate axes (see Fig. 1) the bands belonging to A class are z polarized while those corresponding to B have x and y polarization. The bands having x polarization corresponds to out-of-plane vibrations while those of y polarization are in-plane vibrations similarly to the case of planar 4-PhPy. However, it should be noted that these vibrational modes can approximately be separated since their polarized transitions are “mixed”. The correlation between symmetry classes of both symmetry groups C_{2v} and C_2 is presented in Fig. 5.

Calculated frequencies of low symmetry 4-PhPy are scaled by means of several correction factors¹ calculated by the least-squares procedure proposed in [14] and also listed in Table 1. It should be noted that we found some disagreements between symmetry assignment proposed by Bayari et al. [3], Zawada et al. [15] and assignment given by us. These discrepancies mainly concern several bands in high and low frequency part of IR spectrum (see Table 2). Reduced IR-LD spectra show that bands at 1074 and 608 cm^{-1} are doublets and their components have different polarization (see Fig. 3b). As it can be seen on the same figure that the band at 1076 cm^{-1} has y polarization (B_2) while that one at 1070 cm^{-1} is z polarized (A_1). We observe similar picture in the case of low frequency band at

608 cm^{-1} which splits into two components: the first one at 621 cm^{-1} y polarized (B_2) and the other one at 606 cm^{-1} with z polarization (A_1) (see also Fig. 3b).

Our present study shares to a certain extent critical comments of Zawada et al. [15] concerning the qualitative character of symmetry assignment of vibrational modes of 4-PhPy proposed in [3]; nevertheless we found some discrepancies with Zawada’s symmetry assignment too (see Table 2). Therefore, in our subsequent discussion we will use results of our symmetry band assignment of polarized IR spectra.

5. Theory

5.1. Orientational parameters and vibrational transition moments

The orientation of vibrational transition moments with respect to the nematic director $\mathbf{n} \equiv Z$ can be determined by the use of so-called orientational factors or parameters K_f . The later depend also on the orientation of the transition moments within molecular coordinate system and can be described by the following expression [6]:

$$K_f = \langle \cos^2 \Omega_f \rangle = \sum_{u,v} K_{u,v} \cos \phi_u^f \cos \phi_v^f, \quad u, v = x, y, z \quad (1)$$

where the brackets $\langle \cdot \rangle$ denote averaging over all orientations of the solute molecules, while $\Omega_f = (\mathbf{M}_f, Z)$ is the angle between the transition moment \mathbf{M}_f and the Z -axis of the laboratory coordinate system² (see Fig. 6). K_{uv} are elements of the orientation tensor, \mathbf{K} , that are also called orientational factors or parameters [6], while the orientation of the f th transition moment \mathbf{M}_f with respect to the molecular

¹ A separate scale factor determined by formula 10 in Ref. [14] is used for each type of vibrations (stretching $\nu_{\text{C-H}} - 0.957$, $\nu_{\text{Ar}} - 0.969$ and deformation in-plane $\delta_{\text{C-H}} - 0.972$; $\delta_{\text{Ar}} - 0.973$ and out of plane $\gamma_{\text{C-H}} - 0.971$).

² This axis is usually used to define the uniaxial direction in nematic liquid crystals and stretched polymers.

Table 1

The fundamental vibrational frequencies of 4-PhPy observed by infrared spectroscopy in solid state (KBr pellet), isotropic (CCl₄) and anisotropic (ZLI1695) solvents

4-PHPY(C _{2v})			4-PHPY(C ₂)				
Symmetry and assignment	KBr; PE pallet	DFT calc.	Symmetry and assignment	CCl ₄	ZLI 1695	DFT calc.	K _f
20 A₁(z)			27 A(z)				
ν _{CH} (Ar) ^a	3083	3090	ν _{CH} (Ar)	3079	3081	3082	0.462
ν _{CH} (Ph)	—	3077	ν _{CH} (Py)	—	—	3078	—
ν _{CH} (Ar)	3058	3067	ν _{CH} (Ph)	3061	3059	3058	—
ν _{CH} (Ph)	3036	3046	ν _{CH} (Ph)	—	3037	3044	—
ν _{CH} (Py) ^b	3028	3028	ν _{CH} (Py)	—	3028	3029	0.461
ν _{ring} (Ph)	1609	1610	ν _{ring} (Ph)	1609	1609	1608	0.465
ν _{ring} (Py)	1599	1597	ν _{ring} (Py)	1594	1596	1598	—
ν _{ring} (Ar)	1511	1512	ν _{ring} (Ar)	1506	1506	1502	0.465
ν _{ring} (Ar)	1483	1481	ν _{ring} (Ar)	1482	1482	1480	0.463
δ _{CH} (Ar) ^c , δ _{ring} (Py) ^d	1279	1265	δ _{ring} (Py), δ _{CH} (Ar)	1279	1280	1279	—
δ _{CH} (Py)	1219	1232	δ _{CH} (Py)	1218	1220	1218	—
δ _{CH} (Ph)	—	1190	δ _{CH} (Ph)	1182	1182	1179	—
δ _{CH} (Py)	1074	1076	δ _{CH} (Py)	1072	1072	1070	0.452
δ _{CH} (Ph)	1041	1042	δ _{CH} (Ph)	1042	1044	1043	0.457
δ _{ring} (Ar)	1017	1009	δ _{ring} (Ar)	1016	1018	1012	0.460
δ _{ring} (Ar)	1003	991	δ _{ring} (Ar)	1001	1002	990	—
δ _{ring} (Ar)	966	982	δ _{ring} (Ar)	991	991	984	—
δ _{ring} (Ar)	747	738	δ _{ring} (Py)	—	967	969	—
δ _{ring} (Ar)	608	601	δ _{ring} (Ph)	—	958	952	—
ν _{C-Py} ^e	326	322	δ _{ring} (Py)	871	869	868	—
			δ _{CH} (Ph), δ _{ring} (Ar)	—	—	839	—
			δ _{CH} (Ar), δ _{ring} (Ar)	—	745	741	0.454
			δ _{ring} (Ar)	609	607	604	0.464
			δ _{ring} (Ar)	—	—	406	—
			δ _{ring} (Py)	—	—	381	—
			ν _{C-Py} , δ _{CH} (Ar)	—	—	304	—
			δ _{ring} (Ar), τ	—	—	67	—
19 B₂(y)			30 B(x, y)				
ν _{CH} (Ar)	—	3089	ν _{CH} (Ar)	—	3075	3078	0.335
ν _{CH} (Ar)	3075	3075	ν _{CH} (Ar)	—	—	3073	—
ν _{CH} (Ph)	3052	3053	ν _{CH} (Ph)	—	—	3050	—
ν _{CH} (Py)	—	3026	ν _{CH} (Py)	3030	3029	3026	—
ν _{ring} (Ph)	1588	1589	ν _{ring} (Ph)	—	—	1587	—
ν _{ring} (Py)	1543	1552	ν _{ring} (Py)	1551	1550	1550	0.327
ν _{ring} (Ph)	1445	1445	ν _{ring} (Ph)	1447	1449	1442	—
ν _{ring} (Py)	1409	1407	ν _{ring} (Py)	1409	1409	1405	0.333
δ _{CH} (Ar)	1342	1338	δ _{CH} (Ar)	1329	1327	1326	—
δ _{CH} (Ar)	1332	1323	δ _{CH} (Ar)	1309	1313	1321	—
δ _{CH} (Ar)	1314	1289	δ _{CH} (Ar)	—	—	1293	—
δ _{CH} (Py)	1233	1250	δ _{CH} (Ar)	—	—	1249	—
δ _{CH} (Ph)	1164	1159	δ _{CH} (Ph)	1152	—	1156	—
δ _{CH} (Py)	1102	1108	δ _{CH} (Py)	—	—	1088	—
δ _{CH} (Ar)	1074	1082	δ _{CH} (Ar)	1076	1076	1080	0.360
δ _{ring} (Py)	668	668	γ _{CH} (Ph) ^f	972	972	976	—
δ _{ring} (Ph)	—	614	γ _{CH} (Py)	—	—	956	0.357
δ _{C-C} (Py, Ph)	—	406	γ _{CH} (Ar)	915	916	912	—
δ _{C-C} (Py, Ph)	—	184	γ _{CH} (Py)	827	828	825	0.200
11 B₁(x)			γ _{CH} (Ar)	—	761	760	0.183
γ _{CH} (Ph)	974	972	γ _{CH} (Ar)	—	735	736	0.183
γ _{CH} (Py)	965	949	γ _{CH} (Ph)	697	696	695	0.201
γ _{CH} (Ph)	918	900	δ _{ring} (Py)	671	—	668	0.194
γ _{CH} (Ar)	830	822	δ _{ring} (Ph)	621	—	625	0.363
γ _{CH} (Ar)	761	756	γ _{ring} (Ar), τ ^g	562	560	558	0.251
γ _{C-Ph} , γ _{CH} (Ar)	731	726	γ _{C-Ph} , γ _{ring} (Ph) ^h	494	491	489	0.183
γ _{CH} (Ph)	687	675	δ _{C-Py} , δ _{ring} (Ph)	—	—	367	—
γ _{CH} (Ar), τ ⁱ	561	558	γ _{C-Py}	—	—	260	—

Table 1 (continued)

4-PHPY(C_{2v})			4-PHPY(C_2)			
Symmetry and assignment	KBr; PE pallet	DFT calc.	Symmetry and assignment	CCl_4	ZLI 1695	DFT calc. K_f
$\gamma_{ring}(Ar)$	442	445	$\delta_{C-C}(Py, Ph)$	–	–	126
γ_{C-Py}	228 ^j	222	γ_{C-Py}	–	–	92
γ_{C-Py}	–	95				

The spectral bands are compared with and assigned to predicted fundamentals by DFT calculations.

^a ν_{CH} – CH stretching vibration of both aromatic rings.

^b ν_{ring} ($x = Ph, Py$ and Ar) – ring stretching vibrations of Phenyl, Pyridine and whole aromatic system.

^c δ_{CH} ($X = Ph, Py$ and Ar) CH in -plane deformation vibration of Phenyl, Pyridine and whole aromatic ring system.

^d $\delta_{ring}(X = Ph, Py$ and $Ar)$ – ring in-plane deformation vibration of Phenyl, Pyridine and whole aromatic system, respectively.

^e ν_{C-X} ($x = Py$) – Phenyl-Pyridine C–C stretching vibrations.

^f γ_{CH} ($X = Ph, Py$ and Ar) C–H out-of-plane deformation vibration of Phenyl, Pyridine and whole aromatic ring system.

^g γ_{ring} – ($X = Ph, Py$ and Ar) ring out-of-plane deformation vibration of Phenyl, Pyridine and whole aromatic ring system.

^h γ_{C-X} C–C ($x = Py$ or Ph) out-of-plane deformation vibrations.

ⁱ τ – torsional vibration of both aromatic rings.

^j FAR IR spectral data ($150 < \nu < 400 \text{ cm}^{-1}$) were obtained by PE technique.

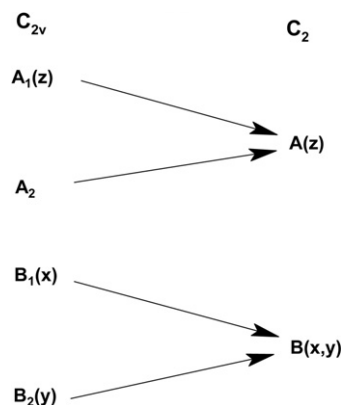


Fig. 5. Correlation diagram between symmetry species of both C_{2v} and C_2 symmetry groups.

Table 2

The difference in symmetry band assignment observed for several fundamentals of 4-PhPy in Ref. [3,14] and in this work

Frequency	Symmetry band assignment		
$\nu_{exp} (\text{cm}^{-1})$	Ref. [3]	Ref. [14]	This work
1588	A_1	B_2	B_2
1543	B_2	A_1	B_2
1232	B_2	A_1	A_1
1219	A_1	B_2	B_2
1182	B_2	A_1	A_1
1102	B_2	A_1	A_1
965	B_1	A_1	B_1
830	A_1	B_1	B_1
561	B_2	B_1	B_1
442	A_1	B_1	B_1

axes x , y , and z is described by direction cosines $\cos(\mathbf{M}_f, u) = \cos \varphi_u^f$, $u = x, y, z$, for which the following relation is valid:

$$\cos^2 \varphi_x^f + \cos^2 \varphi_y^f + \cos^2 \varphi_z^f = 1. \quad (2)$$

For molecules of C_{2v} or higher symmetry evaluation of average orientation is very straightforward since symmetry constrains direction of vibrational transition moments to the

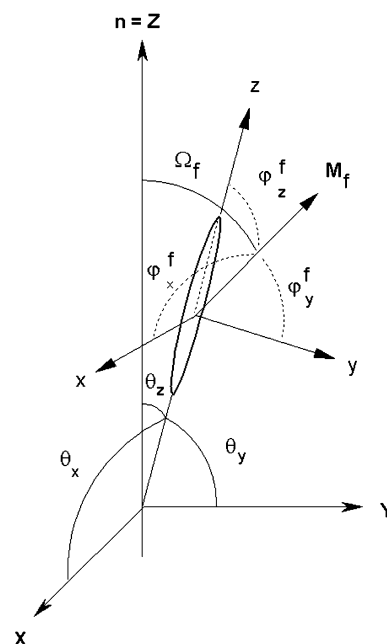


Fig. 6. The orientation of the solute molecule with respect to nematic director \mathbf{n} and the orientation of an arbitrary vibrational transition moment \mathbf{M} with respect to molecular axis system x, y, z . Angles φ_i^f ($i = x, y, z$) define transition moment orientation in molecular frame, while θ_i^f ($i = x, y, z$) define the orientation of long molecular axis in respect to nematic director \mathbf{n} .

axes x , y and z of molecular framework, whose orientational factors can simply be determined by the following formula[6]: $K_{uu} = K_u = R_u/(2 + R_u)$, $u = x, y, z$. R_u are measured dichroic ratios and the orientational tensor \mathbf{K} acquires a diagonal form $K_{uv} = K_{ii}\delta_{uv}$, where its trace is equal to one:

$$\text{Tr}(\mathbf{K}) = K_x + K_y + K_z = 1.$$

However, when molecular symmetry is lowered in result of conformational change caused by environmental constraints, as it is the case with 4-PhPy, $C_{2v} \rightarrow C_2$, molecular axis C_2 (z) remains a symmetry axis only. This implies that

z polarized transitions remain z polarized, while x and y polarized transitions are ‘mixed’, their directions depending on the dihedral angle (see Fig. 1) [5].

When an arbitrary molecular frame is chosen the orientational tensor K_{uv} should have five independent unknowns and there are also two unknown independent direction cosines $\cos \phi_u^f$, for each transition moment M_f (see Eq. (2)). The number of unknown values K_{uv} can be reduced if the principal molecular axis system is used. In such a molecular frame the orientational tensor acquires a diagonal form similarly to the case of high symmetry molecules. Then orientation of an arbitrary transition moment M_f in respect to nematic director given by Eq. (1) can be rewritten in the form:

$$K_f = K_{x'} \cos^2 \phi_{x'}^f + K_{y'} \cos^2 \phi_{y'}^f + K_{z'} \cos^2 \phi_{z'}^f \quad (3)$$

In this molecular frame the axes x' , y' and z' coincide with the resulting eigenvectors while the eigenvalues correspond to the orientational factors $K_{u'}$ [6]. Although the number of the unknown parameters significantly decreases, the task for determination of $K_{u'}$ values cannot be unambiguously solved without any prior knowledge about the mutual orientation of a few transition moments. Principally, this information can be extracted from another experimental or theoretical source see for example Ref. [16,17].

5.2. Method development

In a twisted 4-PhPy one of the principal axes of the orientational tensor, for instance z , should be parallel to the cross section of both planes of aromatic rings (see Fig. 1), i.e., $K_{xz} = K_{yz} = 0$. The K_z value can be determined directly from the dichroic ratio R_z by interactive subtraction $A_{\parallel}(v) - R_z \cdot A_{\perp}(v)$ as the bands corresponding to the transitions polarized parallel to the z -axes simultaneously disappear (see Fig. 3b, curve $\Delta A_{xy}(v)$). When directions of molecular axes x and y are arbitrarily chosen in respect to the nematic director \mathbf{n} orientational parameters K_x , K_y and K_{xy} remain unknown. If a principal axes system is used, the off-diagonal element K_{xy} vanishes. Thus, the orientational parameters K_x and K_y can be determined by a set of two equations similar to Eq. (3) [5]:

$$K_{x_i} = K_x \cos^2(\varphi/2) + K_y \sin^2(\varphi/2) \quad (4)$$

$$K_{y_i} = K_x \sin^2(\varphi/2) + K_y \cos^2(\varphi/2), \quad (i = 1, 2) \quad (5)$$

where φ is the unknown dihedral angle between aromatic rings, while K_{x_i} and K_{y_i} are orientational factors which can be determined directly from dichroic ratios measured by out- and in-plane C–H deformation vibrations of aromatic rings (see Fig. 3b, curves $\Delta A_{xz}(v)$ and $\Delta A_{yz}(v)$). In principle these frequency modes of 4-PhPy are difficult to localize within each aromatic subunit. However, visualization³ of calculated in-plane and out-of-plane frequency

modes shows that some of them can approximately be related to one of both aromatic rings. This is the reason to use indexes 1 and 2 for experimentally determined K_{x_i} and K_{y_i} values. They are very close to the orientational parameters of local coordinate systems shown in Fig. 1. Then, K_x and K_y solution of set of Eqs. (4) and (5), can be found by the following expressions:

$$K_x = \frac{1 - K_z}{2} - \frac{K_{y_i} - K_{x_i}}{2} \sqrt{(1 + \tan^2 \varphi)} \quad (6)$$

$$K_y = \frac{1 - K_z}{2} + \frac{K_{y_i} - K_{x_i}}{2} \sqrt{(1 + \tan^2 \varphi)}, \quad (i = 1, 2), \quad (7)$$

6. Results and discussion

As it can be seen from Eqs. (6) and (7) the IR-LD measurements of a liquid crystal solution do not provide accessible information about the twist angle φ because the unknown orientational parameters K_x and K_y are functions of this independent variable. For that reason the other experimental or theoretical approach should be used for determination of the dihedral angle.

Since the decrease of conjugation in aromatic systems leads to an increase of the frequency of ring out-of-plane deformation vibrations [18] their shift can be used as a qualitative indicator of the conformational state of a solute molecule and can provide useful information about the intermolecular solute–solvent interactions [7]. It is an explanation of frequency increase of out-of-plane vibrations of biphenyl and bipyridine in non-polar solvents where an internal rotation of aromatic subunits is possible for example [19]. A similar tendency is qualitatively confirmed by our DFT frequency calculations for this type of deformation vibration when dihedral angle φ is varied in the interval (0–90°) (see Fig. 7). In the same figure are

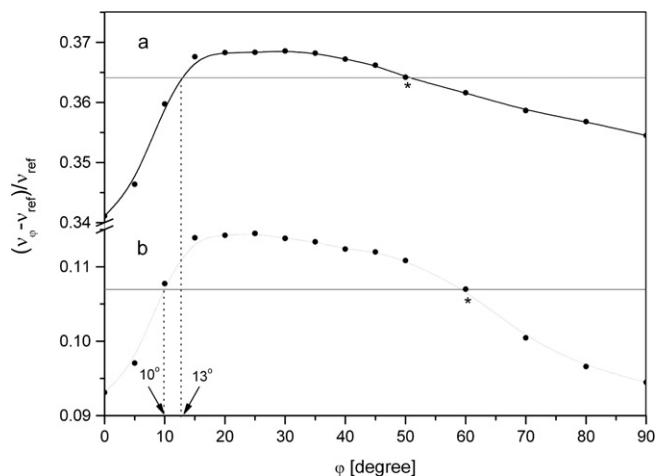


Fig. 7. Two plots (a) and (b) present the relationship between frequency ratios $(v_\varphi - v_{\text{ref}})/v_{\text{ref}}$ and dihedral angle φ , where v_φ is the frequency of out of plane vibration at 828 cm^{-1} which value depends on the relative orientation of both aromatic rings while for a reference frequency v_{ref} two bands at 745 and 607 cm^{-1} were chosen since they have not such dependence.

³ MOLEKEL 4.0, P. Flükiger, H.P. Lüthi, S. Portmann, J. Weber, Swiss Center for Scientific Computing, Manno (Switzerland), 2000.

presented both theoretical and experimental frequency data using the following frequency ratios $(\nu_\varphi - \nu_{\text{ref}})/\nu_{\text{ref}}$, where ν_φ is the frequency of out of plane vibration at 828 cm^{-1} ($B(x, y)$) which is sensitive to internal rotation, while in the case of ν_{ref} two reference frequencies at 745 cm^{-1} ($A(z)$) and 607 cm^{-1} ($A(z)$) that have no such dependence were chosen (see Fig. 7). Experimental and theoretical frequency data presented this way make possible to reduce in a certain extent the solvent and scaling frequency effect of the studied vibrational modes.

The sought twist angle was found to be $10\text{--}13^\circ \pm 5^\circ$ in result of intersection of theoretical data curve obtained by calculated frequencies at different values of φ and the straight line corresponding to single experimental frequency (see Fig. 7).

This rough estimation of the angle value is in the expected interval ($0\text{--}30^\circ$) since the dihedral angle of biphenyl is 0° in solid state [5], while in non-polar solvents it was found to be $20\text{--}30^\circ$ [4,20]. It is not surprising to observe a smaller value of the twist angle of 4-PhPy in liquid crystalline phase in comparison with those of isotropic one since parallel packing of anisometric molecules implies a contraction of intermolecular distances between solute and solvent in a direction perpendicular to the nematic director. This finding is also supported by the fact that the transition isotropic liquid to nematic liquid crystal is a first order phase transition which implies a certain change of the density of the sample [21,22]. Thus, the transition from random to ordered phase may provoke a compression of the intrinsic volume of the guest molecule that leads to decrease in internal rotational angle. This effect has similar expression to those of pressure on the internal rotation angle of biphenyl in carbon disulfide [7].

The second value of φ observed in the interval $49\text{--}58^\circ$ (see asterisk in Fig. 7) does not seem to be realistic since in the liquid crystal solution it is not very likely to exist two different values for a dihedral angle. More over, the values of $\varphi = 49^\circ$, 58° exceed this one for gas phase $\varphi \sim 44^\circ$ and apparently lead to a larger intrinsic volume in condensed phase. For that reason an average value of $\varphi = 12^\circ$ was chosen in order to calculate orientational parameters K_x and K_y from Eqs. (6) and (7).

During preparation of reduced IR-LD spectra small differences were found by determination of K_f values for in-plane vibrations (e.g. $1076\text{ cm}^{-1} K_{y_1} = 0.360$ and $1409\text{ cm}^{-1} K_{y_2} = 0.333$) and for C—H out-of-plane vibrations (e.g. $761\text{ cm}^{-1} K_{x_1} = 0.183$ and $828\text{ cm}^{-1} K_{x_2} = 0.201$) (see also Table 1). These deviations may due to from one hand of the spectral overlap and from another hand of a weak vibrational coupling between aromatic rings [5]. The last effect may cause a small frequency shift and a distortion of the transition moment orientation with respect to the local coordinate axes x_i and y_i ($i = 1, 2$) of both aromatic subunits.

Using Eqs. (6) and (7) and above K_f data the following values for $K_x = 0.179$; 0.201 and $K_y = 0.356$; 0.334 , were

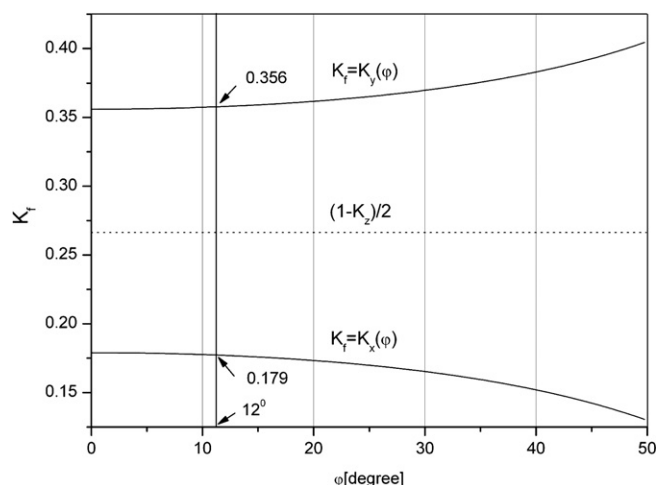


Fig. 8. Graphical illustration of conformational dependence of orientational parameters K_x and K_y from the dihedral angle φ between aromatic rings. K_x and K_y values are determined from intersection points of the vertical line at 12° and both curves $K_x(\varphi)$ and $K_y(\varphi)$ generated by Eqs. (6) and (7).

obtained. $K_z = 0.465$ was initially determined from dichroic ratio $R_z = 1.738$.

The results obtained for orientational parameters K_x and K_y are close and can be explained by mentioned above deviations of K_f values.

The following set of orientational factors ($K_{x_1} = 0.183$; $K_{y_1} = 0.360$; $K_z = 0.465$) was used to illustrate conformational dependence of K_x and K_y on the twist angle φ (see Fig. 8). As it can be seen from the same figure both functions $K_x(\varphi)$ and $K_y(\varphi)$ change slowly and smoothly in the interval $\varphi = \{0\text{--}30^\circ\}$, where the twist angle value for nematic phase is expected to appear. This behavior of both curves implies that small variations around a certain dihedral angle in mentioned above interval should not lead to sudden change in orientational parameters K_x and K_y .

7. Conclusions

In the paper we studied a conformational dependence of orientational parameters K_x and K_y on the dihedral angle φ between both aromatic rings of 4-PhPy.

Relations $K_x(\varphi)$ and $K_y(\varphi)$ given by Eqs. (6) and (7) (Fig. 8) show that both orientational parameters K_x and K_y change slowly and smoothly in the region of $\varphi = \{0\text{--}30^\circ\}$, where the expected twisting angle value for nematic solution is found. The value of 12° is determined by the proposed qualitative approach which gives a rough estimation of the sought dihedral angle in anisotropic phase. The trace of both curves $K_x(\varphi)$ and $K_y(\varphi)$ (see Fig. 8) shows that small deviations ($\delta\varphi \sim \pm 5^\circ$) around the target value of φ in the pointed above interval do not lead to a sudden change in orientational parameters K_x and K_y .

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