

IR-LD SPECTROSCOPY OF BENZIL ORIENTED AS SOLUTION IN NEMATIC LIQUID CRYSTAL AND MELTED POLYCRYSTALLINE SOLID SAMPLE

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An IR-LD spectral analysis was performed on benzil as a solution in nematic liquid crystal and as melted polycrystalline solid sample, using the orientation technique. An experimental vibrational assignment of IR-characteristic bands both in solution and in solid state was made, thus explaining some of the crystal field effects in solid-state on the IR-maxima.

Key words: benzil; IR-LD spectroscopy; solution; solid-state; overtone

ИНФРАЦРВЕНА СПЕКТРОСКОПИЈА СО ЛИНЕАРЕН ДИХРОИЗАМ НА БЕНЗИЛ ОРИЕНТИРАН ВО НЕМАТИЧЕН ТЕЧЕН КРИСТАЛ И ВО СТОПЕН ПОЛИКРИСТАЛЕН ЦВРСТ ПРИМЕРОК

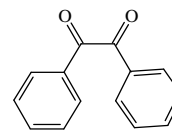
Со инфрацрвена спектроскопија со линеарен дихроизам (IR-LD) е извршена спектрална анализа на бензил во стопен поликристален цврст примерок од нематични течни кристали и поликристални примероци во цврста состојба, користејќи ја ориентационата техника. Извршена е експериментална вибрациона асигнација на карактеристичните инфрацрвени ленти во раствор и во цврста состојба. На тој начин се објаснети некои од ефектите на кристалното поле врз максимумите во спектрите на примероци во цврста состојба.

Клучни зборови: бензил; инфрацрвена спектроскопија со линеарен дихроизам; раствор; цврста состојба

INTRODUCTION

Benzil, 1,2-diphenylethane-1,2-dione (Scheme 1), is a photoinitiator that breaks down into free radicals upon exposure to ultraviolet radiation, and is an example of optically active compound in the crystalline state only [1]. Its potent activation of microsomal epoxide hydrolase *in vitro* was an object of a series of theoretical [2], crystallographic [3, 4] and infrared spectral [2, 5, 6] studies. Detailed experimental IR-band assignment including the overtones is possible by application of linear-dichroic infrared spectral (IR-LD) analysis, which is an object of present work. Presented here are the results of IR-LD spectral analysis of benzil as a

solution in nematic liquid crystal and as melted polycrystalline solid sample.



Scheme 1

EXPERIMENTAL

Benzil was purchased from Aldrich.

The IR-spectra were recorded on a Bomem-Michelson 100 FTIR-spectrometer (4000–400 cm⁻¹)

equipped with a Perkin Elmer wire-grid polarizer. The oriented samples were obtained in two ways: (i) film, crystallized between KBr plates annealed at 170°C, and (ii) a solution in nematic mesophase. A 4'-cyano-4'-alkylbicyclohexyl mixture (ZLI 1695, Merck) was used for the orientation of the benzil. The orientation technique and the procedure used for the IR-LD data interpretation have been described in details elsewhere [7, 8]. The *difference-reduction* procedure for polarized IR-spectra interpretation involves subtraction of a perpendicular spectrum, (IR_s), obtained at a 90° angle between the polarized light beam electric vector and the orientation of the sample, from a parallel spectrum (IR_p) obtained at a co-linear mutual orientation. The recorded *difference* ($IR_p - IR_s$) spectrum divides the parallel (A_p) and perpendicular (A_s) integrated absorbances of each band into positives, originating from transition moments that form average angles with the orientation direction (\mathbf{n}) between 0° and 54.7°, and negative ones, corresponding to transition moments between 54.7° and 90°. In The perpendicular spectrum is multiplied by the parameter c , subtracted from the parallel spectrum, and c is varied until a band or set of bands are eliminated. The simultaneous disappearance of bands in the obtained ($IR_p - cIR_s$) *reduced* IR-LD spectrum indicates a co-linearity of the corresponding transition moments, thus providing information regarding the mutual disposition of the molecular fragments. This elimination method is graphically carried out using a subtracting procedure attached to the program for processing of IR spectra.

RESULTS AND DISCUSSION

The difference IR-LD spectra of benzil oriented as a solution in nematic liquid crystal (Fig. 1.1) and as polycrystalline melted film (Fig. 1.2) indicated a significant degree of orientation of the guest molecule, independent of the technique used. The characteristic IR-frequencies are listed in Table 1.

The corresponding in-plane and out-of-plane modes in separate aromatic rings are noted using the Wilson notation, assuming that the discussed structural fragments in the benzil molecule possessed C_{2v} symmetry.

According to X-ray data [3, 4] benzil crystallizes at room temperature in a trigonal system with

space group D_3^4 ($P3_121$). The molecule is composed of two nearly planar benzoyl groups closing a torsion angle of 108°. According to known theoretical data [2], the molecule possesses a C_2 symmetry, causing the existence of in-phase and out-of-phase splitting in the crystal and in the solution as well.

Table 1

IR-characteristic bands of benzil in 1700 – 400 cm^{-1} range in solution and in solid state

Phase		Assignment*
Solution ν / cm^{-1}	Solid-state ν / cm^{-1}	
1683, 1674	1681, 1673, 1660, 1654	$\nu^{as}_{C=O}, \nu^s_{C=O}$
1597	1597	8a (A_1)
1581	1579	8b (B_2)
1492	1490	19a (A_1)
1463	1465	19b (B_2)
1317	1324	3 (B_2)
1174	1170	9a (A_1)
1143	1140	9b (B_2)
1072	1070	18a (A_1)
1025	1025	18b (B_2)
1000	999	1 (A_1)
877	869	d_1
719	725	11 (B_1)
688	679	4 (B_1)

* According Wilson notation [9]

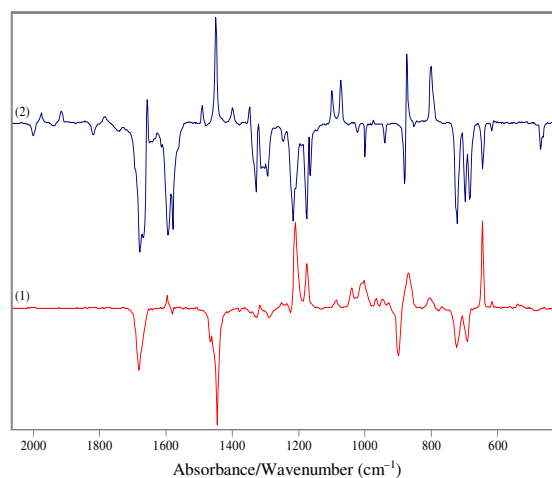


Fig. 1. Difference IR-LD spectra of benzil oriented as a solution in nematic liquid crystal (1) and melted polycrystalline solid sample (2)

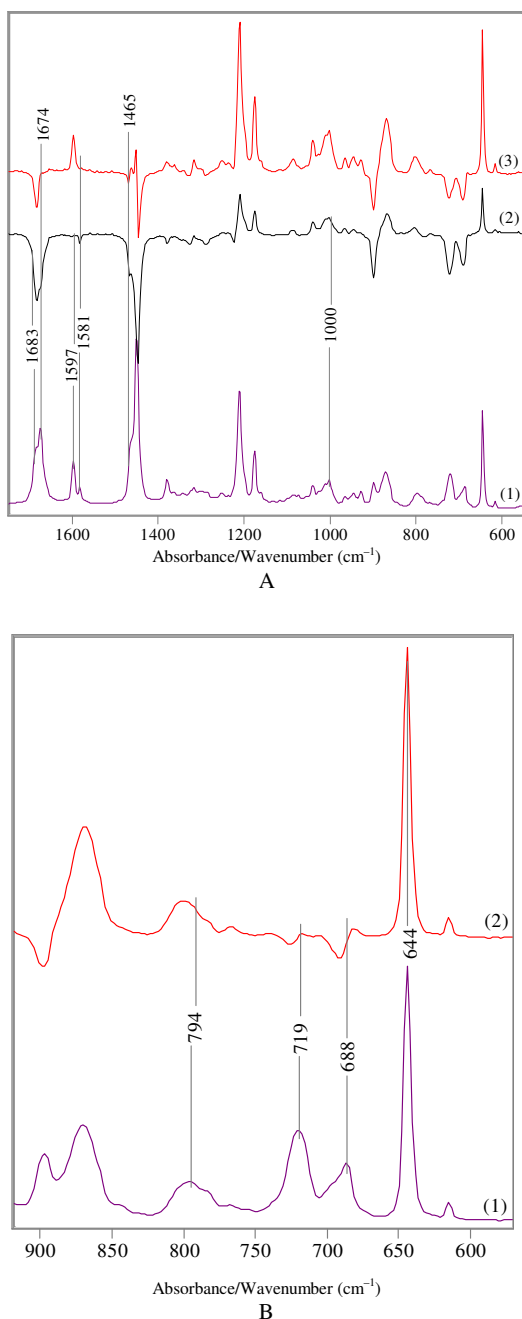


Fig. 2. Non-polarized IR- (1) and reduced IR-LD spectra of benzil oriented as a solution in nematic liquid crystal after elimination of peaks at 1597 cm^{-1} (A(2)), 1674 cm^{-1} (A(3)) and 719 cm^{-1} (B(2))

IR-LD analysis of oriented benzil as nematic liquid crystal solution

The non-polarized IR-spectrum (Fig. 2.1) is characterized with pairs of maxima at 1683 cm^{-1} and 1674 cm^{-1} corresponding to $\nu^{\text{as}}_{\text{C=O}}$ and $\nu^{\text{s}}_{\text{C=O}}$ stretching modes [2] (Table 1). The peaks at 1597

cm^{-1} and 1581 cm^{-1} are assigned to 8a and 8b in-plane skeletal frequencies of mono-substituted benzenes. The $1000 - 500\text{ cm}^{-1}$ region shows series of peaks at 794 cm^{-1} , 719 cm^{-1} , 688 cm^{-1} and 644 cm^{-1} assigned in [2] as $11-\gamma_{\text{CH}}$, $4-\gamma_{\text{Ar}}$, 6a and 6b modes of phenyl fragments (Fig. 3.1). However, detailed assignment of IR-maxima and corrections can be made in the following IR-LD spectral analysis.

The reducing-difference procedure on polarized IR-LD spectra interpretation leads to the following results: (i) The elimination of the 1597 cm^{-1} peak (Fig. 2A.2) resulted in a observation of a 1581 cm^{-1} peak and disappearance of the 1000 cm^{-1} maximum. This new peak corresponds to 1 in-plane (A_1), and the 1597 cm^{-1} peak can be assigned as 8a mode; (ii) The elimination of the 1674 cm^{-1} peak leads to the disappearance of the 1581 cm^{-1} and 1465 cm^{-1} peaks (Fig. 2A.3), assigned as 8b and 19b modes. The results correlate well with the theoretical data [2], where the values are 1580 cm^{-1} and 1458 cm^{-1} . (iii) The simultaneous elimination of the 719 cm^{-1} and 688 cm^{-1} peaks (Fig. 2B.2) helped assign their character as $11-\gamma_{\text{CH}}$ and $4-\gamma_{\text{Ar}}$ of mono-substituted benzenes, in contrast to the theoretical data, where the peaks are assigned as $4-\gamma_{\text{Ar}}$ and 6a [2]. Moreover, if the 688 cm^{-1} maximum corresponds to A_1 modes, it must be eliminated with the 8a peak (Fig. 2.2), an outcome that is not observed when Figs. 2A.2 and 2B.2 are compared.

IR-LD analysis of oriented benzil as melted polycrystalline solid

In contrast to the IR-spectrum in solution, the non-polarized solid-state spectrum in the $1720 - 1640\text{ cm}^{-1}$ range is characterized with multiple bands, where the deconvolution and curve-fitting procedure resulted in series of peaks at 1681 cm^{-1} , 1673 cm^{-1} , 1660 cm^{-1} and 1654 cm^{-1} , respectively (Table 1). This result could be explained with crystal field splitting in solid-state. The detailed IR-characteristic bands assignment in solid-state of the compound studied, as well as the overtone and combination mode determination, is made by the IR-LD analysis described below.

The elimination of the 3315 cm^{-1} peak leads to disappearance of only the 1657 cm^{-1} peak, thus indicated the overtone character of the first maximum (Fig. 3A.2).

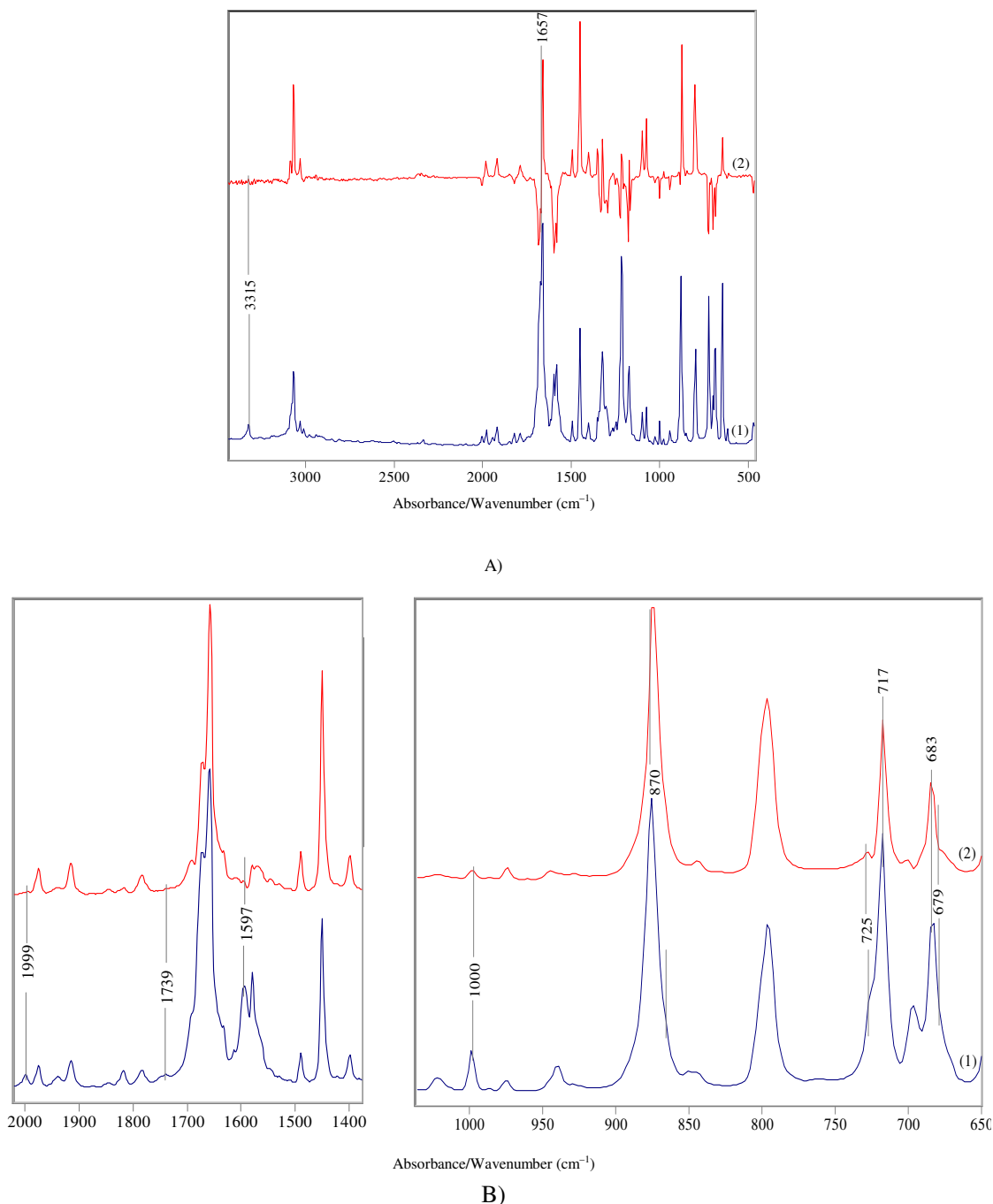


Fig. 3. Non-polarized IR- (1) and reduced IR-LD spectra of benzil oriented as melted polycrystalline solid sample after elimination of peaks at 3315 cm^{-1} (A(2)) and 1999 cm^{-1} (B(2))

The elimination of the 1999 cm^{-1} maximum (Fig. 3B.2) caused the disappearance of the 1739 cm^{-1} , 1597 cm^{-1} , 999 cm^{-1} , 873 cm^{-1} , 725 cm^{-1} and 679 cm^{-1} peaks. This result indicated the character of the first two maxima as $1998\text{ cm}^{-1} = 2 \times 999\text{ cm}^{-1}$ and $1740 = 2 \times 870$, thus correlating well with previous data [6]. The peaks at 999 cm^{-1} and 870 cm^{-1}

correspond to 1 (in-plane A_1) mode and d_1 [2]. The last procedure indicated that the elimination of pairs of $11-\gamma_{\text{CH}}$ and $4-\gamma_{\text{Ar}}$ out-of-plane peaks at 725 cm^{-1} and 679 cm^{-1} gives rise to neighboring peaks at 717 cm^{-1} and 683 cm^{-1} with the same character. This fact is a result of the near perpendicular orientation of both benzenes in the frame of the ben-

zil molecule, closing an angle of 108° , as determined by single crystal X-ray diffraction in [3, 4].

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