

Two-dimensional correlation infrared spectroscopy studies on the thermal-induced mesophase of 4-nitrobenzohydrazide derivative[☆]

Binglian Bai^{a,b,*}, Jue Wei^a, Nicolas Spegazzini^b, Yuqing Wu^c, Haitao Wang^d, Min Li^d, Yukihiko Ozaki^b

^a College of Physics, Jilin University, Changchun, PR China

^b Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, 2-1 Gakuen, Sanda 669-1337, Japan

^c State Key Lab for Supramolecular Structure and Material, Jilin University, Changchun, PR China

^d College of Materials Science and Engineering, Jilin University, Changchun, PR China

ARTICLE INFO

Article history:

Received 20 October 2013

Received in revised form

27 November 2013

Accepted 27 November 2013

Available online 7 December 2013

Keywords:

Two-dimensional correlation analysis

Infrared spectroscopy

Intermolecular hydrogen bonds

Mesophase

Liquid crystals

Hydrazide derivative

ABSTRACT

Two-dimensional (2D) correlation infrared (IR) spectroscopy has been applied to explore the effect of hydrogen bondings (HBs) on the structure of mesophase in the dissymmetrical 4-nitrobenzohydrazide derivative, N-(4-cetyloxybenzoyl)-N'-(4'-nitrobenzoyl) hydrazine (C16-NO₂). The strength and species of HBs as well as the heat-induced structural variations in mesophase have been investigated. It has been found from 2D correlation IR spectroscopy that the sequential order of changes in the different functionalities in the course of liquid crystalline formation is that, firstly, the alkyl chain changes from the significant population of the *trans* conformation to the significant population of *gauche* conformation; then, the intermolecular HB between C=O and N-H groups is weakened, some even being broken, and consequently, the intermolecular distance is enlarged; finally, the skeleton of phenyl ring has enough space to change their conformation to weaken the π - π stacking interaction. In addition, besides a few free and some medium bonded N-H and C=O groups, strongly bonded N-H and C=O groups still predominantly exist in the mesophase.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Self-assembled liquid crystalline materials, formed through non-covalent interactions, have attracted much attention because they are good candidates for the next generation of functional materials [1–3]. Hydrazide units have been used to build supramolecular liquid crystals based on hydrogen-bondings (HBs), and several related systems have been reported by us recently [4–11]. Essentially, the intermolecular HBs in hydrazide derivatives can be speculated well by performing concentration- and temperature-dependent NMR spectra as well as the corresponding FT-IR spectra. For example, temperature-dependent ¹H NMR spectroscopic experiments in 20% DMSO-d₆/CDCl₃ of TC6 showed that both NH-1 (near to alkoxyphenyl) and NH-2 (near to central phenyl) have large shifts (6.45×10^{-3} ppm K⁻¹ and 6.05×10^{-3} ppm K⁻¹, respectively) with temperature (generally, internally hydrogen-bonded amides are expected to show a much smaller shift

(< 3.0×10^{-3} ppm K⁻¹) with temperature). And we also calculated the association constants (*K*) of 7.13×10^3 M⁻¹ and 1.53×10^3 M⁻¹ on the basis of NH-1 and NH-2 by the concentration-dependent ¹H NMR spectroscopic experiments in CDCl₃ [4]. However, the strength and species of HB cannot be deduced well by the normal NMR or FT-IR spectra.

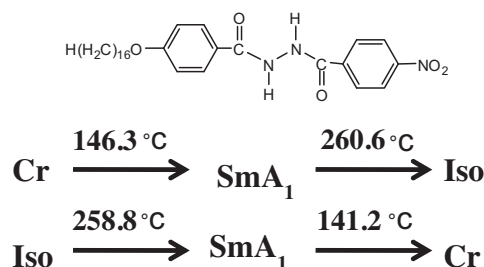
2D correlation spectroscopy has recently gained much attention from the points of both basic science and practical applications [12–15]. 2D correlation spectroscopy simplifies the investigation of complex spectra, enhancing spectral resolution by spreading peaks along the second dimension, enabling one to extract information that cannot be obtained straightforwardly from conventional spectra. And 2D correlation analysis has received great attention for its another ability: it can discern the specific order of events taking place under the influence of a controlling physical perturbation, such as temperature, concentration, time and so on [15–19].

2D correlation analysis has particular advantages in studying the supramolecular liquid crystals. For example, Wu et al. classified the hydrogen-bonding (HB) species in the azobenzene liquid crystals [20]. Later, they explored the phase transition and heat-induced structural variations of the hydrogen-bonded liquid crystal complex (DBS:BD:DBS) [21]. Shen et al. reported the liquid-crystalline phase development of a mesogen-jacketed polymer (PMPCS) using 2D IR correlation analysis [22]. Zhao et al. studied the thermal

[☆] Selected paper presented at 7th International Conference on Advanced Vibrational Spectroscopy, Kobe, Japan, August 25–30, 2013.

* Corresponding author at: College of Physics, Jilin University, Changchun, PR China. Tel.: +86 43185168254.

E-mail address: baibinglian@jlu.edu.cn (B. Bai).



Scheme 1. The chemical structure and the transition temperature of C16-NO₂ [11]. Cr, SmA₁ and Iso indicate crystalline state, monolayer smectic A phase and isotropic liquid, respectively. The peak maximum was taken as the phase transition temperature in DSC curves.

phase transition of a ferroelectric liquid crystal with a monotropic transition temperature [23]. In the present study, we will apply both temperature-dependent FTIR and 2D IR spectra to explore the strength and species of HB as well as the heat-induced structural variations of C_n-NO₂ in mesophase (see Scheme 1). In our previous paper, we have speculated through the temperature-dependent ¹H NMR spectroscopic experiments in 20% DMSO-d₆/CDCl₃ that the primary involvement of N–H protons in C_n-NO₂ is an intermolecular hydrogen bonding [11].

2. Experimental

2.1. Materials

The synthesis of C16-NO₂ was the same as described in previous study [11]. The product was characterized by Fourier transform infrared (FT-IR), ¹H NMR spectra and elemental analysis.

2.2. Measurements

FT-IR spectra were measured by using a Perkin-Elmer Spectrum One B instrument. Samples for IR measurement were prepared by casting onto a KBr plate from a chloroform stocked solution to form a thin film, which was then covered with another KBr window. This sandwiched sample cell was held on a hot stage for the following temperature-dependent IR spectra measurement.

FTIR spectra were collected in the temperature range of 30–250 °C with an interval of 5 °C, and the spectra collected in the temperature range 160–220 °C were used to perform the 2D IR correlation analysis. The 2D contour maps were calculated and plotted by 2Dshige software [17,18]. In the 2D contour maps, the unshaded regions indicate positive correlation intensities, while the shaded regions are for the negative ones.

3. Results and discussion

3.1. Temperature-dependent IR spectra and band assignments of C16-NO₂ [4–11,24]

Fig. 1 shows temperature-dependent IR spectra of C16-NO₂ in the spectral region of 3500–1100 cm⁻¹ on the first heating run. And the assignments of IR bands for C16-NO₂ at the liquid crystalline (220 °C) and crystalline (30 °C) phase are presents in Table 1 [4–11,24]. It can be seen that only hydrogen-bonded N–H (3207 cm⁻¹) and strong hydrogen-bonded C=O stretching vibration bands are observed at 1654 (very weak), 1591 and 1567 cm⁻¹ [11,24], and no “free” (non-bonded) N–H (a relatively sharp peak with a frequency higher than 3400 cm⁻¹) or C=O (the frequency higher than 1700 cm⁻¹) stretching vibration bands were detected at room temperature, which indicates that almost all the N–H

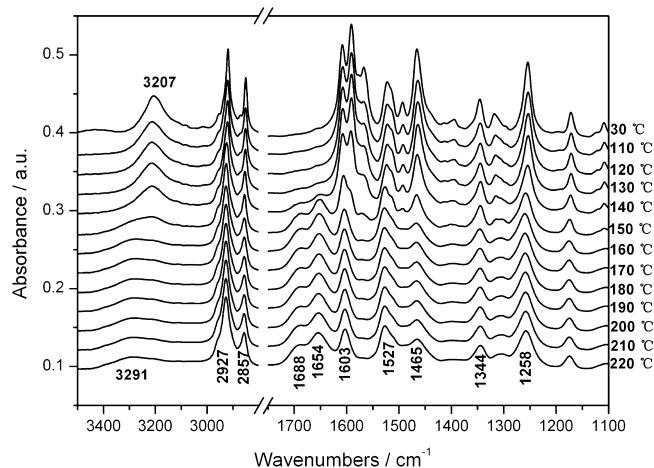


Fig. 1. The temperature dependent FT-IR spectra of C16-NO₂ in the spectral regions of 3500–1100 cm⁻¹ at 30 °C and 110–220 °C.

groups are associated with the C=O groups via N–H...O=C HB in the crystalline phase. Upon heating, the ν(N–H) band is almost unchanged in crystalline phase, only exhibits a sudden change at the crystalline–smectic transition (146 °C). The ν(N–H) band appears at around 3291 cm⁻¹, as well as a shoulder at 3209 cm⁻¹ in the smectic phase. This change is accompanied by a shift of amide I bands from 1591 and 1567 cm⁻¹ to 1688 and 1654 cm⁻¹. The absorptions at 3291, 3209 cm⁻¹ of N–H group and 1688, 1654 cm⁻¹ of C=O group strongly indicate that the HB still exists in the smectic phase, though it has become much weaker.

Fig. 2 shows temperature dependences of ν(N–H), ν_{as}(CH₂) and ν_s(CH₂) of C16-NO₂. It is noted that a higher frequency shift of ν(N–H) is observed on going from the crystalline to the smectic A phase. However, the conformational transitional temperature of ν_{as}(CH₂) and ν_s(CH₂) is indicated below the melting point (146 °C). It suggests that below the melting point, the alkyl chain changes from the significant population of the *trans* conformation (ν_{as}(CH₂)-2919 cm⁻¹, ν_s(CH₂)-2851 cm⁻¹) to the significant population of *gauche* conformation (ν_{as}(CH₂)-2926 cm⁻¹, ν_s(CH₂)-2855 cm⁻¹).

3.2. Two-dimensional IR correlation analysis

Fig. 3A shows a contour map representation of the synchronous 2D correlation spectrum of C16-NO₂ in the spectral region between 3100 and 3450 cm⁻¹ in the temperature range of 160–220 °C. An intense auto-peak at the diagonal position is observed at 3218 cm⁻¹, corresponding to stretching mode of strong hydrogen bonded N–H groups. The auto-peak for the weakly hydrogen

Table 1

Assignments of IR bands for C16-NO₂ at the liquid crystalline (220 °C) and crystalline (30 °C) phase.

30 °C (Cr)	220 °C (SmA ₁)	Assignment
3207	3291	ν(N–H)
2955, 2919	2958, 2927	ν _{as} (CH ₂), ν _{as} (CH ₂)
2872, 2851	2873, 2857	ν _s (CH ₂), ν _s (CH ₂)
1608, 1577 (weak)	1603, 1571 (weak)	Phenyl ring stretching, ν(C=C)
1654, 1591, 1567	1688, 1654	Amide I, ν(C=O)
1523	1527	Amide II
1514, 1346	1514, 1345	ν _{as} , ν _s (NO ₂)
1465	1465	CH ₂ scissoring, δ(CH ₂)
1317	1307	Amide III
1254	1258	Phenyl-O stretching, ν(Ar–O)
844	845	Phenyl ring out-of-plane bending, δ(Ar–H), para-(CH ₂) _n rocking, n ≥ 4
720	716	

Download English Version:

<https://daneshyari.com/en/article/1249965>

Download Persian Version:

<https://daneshyari.com/article/1249965>

[Daneshyari.com](https://daneshyari.com)