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Electronic Spectra of N-(P-Methoxybenzylidene)-P-N-Butylaniline (MBBA)

M. Mizuno [a] , T. Shinoda [a] , H. Mada [b a] & S. Kobayashi [b a]
[a] National Chemical Laboratory for Industry, Shibuya-ku, Tokyo, 151, Japan
[b] Department of Electronic Engg., Tokyo University of Agriculture and Technology, Koganei, Tokyo, 184, Japan
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ELECTRONIC SPECTRA OF N-(P-METHOXYBENZYLIDENE)-P-N-BUTYLANILINE (MBBA)

M.MIZUNO, T. SHINODA,
National Chemical Laboratory for Industry,
Shibuya-ku, Tokyo 151, Japan
H. MADA and S. KOBAYASHI
Department of Electronic Engg., Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan

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Abstract The ultraviolet absorption spectra of MBBA in the metastable and stable solids, the nematic, and the isotropic liquid states have been measured. Furthermore the spectra of dilute solutions and the linear dichroism spectra of nematic single liquid crystal in a homogeneous orientation have also been observed.

The polymorphism in solid-MBBA has been evidenced previously by the calorimetric measurements[1,2] and Raman scattering[3,4]. In the previous paper[2], one of the present authors T.S. and her coworkers have suggested that the result of Raman scattering is interpreted by taking into account the difference in the twist angles of the aniline and benzylidene rings out of the H-C=N plane in the different solid states[4]. In the present letter, the results of ultraviolet absorption for the different states of MBBA are reported.

The sample of MBBA was obtained from Tokyo Ōka Kogyo Co., Ltd. and its purity was the same as that used in the previous calorimetric measurement[2]. The UV spectra in the 190 -400 nm region were obtained with a Cary 14M recording spectrophotometer. The sample cell is composed of a pair of the parallel quartz plates and its edges were sealed by using an Epoxy resin or fused quartz. The optical path length of a sample cell was obtained from the measurement of interferogram on the blank cell[5]. After the determination of the gap of the cell, the specimen in the nematic state was deposited into the cell, and then transformed into the isotropic liquid state by heating once.

Figure 1 represents four different curves showing the absorption spectra of metastable ($2.0_6 \pm$ 0.02°C) and stable ($1.9_3 \pm$ 0.01°C) solids, a nematic (25.8 - 25.9°C), and an isotropic liquid (51.3°) of MBBA, respectively. The metastable state was established by cooling from the nematic state, and the stable state by annealing from 80 K to 0°C several times. The cell with 0.820 μm path length was used. As shown in Figure 1, the wavelengths of the absorption maxima do not shift, and the molar absorptivity increases with transforming from nematic to isotropic liquid. By transforming from metastable to stable solid, the strong absorption band appeared in 230 - 250 nm becomes weak, and the very weak absorption band near 340 nm comes out.

Other measurements of UV spectra were carried out on MBBA (in nematic) dissolved in ethanol (3.40×10^{-5} mol/ℓ) and cyclohexane (5.37×10^{-5} mol/ℓ), respectively

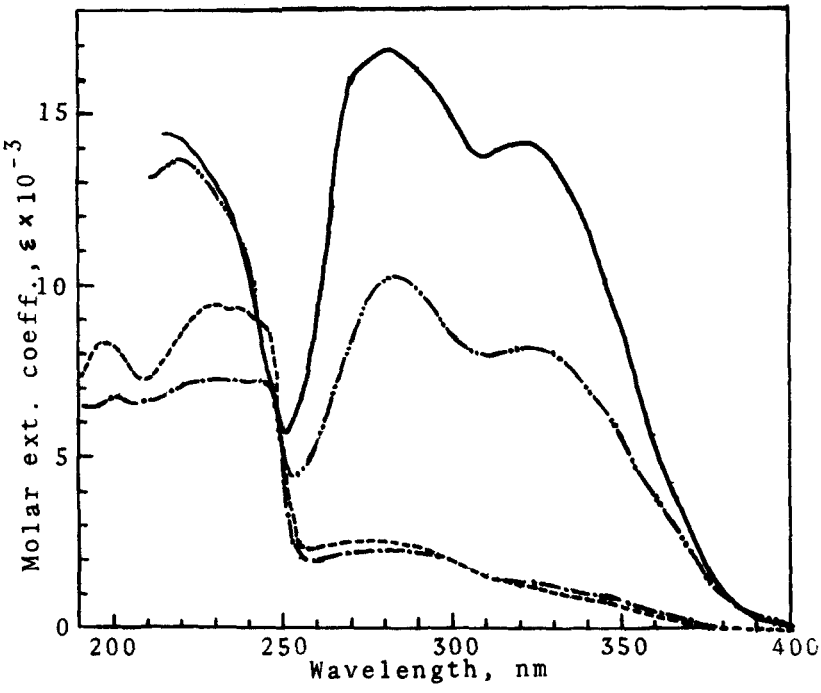

Figure 1. Electronic spectra of MBBA in the different condensed states: ——isotropic liquid; —·—·—·— nematic; - - - - metastable solid; —·—·stable solid.

The results are shown in Figure 2. The absorption band near 320 nm indicates the largest effect due to solvent among the three strong bands.

In order to know the anisotropy in UV spectra the linear dichroism spectra of nematic single liquid crystal in a homogeneous orientation were also measured; this alignment was prepared by a conventional rubbing technique[6]. The gap of the cell was 0.763 μm. Temperature was kept up at 23.4 - 24.3°C. The experimental results are shown in Figure 3. In the

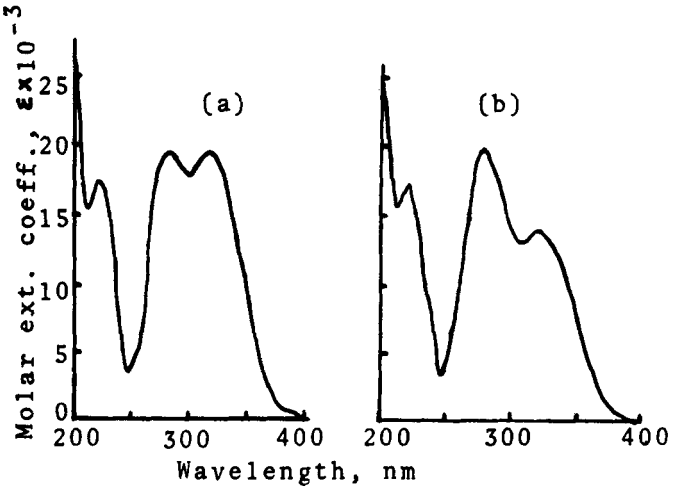

Figure 2. Electronic spectra of MBBA in solvents: (a) ethanol, (b) cyclohexane.

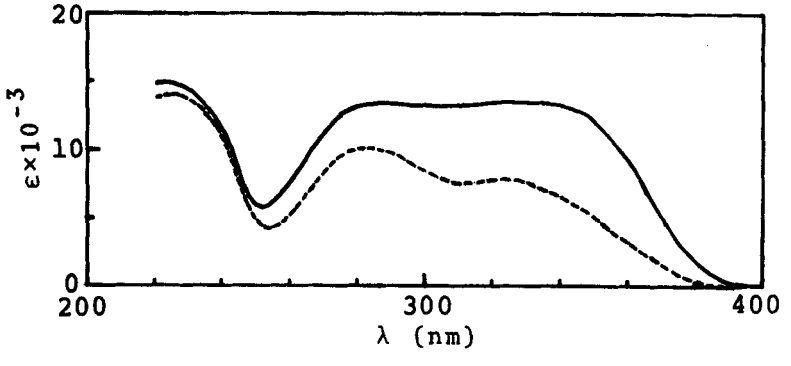

Figure 3. Linear dichroism spectra of MBBA in nematic single liquid crystal: —— $\varepsilon_{\parallel}$; ----- $\varepsilon_{\perp}$.

three strong bands the molar extinction coefficient (ε_{max}) of the absorption maxima and the azimuth angle (θ) may be related approximately by the ellipsoid. The formulas obtained from the observed values are the following:

$(1/\varepsilon_{max})^2 = (\sin\theta/7.69)^2 + (\cos\theta/12.36)^2$; 325 nm band
$(1/\varepsilon_{max})^2 = (\sin\theta/9.95)^2 + (\cos\theta/13.08)^2$; 285 nm band
$(1/\varepsilon_{max})^2 = (\sin\theta/14.08)^2 + (\cos\theta/15.00)^2$; 225 nm band.

The wavelength (λ_{max}) and molar ext. coeff. (ε_{max}) of the absorption maxima in the observed spectra of MBBA are summarized in Table 1.

TABLE 1 Absorption maxima of MBBA

	λ_{max}(nm)	ε_{max}
isotropic liquid	323.0	14140
	282.5	16820
	216.9	16820
nematic	324.7	8120
	283.2	10240
	219.9	13630
metastable solid	272.6	2470
	230-245	9420-8800
	197.2	8410
stable solid	330-340	1300
	281.1	2240
	230-247	7300
	199.8	6790
in ethanol	320.0	19050
	283.8	19610
	222.2	17900
in cyclohexane	321.5	13410
	279.2	19680
	221.8	15210
$\varepsilon_{\parallel}$ in nematic	326.1	13480
	288.4	13500
	224.5	15000
$\varepsilon_{\perp}$ in nematic	324.7	7900
	283.4	10160
	224.8	14080

The observed densities of MBBA[7] were used for isotropic liquid and nematic, and assumed density value of 1.05 was employed for solids to estimate molar extinction coefficients.

We are continuing this investigation from the points of view of molecular conformation and interaction.

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