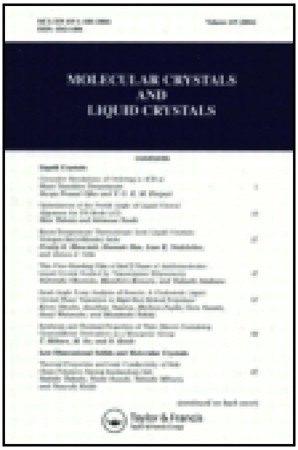


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Infrared Spectroscopic Studies of the Nematogenic Homologous Series p-(p-ethoxyphenylazo) phenyl alkanoates

P. K. Rajalakshmi [a] , N. C. Shivaprakash [a] & J. Shashidhara Prasad [a]

[a] Department of Physics, University of Mysore, Mysore, 570 006, India

To cite this article: P. K. Rajalakshmi , N. C. Shivaprakash & J. Shashidhara Prasad (1980): Infrared Spectroscopic Studies of the Nematogenic Homologous Series p-(p-ethoxyphenylazo) phenyl alkanoates, Molecular Crystals and Liquid Crystals, 60:4, 311-318

To link to this article: http://dx.doi.org/10.1080/00268948008071440

Mol. Cryst. Liq. Cryst., 1980, Vol. 60, pp. 311–318
0026-8941/80/6004–0311$04.50/0

Infrared Spectroscopic Studies of the Nematogenic Homologous Series *p*-(*p*-ethoxyphenylazo)phenyl alkanoates

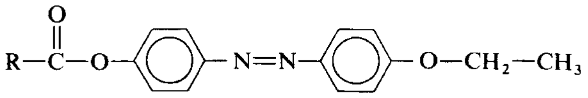
P. K. RAJALAKSHMI, N. C. SHIVAPRAKASH and
J. SHASHIDHARA PRASAD
Department of Physics, University of Mysore, Mysore 570 006, India.

(*Received November 13, 1979*)

Infrared (500–2000 cm^{-1}) spectra of *p*-(*p*-ethoxyphenylazo)phenyl alkanoates (valerate, hexanoate, heptanoate and undecylenate) have been examined in the solid state. An attempt has been made to correlate the variations in the intensities and frequency shifts with the known crystal structures determined by X-ray diffraction methods. The gradual shift towards smaller wavelength in the carbonyl (C=O) stretching frequency and the relative increase in the intensity of the carbonyl frequency as the chainlength increases may be correlated with the increased deviation from planarity of the molecule.

INTRODUCTION

It is quite well established that the molecular structure of mesogenic materials in the crystalline state pre-determines the orientation of molecules in the liquid crystalline state and also contributes to the understanding of the change in physical properties such as thermal stabilities, within the homologous series. In view of this, NMR[1] and X-ray diffraction[2–4] studies have been used to get insight about the molecular structures. Presently we have employed the infrared spectroscopic technique in the solid state to correlate the frequency shifts and intensity variations with the crystal structure variations for the homologous series



R = butyl, pentyl hexyl and oleyl.

EXPERIMENTAL

All chemicals were purchased from Eastman Organic Chemicals Division. The samples were recrytallized before use. All the infrared spectra were obtained on a Zeiss UR 10 spectrophotometer equipped with LiF, NaCl and KBr prisms and providing a recording spectral range of 400–5000 cm^{-1}. The spectra were recorded at room temperature (percentage absorbance versus wavelength) on charts of 10 cm width. The chart was self calibrated every 10 and 100 cm^{-1} with the NaCl prism, the wavenumber accuracy was

TABLE I

p-(*p*-ethoxyphenylazo)phenyl valerate

Band wavelength (μ)	Band wave number cm^{-1}	Intensity[a]	Assignment[b]
5.19	1928	s	
5.42	1846	w	
5.54	1804	s	$\nu(C{=}O)$
6.27	1595	m	$\beta_{ske}(C{=}C)$
7.00	1428	w	$\delta_{sy}(CH_2)$
7.29	1372	m	$\delta_{sy}(CH_3)$: Nujol
7.71	1297	m	
8.00	1250	m	$\beta(C{-}H)$
8.17	1224	m	
8.33	1200	vw	$\nu_{asy}(C{-}O{-}C)$
8.58	1165	s	$\beta(C{-}H)$
9.00	1111	vw	
9.25	1081	s	
10.54	949	s	
11.04	906	m	
11.17	895	w	
11.37	879	w	$\gamma(C{-}H)$
11.58	863	sh	$\gamma(C{-}H)$
11.83	845	w	$\gamma(C{-}H)$
12.00	833	s	$\gamma(C{-}H)$
12.50	800	vs	$\gamma(C{-}H)$
13.00	769	m	
13.29	752	m	
13.46	743	s	$\gamma(C{-}H)$
13.79	725	m	$r(CH_2)$
13.92	718	w	
14.21	704	m	$\gamma(C{-}C)$
14.67	682	s	$\gamma(C{-}H)$
14.87	672	m	$\gamma(C{-}H)$
15.92	628	s	$\beta(C{-}C)$
17.54	570	s	$\varphi(C{-}C)$

[a] vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

[b] See footnote for Table IV.

±1.5 cm^{-1} at 700 cm^{-1} and ±3.5 cm^{-1} at 1500 cm^{-1}. The spectra were registered with Nujol as mulling medium between KBr plates. Tables I to IV give the corrected band positions, relative intensities and assignments of the frequencies observed in the solid state for *p*-(*p*-ethoxyphenylazo)phenyl alkanoates and the spectra are reproduced in Figures 1 to 4.

TABLE II

p-(*p*-ethoxyphenylazo)phenyl hexanoate

Band wavelength (μ)	Band wave number cm^{-1}	Intensity[a]	Assignment[b]
5.37	1860	m	
5.52	1811	s	$\nu(C{=}O)$
6.33	1579	m	$\beta_{ske}(C{=}C)$
7.00	1428	vw	$\delta_{sy}(CH_2)$
7.29	1371	m	$\delta_{sy}(CH_3)$: Nujol
7.67	1304	m	
8.00	1250	m	$\beta(C{-}H)$
8.25	1212	m	$\nu_{asy}(C{-}O{-}C)$
8.46	1182	sh	
8.54	1171	s	$\beta(C{-}H)$
8.92	1121	s	
9.25	1081	s	$\beta(C{-}H)$
10.04	996	m	$\beta(C{-}H)$
10.42	960	s	
11.08	902	s	
11.33	882	vs	$\gamma(C{-}H)$
11.46	873	vs	
12.00	833	s	$\gamma(C{-}H)$
12.42	805	vs	
12.96	772	w	
13.17	759	m	
13.83	723	s	$r(CH_2)$
14.17	706	m	$\gamma(C{-}C)$
14.58	686	s	
14.92	670	s	$\gamma(C{-}H)$
15.75	635	s	
16.00	625	s	$\beta(C{-}C)$
17.42	574	s	$\varphi(C{-}C)$

[a] vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

[b] See footnote for Table IV.

TABLE III

p-(*p*-ethoxyphenylazo)phenyl heptanoate

Band wavelength (μ)	Band wave number cm^{-1}	Intensity[a]	Assignment[b]
5.04	1983	w	
5.19	1928	s	
5.48	1825	s	$\nu(C{=}O)$
6.25	1600	m	$\beta_{ske}(C{=}C)$
7.00	1428	w	$\delta_{sy}(CH_2)$
7.25	1379	s	$\delta_{sy}(CH_3)$: Nujol
7.62	1311	m	
7.96	1256	m	$\beta(C{-}H)$
8.17	1224	m	$\nu_{asy}(C{-}O{-}C)$
8.54	1171	s	$\beta(C{-}H)$
9.17	1091	s	
10.33	967	s	
11.25	889	vw	$\gamma(C{-}H)$
11.75	851	sh	$\gamma(C{-}H)$
11.92	839	s	$\gamma(C{-}H)$
12.50	800	s	$\gamma(C{-}H)$
12.83	779	w	
12.92	774	m	
13.08	764	sh	
13.17	759	sh	
13.42	745	w	$\gamma(C{-}H)$
13.67	731	m	
13.83	723	w	$r(CH_2)$
13.96	716	m	
14.17	706	w	$\gamma(C{-}C)$
14.58	686	s	
14.96	668	vw	$\gamma(C{-}H)$
15.75	635	s	
15.87	630	s	
17.50	572	s	$\varphi(C{-}C)$

[a] vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

[b] See footnote for Table IV.

TABLE IV

p-(*p*-ethoxyphenylazo)phenyl undecylenate

Band wavelength (μ)	Band wave number cm^{-1}	Intensity[a]	Assignment[b]
5.27	1898	w	
5.42	1839	s	$\nu(C{=}O)$
5.50	1818	s	
6.27	1595	m	$\beta_{ske}(C{=}C)$
6.44	1553	m	

(*continued*)

TABLE IV (*continued*)

Band wavelength (μ)	Band wave number cm^{-1}	Intensity[a]	Assignment[b]
6.89	1450	vw	$\delta_{asy}(CH_3)$; $\delta_{asy}(CH_2)$
7.00	1428	vw	$\delta_{sy}(CH_2)$
7.25	1379	s	$\delta_{sy}(CH_3)$; Nujol
7.54	1326	vw	
7.75	1290	s	
7.92	1263	w	
8.12	1231	m	ν_{asy}(C—O—C)
8.25	1212	w	
8.50	1176	vs	β(C—H)
9.25	1081	s	β(C—H)
10.00	1000	m	CH_2=CH
10.12	988	m	
10.50	952	s	
10.96	912	sh	
11.17	895	vw	
11.33	882	vw	γ(C—H)
11.46	873	vw	γ(C—H)
11.83	845	m	γ(C—H)
12.46	803	s	γ(C—H)
12.75	784	m	
13.00	769	m	
13.21	757	m	
13.79	725	s	r(CH_2)
14.17	706	m	γ(C—C)
14.75	678	s	γ(C—H)
14.96	668	m	
15.58	642	sh	
15.83	631	s	
16.12	620	s	β(C—C)
16.42	609	m	
17.50	572	vs	φ(C—C)

[a] vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

[b] ν(C=O) = C=O stretching.
β_{ske}(C=C) = C=C skeletal in-plane deformation in benzene.
$\delta_{sy}(CH_2)$ = CH_2 symmetric deformation vibration.
$\delta_{sy}(CH_3)$ = CH_3 symmetric deformation vibration.
β(C—H) = C—H in-plane deformation.
ν_{asy}(C—O—C) = C—O—C asymmetric stretching vibration.
γ(C—H) = C—H out-of-plane deformation.
r(CH_2) = CH_2 rocking deformation.
γ(C—C) = C—C out-of-plane deformation.
β(C—C) = C—C in-plane deformation.
φ(C—C) = Out of-plane ring deformation.
$\delta_{asy}(CH_2)$ = CH_2 asymmetric deformation vibration.
$\delta_{asy}(CH_3)$ = CH_3 asymmetric deformation vibration.

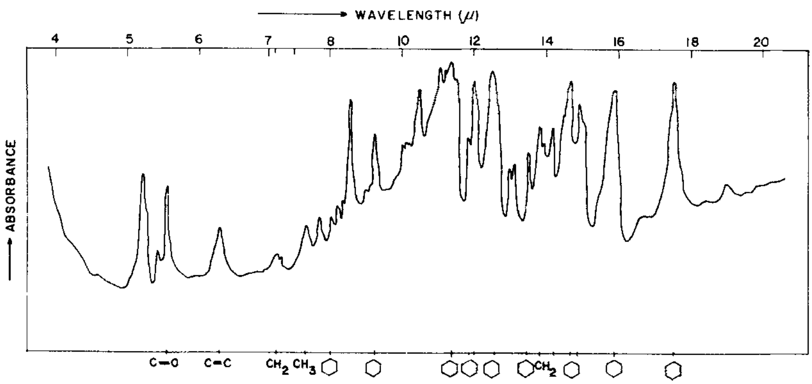


FIGURE 1 Percentage absorbance versus wavelength for *p*-(*p*-ethoxyphenylazo)phenyl valerate.

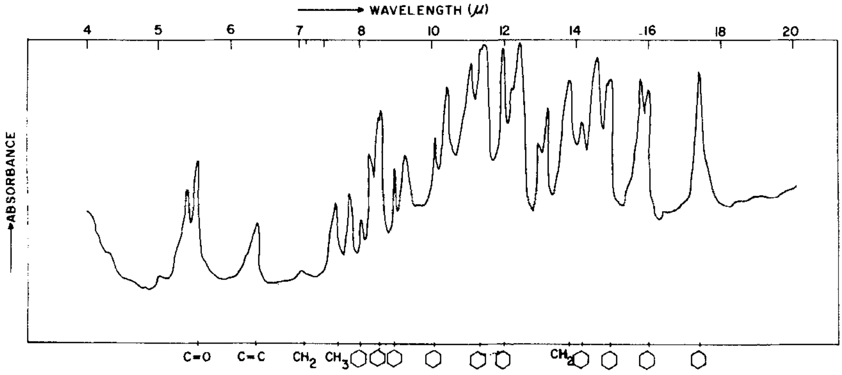


FIGURE 2 Percentage absorbance versus wavelength for *p*-(*p*-ethoxyphenylazo)phenyl hexanoate.

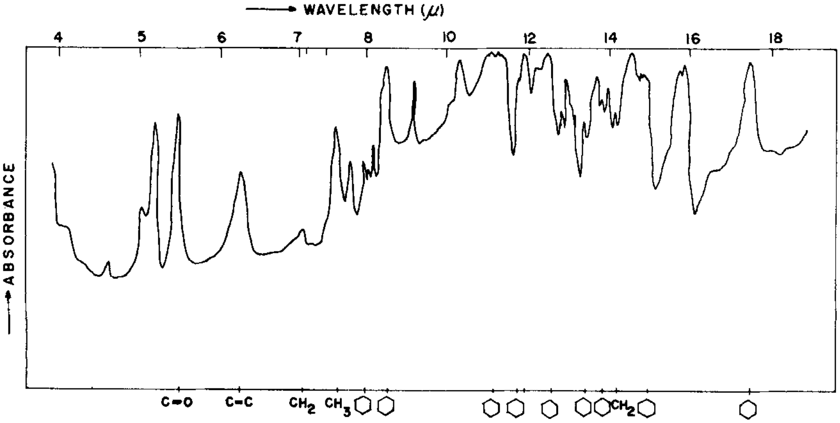


FIGURE 3 Percentage absorbance versus wavelength for *p*-(*p*-ethoxyphenylazo)phenyl heptanoate.

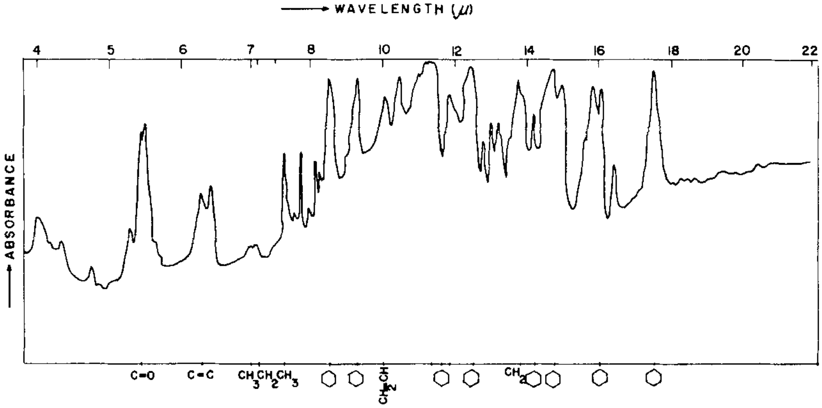


FIGURE 4 Percentage absorbance versus wavelength for *p*-(*p*-ethoxyphenylazo)phenyl undecylenate.

RESULTS AND DISCUSSION

A survey of the assignment reveals that except for an additional peak in the case of the undecylenate around 1000 cm^{-1} due to the $CH_2{=}CH$ group, there are not many changes in either the relative intensities or in the frequencies as we go up the homologous series, barring the case of the carbonyl stretching frequency and the C—O—C asymmetric stretching vibration. There is a gradual shift in the carbonyl (C=O) stretching frequency as the alkyl chain length increases. The shift is towards smaller wavelength (1804, 1811, 1825 and 1839 cm^{-1}) as we go from valerate to undecylanate. Similarly, a shift is also observed in the case of C—O—C asymmetric stretching vibrations (1200, 1212, 1224, 1231). Also the relative intensity of the carbonyl frequency increases from valerate to undecylenate. These changes could be associated with the changes observed in the molecular structure in the crystalline state of these molecules. From the X-ray diffraction studies[2–4] we notice that the angle between the two benzene planes gradually increases from 7 to 31° as we go from valerate to undecylenate which will contribute for the deviation from planarity of the molecule. This will result in the carbonyl dipoles deviating more and more from the preferential directions of the molecule as one goes up the series, thereby causing a shift in frequency and variation in the intensity, as the carbonyl group is directly linked to one of the benzene ring through C—O—C group.

CONCLUSIONS

The changes in the relative intensities and the frequency shift of the carbonyl frequency are indicative of the deviation from planarity of the skeleton of the homologous series *p*-(*p*-ethoxyphenylazo)- phenyl alkanoates.

Acknowledgements

We thank the Director, Indian Institute of Science, Bangalore, for providing Infrared spectrometer facilities. Two of us (PKR and NCS) are grateful to the Council of Scientific and Industrial Research, New Delhi, for the award of Fellowships. JSP would like to thank University Grants Commission, India for a career award.

References

1. J. Shashidhara Parsad, *Acta Ciencia Indica.*, **1**, (4) 340 (1975).
2. J. Shashidhara Prasad, *Acta Cryst.*, 'B' **35**, 1404 (1979).
3. J. Shashidhara Prasad, *Acta Cryst.*, 'B' **35**, 1407 (1979).
4. J. Shashidhara Prasad, *Z. Kristallographie*, **147**, S-149 (1978).