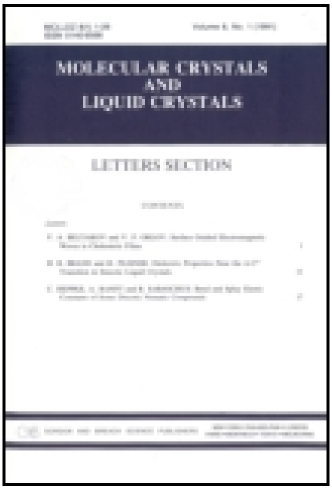
This article was downloaded by: [University Of Gujrat]
On: 11 December 2014, At: 13:33
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Theoretical Calculations on Hydroxybutyl 4-aroyloxybenzoates: Synthesis and Mesomorphic Properties of their H-bonded Complexes with Poly(4-vinylpyridine)

Khushi Muhammad[a], Muhammad Qaiser Fatmi[b] & Shahid Hameed[a]
[a] Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan
[b] Department of Biosciences, COMSATS Institute of Information Technology, Chak Shahzad, Islamabad, Pakistan
Published online: 27 May 2014.

To cite this article: Khushi Muhammad, Muhammad Qaiser Fatmi & Shahid Hameed (2014) Theoretical Calculations on Hydroxybutyl 4-aroyloxybenzoates: Synthesis and Mesomorphic Properties of their H-bonded Complexes with Poly(4-vinylpyridine), Molecular Crystals and Liquid Crystals, 593:1, 93-103, DOI: 10.1080/15421406.2013.867226

To link to this article: http://dx.doi.org/10.1080/15421406.2013.867226

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Mol. Cryst. Liq. Cryst., Vol. 593: pp. 93–103, 2014
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.867226

Theoretical Calculations on Hydroxybutyl 4-aroyloxybenzoates: Synthesis and Mesomorphic Properties of their H-bonded Complexes with Poly(4-vinylpyridine)

KHUSHI MUHAMMAD,[1] MUHAMMAD QAISER FATMI,[2]
AND SHAHID HAMEED[3,*]

[1]Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan
[2]Department of Biosciences, COMSATS Institute of Information Technology, Chak Shahzad, Islamabad, Pakistan
[3]Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan

Important parameters of hydroxybutyl 4-aroyloxybenzoate ligands were calculated and correlations were made between theoretical and experimental results. In addition, supramolecular side-chain liquid crystalline polymers of the ligands with poly(4-vinylpyridine) were synthesized. Hydrogen bond formation was ascertained by Fourier tranform infra-red spectroscopy. The stabilities of the complexes were determined by thermogravimetric analysis. The mesomorphic behavior was investigated using differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction analysis. Semiempirical study revealed that a ratio of ∼1.2 in the lengths of flexible and rigid parts of the molecules is the most favorable for a wider liquid crystal (LC) temperature range.

Keywords Nematic complexes; PM6 semiempirical calculations; poly(4-vinylpyridine); supramolecular

1. Introduction

Side chain liquid crystalline polymers (SCLCP) have been the field of immense research for the last 20 years owing to their use as optical data storage materials [1–3] and electro-optic light modulators [4]. These materials possess the property of film formation with characteristically oriented pendants and hence are used as orientation layers in ferroelectric liquid crystal displays [5]. These substances also find applications in nonlinear optics [6]. In gas chromatography and HPLC, these are used as stationary phases [7, 8].

These materials may be synthesized either by the polymerization of monomers bearing mesogenic groups [9, 10], or by linking LC ligands to the polymer chains [11–13]. The mesogenic ligands may be attached to the polymer backbone either through covalent bonds or noncovalent interactions including H-bonding, ionic, ion-dipolar [14] and halogen bonding [15]. Hydrogen-bonded SCLCPs synthesized so far involve imidazole [16, 17],

---

[*] Address correspondence to Shahid Hameed, Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan. E-mail: shameed@qau.edu.pk, shahidhameed@daad-alumni.de

stilbazole [14, 18], or bipyridine [19] as H-bond acceptors and carboxylic acids or alcohols as H-bond donors. The covalently bonded and supramolecular SCLCPs, both inherent the undesirable properties of higher densities and higher mesophase temperatures, particularly where the pendants have polar end groups.

A ligand having an ester group in conjugation with benzene rings has sufficient polarity due to its electron withdrawing mesomeric effect. This lateral polarity causes the molecules to arrange; a basic requirement for the induction of liquid crystallinity. Furthermore, some double bond character may be imparted due to delocalization of electron pair of alkoxy oxygen on one side of benzene ring to carbonyl group on the other side; thus bringing forth some rigidity in the structure.

In the present study, some parameters of hydroxybutyl 4-aroyloxybenzoates were calculated using semi-empirical method and the theoretical results were correlated with experimental observations. The H-bonded complexes of the ligands with poly(4-vinylpyridine) were prepared and studied for mesomorphic properties. The length of alkoxy end group was varied from 1 to 12 carbon atoms to explore its effects on phase transition temperatures and mesophase stabilities.

2. Experimental

2.1. Materials

Poly(4-vinylpyridine) was purchased from Aldrich Chemical Co. and used as such. Chloroform was supplied by Riedel-deHaën from which ethanol was removed by the standard procedure.

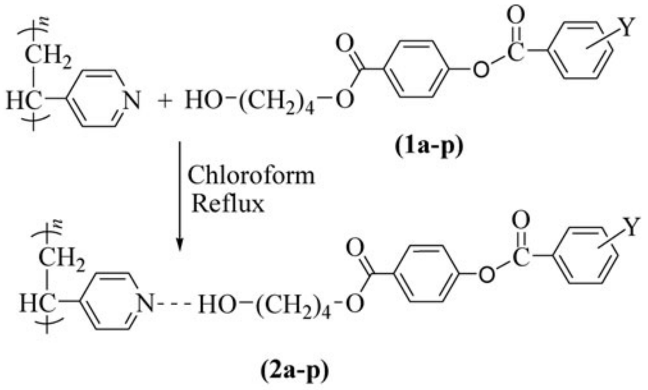
2.2. Characterization

The IR spectra were recorded using Thermo scientific Nicolet 6700 FT-IR spectrophotometer using ATR facility. Thermogravimetric analyses were performed using Mettler Toledo TGA 851e, and phase transition temperatures were determined using Metler Toledo DSC 823e. The LC textures were observed using a polarizing optical microscope (POM) (Olympus BH-2) fitted with a Linkam hot-stage (LK-600PM). All of the photomicrographs were taken under crossed polarizers. Wide-angle X-ray diffractograms (WAXD) were recorded on a Geigerflex D/Max-RB diffractometer. A rotating-anode generator (Cu Kα, 12 kW) was used as the X-ray source. The temperature was controlled by a hot-stage and the samples were protected using nitrogen during measurements.

2.3. Synthesis

The ligands **(1a–p)** were synthesized in a multistep sequence [20] and characterized through modern spectroscopic techniques. H-bonded complexes **(2a–p)** were prepared (Scheme 1) in two different polymer-ligand ratios of 1:0.7 and 1:1.

2.3.1. Synthesis of Complex 2a. For synthesis of complex with polymer ligand ratio of 1:0.7, poly(4-vinylpyridine) (2 mmol, 0.21 g) and ligand **1a** (1.4 mmol, 0.48 g) were dissolved in 10 mL ethanol-free chloroform. The mixture was refluxed for 30 min. Chloroform was removed under reduced pressure and the complex dried in a vacuum desiccator for 48 hr. The quantities of polymer and ligand were 0.21 g and 0.69 g, respectively, for equimolar (2 mmol) complex. IR ($\bar{\upsilon}$, cm^{-1}) 3250 (O—H str.), 2938 (sp^3 C—H str.), 1723(C=O str.),



a) Y = 4-OCH_3
b) Y = 4-OC_2H_5
c) Y = 4-OC_3H_7
d) Y = 4-OC_4H_9
e) Y = 4-$OCH_2CH(CH_3)_2$
f) Y = 4-OC_5H_{11}
g) Y = 4-$(CH_2)_2CH(CH_3)_2$
h) Y = 4-OC_6H_{13}
i) Y = 4-OC_8H_{17}
j) Y = 4-$OC_{10}H_{21}$
k) Y = 4-$OC_{11}H_{23}$
l) Y = 4-$OC_{12}H_{25}$
m) Y = 3-Cl
n) Y = 4-Cl
o) Y = 3-F
p) Y = 4-F

Scheme 1. Preparation of polymer complexes (**2a–p**).

1713 (C=O str.), 1603, 1511, 1455 (C=C arom. str.), 1260, 1224, 1219, 1158, 1062, 1018, 936, 881, 841, 758, 689.

2.3.2. Synthesis of Complex 2b. The complex **2b** was prepared following the same procedure as for **2a**. IR ($\bar{\upsilon}$, cm^{-1}) 3330 (O—H str.), 3069 (sp^2 C—H str.), 2934 (sp^3 C—H str.), 1726 (C=O str.), 1715 (C=O str.), 1602, 1508, 1475 (C=C arom. str.), 1414, 1392, 1309, 1251, 1203, 1158, 1112, 1059, 1040, 892, 848, 818, 761, 691, 664, 562.

2.3.3. Synthesis of Complex 2c. The method of preparation of complex **2c** was same as of **2a**. IR ($\bar{\upsilon}$, cm^{-1}) 3402 (O—H str.), 3074 (sp^2 C—H str.), 2934, 2872 (sp^3 C—H str.), 1726 (C=O str.), 1713 (C=O str.), 1601, 1508, 1464 (C=C arom. str.), 1414, 1255, 1215, 1159, 1118, 1064, 976, 894, 845, 760, 691, 664, 557.

2.3.4. Synthesis of Complex 2d. The complex **2d** was prepared in an analogous manner to complex **2a**. IR ($\bar{\upsilon}$, cm^{-1}) 3254 (O—H str.), 2959, 2936, 2872 (sp^3 C—H str.), 1720 (C=O str.), 1602, 1510, 1466 (C=C arom. str.), 1414, 1379, 1252, 1204, 1160, 1115, 1061, 945, 894, 845, 820, 760, 690, 663, 566.

2.3.5. Synthesis of Complex 2e. The complex **2e** was prepared by the same method as followed for complex **2a**. IR ($\bar{\upsilon}$, cm^{-1}) 3249 (O—H str.), 2952, 2862 (sp^3 C—H str.), 1716 (C=O str.), 1605, 1510, 1472 (C=C arom. str.), 1414, 1263, 1199, 1162, 1100, 1062, 1015, 877, 842, 819, 762, 690, 669.

2.3.6. Synthesis of Complex 2f. The complex **2f** was prepared following the same procedure as described for **2a**. IR ($\bar{v}$, cm^{-1}) 3259 (O—H str.), 2952, 2934, 2856 (sp^3 C—H str.), 1723 (C=O str.), 1704 (C=O str.), 1601, 1510, 1465 (C=C arom. str.), 1414, 1306, 1269, 1242, 1203, 1159, 1118, 1058, 1006, 947, 895, 844, 820, 760, 690, 663, 563.

2.3.7. Synthesis of Complex 2g. The complex **2g** was prepared by the same method as for **2a**. IR ($\bar{v}$, cm^{-1}) 3287 (O—H str.), 2954, 2875 (sp^3 C—H str.), 1732 (C=O str.), 1712 (C=O str.), 1601, 1513, 1465 (C=C arom. str.), 1415, 1260, 1205, 1163, 1112, 1057, 1006, 886, 845, 758, 688, 665, 569.

2.3.8. Synthesis of Complex 2h. The method for synthesis of complex **2h** was same as for **2a**. IR ($\bar{v}$, cm^{-1}) 3317 (O—H str.), 2954, 2927, 2869 (sp^3 C—H str.), 1724 (C=O str.), 1711 (C=O str.), 1603, 1510, 1468 (C=C arom. str.), 1415, 1252, 1205, 1160, 1119, 1058, 1007, 893, 842, 819, 760, 691, 666, 563.

2.3.9. Synthesis of Complex 2i. The complex **2i** was prepared by the same method as for **2a**. IR ($\bar{v}$, cm^{-1}) 3304 (O—H str.), 2922, 2851 (sp^3 C—H str.), 1732 (C=O str.), 1716 (C=O str.), 1602, 1513, 1470 (C=C arom. str.), 1414, 1316, 1260, 1206, 1165, 1120, 1062, 1016, 888, 848, 816, 758, 684, 669, 562.

2.3.10. Synthesis of Complex 2j. The complex **2j** was prepared following the same procedure as for **2a**. IR ($\bar{v}$, cm^{-1}) 3337 (O—H str.), 2919, 2851 (sp^3 C—H str.), 1729 (C=O str.), 1716 (C=O str.), 1602, 1512, 1470 (C=C arom. str.), 1414, 1262, 1209, 1165, 1117, 1058, 1016, 885, 820, 761, 689, 667, 561.

2.3.11. Synthesis of Complex 2k. The method of preparation of complex 2k was analogous to that of **2a**. IR ($\bar{v}$, cm^{-1}) 3361 (O—H str.), 2917, 2851 (sp^3 C—H str.), 1728 (C=O str.), 1709 (C=O str.), 1603, 1510, 1469 (C=C arom. str.), 1415, 1259, 1215, 1160, 1118, 1058, 1009, 954, 891, 845, 760, 692, 667, 568.

2.3.12. Synthesis of Complex 2l. The complex **2l** was prepared following the procedure as described for **2a**. IR ($\bar{v}$, cm^{-1}) 3375 (O—H str.), 2955, 2916, 2848 (sp^3 C—H str.), 1726 (C=O str.), 1712 (C=O str.), 1602, 1508, 1469 (C=C arom. str.), 1416, 1334, 1279, 1248, 1212, 1158, 1119, 1077, 1035, 1009, 953, 892, 843, 760, 692, 666, 575.

2.3.13. Synthesis of Complex 2m. The complex **2m** was prepared following the same procedure as for **2a**. IR ($\bar{v}$, cm^{-1}) 3403 (O—H str.), 3071(sp^2 C—H str.), 2926, 2867 (sp^3 C—H str.), 1730 (C=O str.), 1712 (C=O str.), 1604, 1503, 1477 (C=C arom. str.), 1414, 1274, 1217, 1158, 1120, 1058, 1014, 953, 895, 807, 765, 738, 665, 549.

2.3.14. Synthesis of Complex 2n. The complex **2n** was prepared following the same procedure as for **2a**. IR ($\bar{v}$, cm^{-1}) 3390 (O—H str.), 2967, 2927, 2824 (sp^3 C—H str.), 1731 (C=O str.), 1711 (C=O str.), 1590, 1505, 1485 (C=C arom. str.), 1400, 1367, 1260, 1214, 1158, 1118, 1092, 1058, 1014, 951, 889, 852, 752, 682, 536.

2.3.15. Synthesis of Complex 2o. The complex **2o** was prepared following the procedure as described for **2a**. IR ($\bar{v}$, cm^{-1}) 3383 (O—H str.), 3070 (sp^2 C—H str.), 2927, 2874, 2838 (sp^3 C—H str.), 1733 (C=O str.), 1714 (C=O str.), 1593, 1507, 1483 (C=C arom. str.), 1416, 1269, 1220, 1159, 1119, 1060, 1012, 955, 919, 879, 821, 744670, 559.

2.3.16. Synthesis of Complex 2p. The method of synthesis of complex **2p** was same as for **2a**. IR ($\bar{\upsilon}$, cm^{-1}) 3392 (O—H str.), 2926, 2882, 2825 (sp^3 C—H str.), 1733 (C=O str.), 1717 (C=O str.), 1597, 1507, 1480 (C=C arom. str.), 1414, 1365, 1272, 1229, 1212, 1160, 1119, 1094, 1060, 1013, 955, 892, 853, 798, 759, 683, 656, 510.

3. Results and Discussion

3.1. Synthesis

The formation of H–bond between poly(4-vinylpyridine) and 4-hydroxybutyl 4-(aroyloxy)benzoates was ascertained in IR spectra by a shift in the absorption of hydroxyl group. In all the complexes, the O—H absorptions were shifted to lower wave number by 30 to 55 cm^{-1} when compared to the ligand itself. This may be attributed to the weakening of O—H bond due to the involvement of hydrogen atom in H-bonding with N-atom of poly(4-vinylpyridine). The IR absorptions due to O—H stretching vibrations in ligands and complexes are given in Table 1. The other groups in the complexes show no appreciable change in their absorption maxima.

3.2. Thermal Stabilities

Thermal stabilities of the complexes were determined by thermogravimetric analysis and the data are given in Table 2. Thermograms for all the complexes were single stepped involving 82% to 98% decomposition in the temperature range of 437–476 °C. The thermal stability of complexes synthesized from straight chain ligands increased with increase in the length of alkoxy group up to six carbon atoms (**2h**) and then decreased. The complexes with branched alkoxy (**2e and 2g**) and halogen substituents (**2m--p**) were found less stable

Table 1. Comparison of IR absorptions of O—H in ligands and complexes

Complex	O—H str. (Ligand)	O—H str. (Complex)	Shift in abs.max.
2a	3297	3250	47
2b	3370	3330	40
2c	3437	3402	35
2d	3285	3254	31
2e	3281	3249	32
2f	3296	3259	37
2g	3327	3287	40
2h	3363	3317	46
2i	3334	3304	30
2j	3391	3337	54
2k	3391	3361	30
2l	3430	3375	55
2m	3435	3403	32
2n	3427	3383	44
2o	3429	3390	39
2p	3434	3392	42

Table 2. Thermogravimetric data of synthesized complexes (representative data)

Complex	$T_1{}^a$ (°C)	$T_2{}^b$ (°C)	Extent of decomp.(%)
2b	217	476	94
2d	226	461	87
2f	232	467	88
2h	239	475	90
2i	233	469	88
2l	187	453	82
2m	207	452	93
2p	206	461	98

[a] Initial decomposition temperature.
[b] Temperature of maximum decomposition.

with initial decomposition temperatures comparable with those having longer alkoxy chain (> C_{10}).

3.3. Mesomorphic Properties

The mesophases and their temperature ranges were determined by differential scanning calorimetry and polarizing optical microscopy. Better results were obtained for complexes with polymer ligand ratio of 1:0.7 as compared to those with 1:1 ratio, where the two phases remained separated even after long annealing periods. Complexes with straight alkoxy chains containing 3–8 carbon atoms exhibited a large exothermic peak for melting and another smaller peak which was assigned to LC-isotropic phase transition. Complexes having branched alkoxy groups or halogens showed a single peak (melting transition) in their DSC thermographs and, therefore, were nonmesomorphic. Figure 1 shows DSC traces of representative complexes while the mesophase temperature ranges are presented in Table 3.

The liquid crystalline phase was identified as nematic from the characteristic granular textures observed under the optical polarizing microscope for homogenously aligned samples [21]. The textures developed for ligand **1f** and some of the complexes are depicted in Fig. 2. The focal-conic fan texture of the ligand is shown to indicate its SmA nature for comparison purpose (Fig. 2a). H-bonded complex formation resulted in changing the

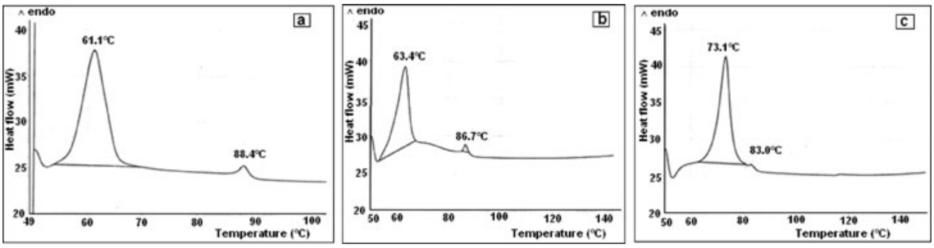


Figure 1. DSC thermographs (first heating scan, heating rate = 10 °C/min) of (a) **2d**, (b) **2f**, and (c) **2i**.

Table 3. Mesophase temperature ranges of complexes

Complex	Mesophase temp. ranges/°C
2a, 2b	Nonmesomorphic
2c	Nematic, 63.0–85.5
2d	Nematic, 61.1–88.4
2e	Nonmesomorphic
2f	Nematic, 63.4–86.7
2g	Nonmesomorphic
2h	Nematic, 73.8–87.4
2i	Nematic, 73.1–83.0
2j-2p	Nonmesomorphic

smectic nature of ligands to nematic, possibly due to atacticity of the polymer main chain which restricts close-packing of pendent mesogenic groups.

The mesophase type was confirmed by X-ray diffraction studies. The polymers with straight alkoxy chain having 3–8 carbon atoms exhibited XRD pattern consisting of a single diffused halo in wide-angle region ($2\theta = 20$–21°). No sharp peaks in either small- or large-angle regions were observed. This result confirms that the polymers show only the nematic phase. Figure 3 shows a representative X-ray diffractogram.

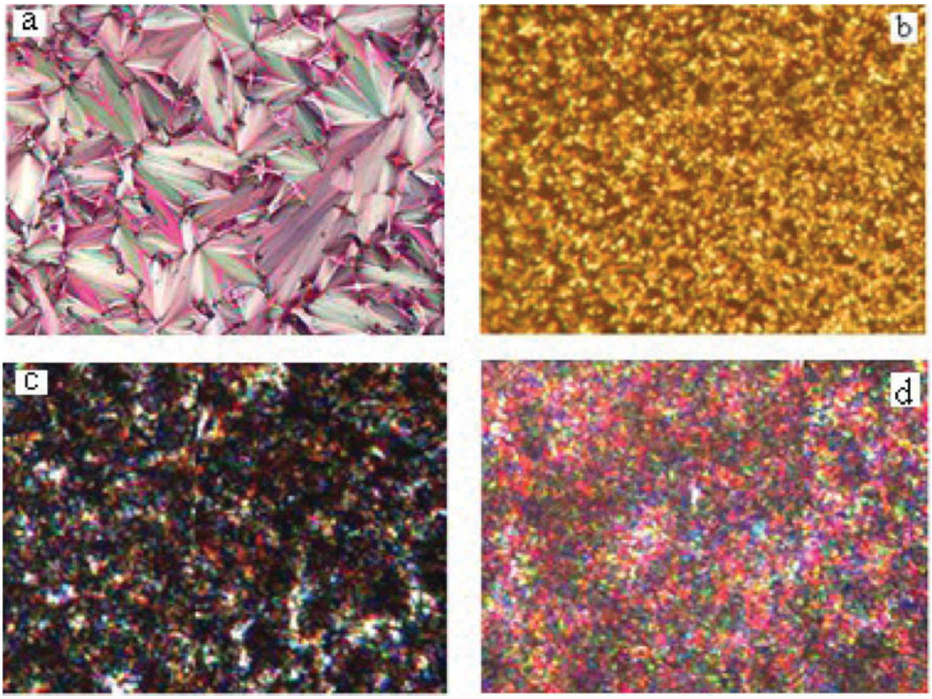


Figure 2. Optical polarizing micrographs of compounds: (a) **1f** taken at 85 °C after annealing for 5 min at 100 °C, (b) **2d** taken at 80 °C after annealing for 5 min. at 110 °C, (c) **2f** taken at 80 °C after annealing for 5 min at 100 °C and (d) **2h** taken at 83 °C after annealing for 5 min at 100 °C.

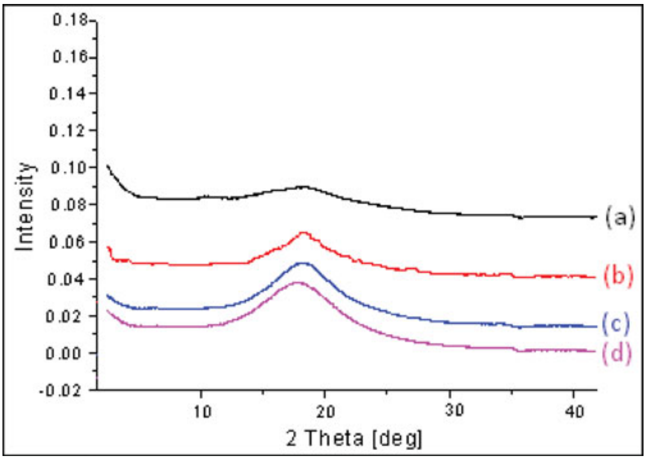


Figure 3. XRD curves for a representative complex **2h** (a) 26 °C (b) 75 °C (c) 80 °C (d) 87 °C.

3.4. Semiempirical Calculations on Ligands

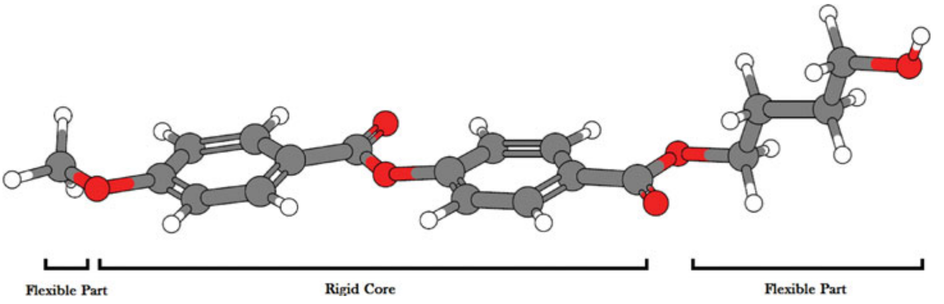
Evaluation of structural and physical properties of compounds is critically important to understand the liquid crystal behavior for practical applications. A semi-empirical method available in molecular orbital package (MOPAC2009) was employed to optimize the geometry of ligands **1a–1p** at parameterization method 6 (PM6) level of theory. Several properties of ligands including the length of flexible chains (F) and rigid core (R), ratio of flexible to rigid parts (F:R ratio), mean polarizability, dipole moment, enthalpy of formation, energy levels of frontier molecular orbitals (E_{HOMO} and E_{LUMO}), and their difference ($\Delta E = E_{HOMO} - E_{LUMO}$) were calculated and the values are given in Table 4.

The size of flexible part relative to the rigid core is an important factor for the induction of liquid crystallinity. The lengths of hydroxybutyl and alkoxy groups were added to get the total length of flexible component. The rigid core length was defined from oxygen atom of alkoxy group to the carboxyl carbon of ester group, which is attached to the hydroxybutyl moiety, as shown in the image of Table 4. The size of the rigid core was measured to be 11.81Å. The F:R ratio varied from 0.56 in halogen containing ligands (**1m–p**) to 1.83 in dodecyloxy substituted ligand **(1l)**. From these calculations and experimental observations[20], it is inferred that F:R ratio ranging from 0.76 to 1.62 exhibits mesomorphism in these compounds. The highest liquid crystal temperature range as observed for compound **1h** corresponds to F:R ratio of 1.19. The ligands **1a** and **1m–p** with too low F/R values of 0.68 and 0.56, respectively, showed no LC behavior.

Polarizability of the molecule is a parameter which affects the optical anisotropy (birefringence) of a macroscopic material [22]. The calculated polarizability values increase with increase in length of alkoxy group with an average increment of $1.7A^3$ per CH_2 group. The polarizability values for halogen-substituted ligands **(1m–p)** are much smaller which is due to electron withdrawing inductive effect of fluorine and chlorine atoms.

Dielectric anisotropy of liquid crystalline compounds is the key material parameter which determines the operating voltage of LCDs and is based on dipole moment of molecules [23]. The calculated dipole moment value of 7.0 D for ligand **1a** is extraordinarily small. The values for the rest molecules generally decrease with increasing alkoxy chain. The dipole moment values for *meta*-haloesters are higher than those of *para*-substituted ones.

Table 4. Structural and physical properties of ligands **1a–1p** using PM6 semiempirical method. The definition of rigid and flexible parts is given in the top image. Red, grey, and white colors represent oxygen, carbon, and hydrogen atoms, respectively



Molecule	Flexible core length (F) (Å)	Rigid core length (R) (Å)	F:R	$\Delta E = E_{LUMO} - E_{HOMO}$(eV)	ΔH_f (kcal/mol)	Mean polarizability (A^3)	Dipole moment (Debye)
1a	8.04	11.81	0.68	8.897	−220.65939	28.67	7.00
1b	8.97	11.81	0.76	8.434	−238.00611	41.67	10.09
1c	10.35	11.81	0.88	8.456	−243.65364	43.47	9.56
1d	11.49	11.81	0.97	8.460	−248.63964	45.40	9.53
1e	10.31	11.81	0.87	8.420	−248.44161	45.51	10.44
1f	12.84	11.81	1.09	8.455	−253.79505	47.28	9.61
1g	11.46	11.81	0.97	8.454	−254.82868	47.25	9.75
1h	14.03	11.81	1.19	8.452	−258.89600	49.16	9.40
1i	16.56	11.81	1.40	8.453	−270.96812	52.90	9.28
1j	19.09	11.81	1.62	8.450	−281.33630	56.60	9.32
1k	20.40	11.81	1.73	8.449	−286.52054	58.44	9.33
1l	21.56	11.81	1.83	8.456	−291.53618	60.27	9.30
1m	6.63	11.81	0.56	8.685	−195.85275	37.96	6.43
1n	6.63	11.81	0.56	8.685	−196.76077	38.23	5.44
1o	6.63	11.81	0.56	8.761	−233.41611	35.99	6.64
1p	6.63	11.81	0.56	8.777	−235.21885	36.02	5.75

Enthalpy of formation (ΔH_f) is viscosity controlling factor of material which affects switching times and power consumption of displays [24]. The calculated enthalpy values show a regular increase with increasing alkoxy chain length. The chloro compounds **1(m,n)** have smaller ΔH_f values than fluoro derivatives **1(o,p)** and hence predicted to be less viscous than fluoro and alkoxy compounds.

The UV/visible absorption and ionization energies of molecules depend upon the energy difference between their frontier molecular orbitals ($\Delta E = E_{HOMO} - E_{LUMO}$); the smaller the value of ΔE, the better photo-responsive is the molecule. Since the calculated ΔE values for alkoxy compounds are almost same, therefore, the alkyl chain length has no effect on the energies of HOMO and LUMO. The values for methoxy and halo compounds are slightly higher.

4. Conclusions

Theoretical calculations of some parameters which influence LC properties were performed on hydroxybutyl 4-aroyloxybenzoate ligands. The theoretical and experimental results revealed that these compounds show LC behavior only when their rigid to soft part length ratio lies in the range of 0.76–1.62. The F:R ratio of 1.19 was found to be the most favorable for wider LC temperature ranges. The thermal and mesomorphic properties of complexes of the ligands with poly(4-vinylpyridine) were also studied. Length of the alkoxy group was found to have a profound effect on the thermal stabilities of alkoxy substituted complexes. The complex **2h** with hexyloxy group was found the most stable of all the complexes, showing first sign of degradation at 239°C. Liquid crystallinity was exhibited by complexes with straight alkoxy group having 3–8 carbon atoms. Maximum LC temperature range was exhibited by the complex **2d**. All the mesomorphic complexes exhibited nematic phase as indicated by the POM textures and confirmed by XRD patterns. The complexes with longer alkoxy groups and halogen substituents were nonmesomorphic as evidenced by DSC thermograms.

Acknowledgments

This work was financially supported by Higher Education Commission of Pakistan through a Ph.D. fellowship to Khushi Muhammad under "Development of S & T Manpower Through Indigenous Ph.D. (300 Scholars)."

References

[1] Bobrovsky, A., Shibaev, V., & Wendorff, J. (2007). *Liq. Cryst.*, *34*, 1–7.
[2] Hvilsted, S., Andruzzi, F., Kulinna, C., Seisler, H. W., & Ramanujam, P. S. (1995). *Macromolecules*, *28*, 2172–2183.
[3] Han, Y. K., & Ko, B. S. (2003). *Opt. Mater.*, *21*, 621–625.
[4] Collings, P. J., & Hird, M. (1997). *Introduction to Liquid Crystals-Chemistry and Physics*, Taylor & Francis: London, UK.
[5] Jin, S.-H., & Kang, S. W. (1998). Patent US Appl. No. 08/465432.
[6] Demartino, R. N., Yoon, H., Stamatoff, J. B., & Buckley, A. (1989). Patent US Appl. No. 07/127088.
[7] Fu, R., Jing, P., Gu, J., Huang, Z., & Chen, Y. (1993). *Anal. Chem.*, *65*, 2141–2144.
[8] Saito, Y. *et al.* (1994). *Chromatographia*, *38*, 295–303.
[9] Huskic, M., & Zigon, M. (2006). *Liq. Cryst.*, *33*, 883–890.
[10] Fujii, N., Kawase, Y., Michinobu, T., & Shigehara, K. (2007). *J. Photopolym. Sci. Tech.*, *20*, 17–18.
[11] Achten, R. *et al.* (2006). *Liq. Cryst.*, *33*, 681–688.
[12] Meng, F. B., Lian, J., Zhang, B. Y., & Sun, Y. (2008). *Eur. Polym. J.*, *44*, 504–513.
[13] Akhtar, T., Paracha, R. N., Hameed, S., Rama, N. H., & Riaz, M. (2007). *Polym-Korea*, *31*, 93–97.
[14] Kato, T., Nakano, M., Moteki, T., Uryu, T., & Ujiie, S. (1995). *Macromolecules*, *28*, 8875–8876.
[15] Nguyen, H. L., Horton, P. N., Hursthouse, M. B., Legon, A. C., & Bruce, D. W. (2004). *J. Am. Chem. Soc.*, *126*, 16–17.
[16] Chao, C.-Y., Li, X., & Ober, C. K. (2004). *Pure Appl. Chem.*, *76*, 1337–1343.
[17] Chao, C.-Y., Li, X., Ober, C. K., Osuji, C., & Thomas, E. L. (2004). *Adv. Funct. Mater.*, *4*, 364–370.
[18] Kato, T., Kihara, H., Uryu, T., Fujishima, A., & Frechet, J. M. J. (1992). *Macromolecules*, *25*, 6836–6841.

[19] Racles, C., & Cazacu, M. (2008). *J. Appl. Polym. Sci.*, *109*, 4000–4009.

[20] Muhammad, K., Hameed, S., Tan, J., & Liu, R. (2011). *Liq. Cryst.*, *38*, 333–348.

[21] Kumar, S. (2001). *Liquid Crystals: Experimental Study of Physical Properties and Phase Transitions*, Cambridge University Press: Cambridge, UK.

[22] Goulding, M. J., Greenfield, S., Coates, D., & Clemitson, R. (1993). *Liq. Cryst.*, *14*, 1397–1408.

[23] Zang, S.-H., Ren, R., Li, X.-M., Li, Q., Song, X.-Y., & Wei, Q.-L. (2006). *Liq. Cryst.*, *33*, 795–801.

[24] Pauluth, D., & Tarumi, K. (2005). *Journal of the SID*, *13/8*, 693–701.