

Synthesis and Liquid Crystal Properties of Alkyloxy-4,4'-biphenyl Esters

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Abstract— A number of biphenyl ester have been synthesized and characterized by spectroscopic analysis. The structures of the esters were varied by attaching different number of alkoxy chains of different lengths. The compounds were examined for their mesogenic behavior under polarizing microscope fitted with a hot and cold stage. The single chain esters exhibit the liquid crystallinity but the double and triple chain analogues do not show liquid crystallinity.

Index Terms— Cluster, Enantiomeric excess, Chiral, Catalyst

1 INTRODUCTION

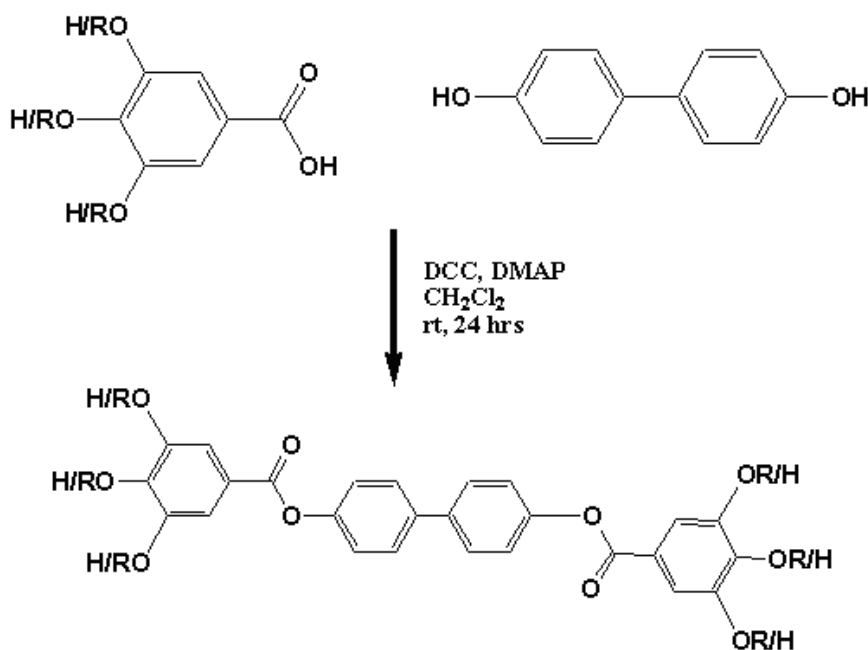
L IQUID crystals are technologically important class of compounds which are being used in electro-optical display systems. In general liquid crystalline compounds are elongated in nature and possess anisotropy of polarity/polarisability¹. However, liquid crystal behavior of organic compounds is very sensitive to its molecular architecture. A slight change in molecular geometry may bring considerable change in its liquid crystal property. Many structural moiety are used to construct liquid crystalline materials. Esters containing benzene or biphenyl nuclei are seen to be very suitable candidate to construct liquid

crystalline molecules¹⁻⁴. Here, in continuation of our research on liquid crystalline materials^{5,6}, we report our attempt to generate liquid crystals based on biphenyl nuclei having two ester linkage.

2 RESULTS & DISCUSSION

Synthesis of the Compounds:

The compounds were synthesized by following reaction scheme shown below –



Scheme 1: Synthetic route to alkyloxyphenyl -4,4'-biphenyl esters

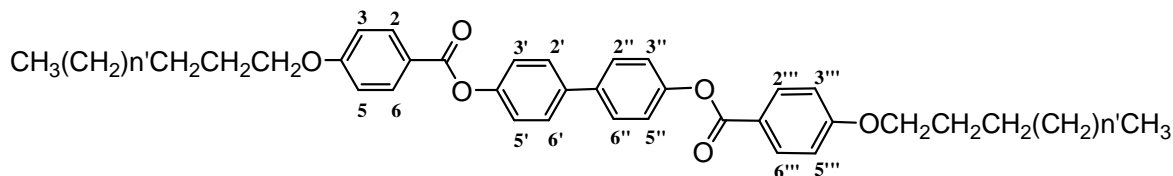
Reaction of alkyloxy benzoic acids with 4,4'-biphenol in presence of dicyclohexylcarbodiimide (DCC), dimethylaminopyridine (DMAP) in dichloromethane at room temperature for 24 hours afforded the esters as white to

off-white solid which were then recrystallised from methanol to get the pure esters. The synthesized compounds were characterized by spectroscopic analysis as described below.

Single Chain Esters

The IR spectra of the single chain esters show absorption band at 3080-3030 cm^{-1} due to aromatic $\nu_{\text{C-H}}$, at 2955-2920

and 2898-2849 cm^{-1} due to aliphatic $\nu_{\text{C-H}}$, strong absorption at 1728 cm^{-1} is a clear identification of carbonyl (ester) $\nu_{\text{C=O}}$ group; absorption band at 1595 and 1510-1452 cm^{-1} due to aromatic $\nu_{\text{C=C}}$, at 1260-1201 and 1069-1011 cm^{-1} may be assigned $\nu_{\text{C-O}}$ absorption.

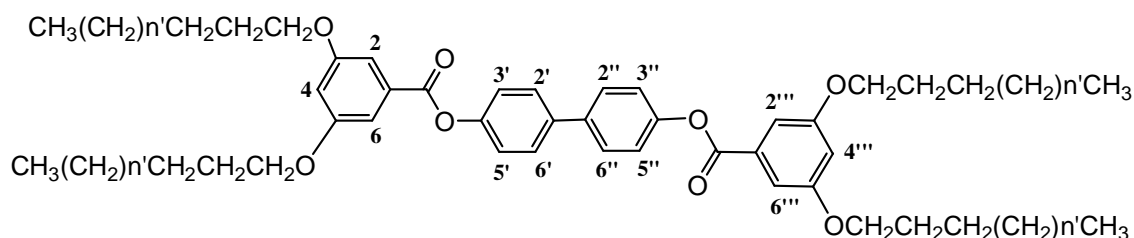


The ^1H NMR spectrums of the single chain compounds showed resonance for the protons of the aromatic ring at δ 6.99 (4H, d, $J=9.0\text{Hz}$) for the ($3''''/5'''' + 3/5$) protons, at δ 8.17 (4H, d, $J=9.0\text{Hz}$) for the ($2''''/6'''' + 2/6$) protons, at δ 7.29 (4H, d, $J=8.6\text{Hz}$) for the ($3''/5'' + 3'/5'$) protons, at δ 7.64 (4H, d, $J=8.6\text{Hz}$) for the ($2''/6'' + 2'/6'$) protons. The alkyloxy chain protons gave five distinct resonance signals: around δ 4.07 for α protons ($-\text{OCH}_2\text{CH}_2-$), δ 1.83 for β protons ($-\text{OCH}_2\text{CH}_2\text{CH}_2-$), δ 1.49 for γ protons ($-\text{OCH}_2\text{CH}_2\text{CH}_2-$), δ 0.91 for terminal CH_3 protons and δ 1.39-1.27 for rest of the aliphatic chain protons.

$\text{OCH}_2\text{CH}_2\text{CH}_2-$), δ 0.91 for terminal CH_3 protons and δ 1.39-1.27 for rest of the aliphatic chain protons.

Double Chain (3,5-) Esters

The IR spectra of the single chain esters showed absorption band at 2918 and 2850 cm^{-1} due to aliphatic $\nu_{\text{C-H}}$; strong absorption at 1739 cm^{-1} is a clear identification of carbonyl (ester) $\nu_{\text{C=O}}$ group; absorption band at 1595 and 1468 cm^{-1} due to aromatic $\nu_{\text{C=C}}$, at 1207-1171 and 1028-1012 cm^{-1} may be assigned $\nu_{\text{C-O}}$ absorption.



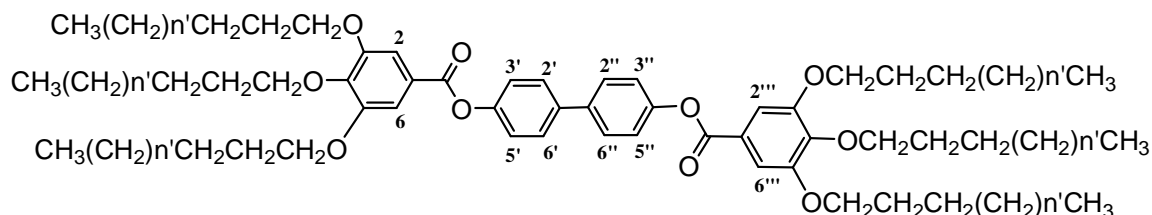
The ^1H NMR spectrums of the double chain compounds showed resonance for the protons of the aromatic ring at δ 7.34 (4H, $J=2.3\text{Hz}$) for the ($2''''/6'''' + 2/6$) protons; at δ 7.29 (4H, d, $J=8.6\text{Hz}$) for the ($3''/5'' + 3'/5'$) protons; at δ 7.64 (4H, d, $J=8.6\text{Hz}$) for the ($2''/6'' + 2'/6'$) protons; at δ 6.73 (2H, $J=2.2\text{Hz}$) for the ($4'''' + 4$) protons.

The alkyloxy chain protons gave five distinct resonance signals: around δ 4.03 for α protons ($-\text{OCH}_2\text{CH}_2-$), δ 1.82 for β protons ($-\text{OCH}_2\text{CH}_2\text{CH}_2-$), δ 1.49 for γ protons ($-\text{OCH}_2\text{CH}_2\text{CH}_2-$), δ 0.90 for terminal CH_3 protons and δ

1.36-1.26 for rest of the aliphatic chain protons.

Triple Chain (3,4,5-) Esters

The IR spectra of the triple chain esters showed absorptions band at 2952-2917 cm^{-1} and 2850 cm^{-1} due to aliphatic $\nu_{\text{C-H}}$; strong absorption at 1735 cm^{-1} is a clear identification of carbonyl (ester) $\nu_{\text{C=O}}$ group; absorption band at 1594 and 1585-1433 cm^{-1} due to aromatic $\nu_{\text{C=C}}$ stretching, at 1229-1199 and 1096 cm^{-1} may be assigned $\nu_{\text{C-O}}$ absorption.



The ^1H NMR spectrums of the triple chain compounds showed resonance for the protons of the aromatic ring at δ 7.43 (4H, s) for the ($2''/6''' + 2'/6$) protons, at δ 7.28 (4H, d, $J=8.5\text{Hz}$) for the ($3''/5'' + 3'/5'$) protons, at δ 7.64 (4H, d, $J=8.5\text{Hz}$) for the ($2''/6'' + 2'/6'$). The alkyloxy chain protons gave five distinct resonance signals: around δ 4.05 for α protons ($-\text{OCH}_2\text{CH}_2-$), δ 1.85 for β protons ($-\text{OCH}_2\text{CH}_2\text{CH}_2-$), δ 1.5 for γ protons ($-\text{OCH}_2\text{CH}_2\text{CH}_2-$), δ 0.9 for terminal CH_3 protons and δ 1.4-1.28 for rest of the aliphatic chain protons.

Table 1: Thermal behaviour of the alkyloxy 4,4'-biphenyl esters.

| R | Thermal behavior |
|----------------------------|---|
| Single Chain Esters | |
| C_6 | $\text{Cr} \xrightleftharpoons[90.4\text{ }^\circ\text{C}]{?} \text{LC} \xrightleftharpoons[154.7\text{ }^\circ\text{C}]{167.2\text{ }^\circ\text{C}} \text{IL}$ |
| C_8 | $\text{Cr} \xrightleftharpoons[128.5\text{ }^\circ\text{C}]{134.3\text{ }^\circ\text{C}} \text{LC} \xrightleftharpoons[225.4\text{ }^\circ\text{C}]{285.2\text{ }^\circ\text{C}} \text{IL}$ |
| C_{10} | $\text{Cr} \xrightleftharpoons[142.3\text{ }^\circ\text{C}]{168.6\text{ }^\circ\text{C}} \text{LC} \xrightleftharpoons[234.9\text{ }^\circ\text{C}]{274.7\text{ }^\circ\text{C}} \text{IL}$ |
| C_{12} | $\text{Cr} \xrightleftharpoons[117.4\text{ }^\circ\text{C}]{134.3\text{ }^\circ\text{C}} \text{LC} \xrightleftharpoons[140.2\text{ }^\circ\text{C}]{203.8\text{ }^\circ\text{C}} \text{IL}$ |
| Double Chain Esters | |
| C_{16} | $\text{Cr} \xrightleftharpoons[52.2\text{ }^\circ\text{C}]{88.9\text{ }^\circ\text{C}} \text{IL}$ |
| C_{18} | $\text{Cr} \xrightleftharpoons[55.2\text{ }^\circ\text{C}]{84.6\text{ }^\circ\text{C}} \text{IL}$ |
| Triple Chain Esters | |
| C_{10} | $\text{Cr} \xrightleftharpoons[59.2\text{ }^\circ\text{C}]{76.4\text{ }^\circ\text{C}} \text{IL}$ |
| C_{14} | $\text{Cr} \xrightleftharpoons[51.3\text{ }^\circ\text{C}]{67.8\text{ }^\circ\text{C}} \text{IL}$ |
| C_{16} | $\text{Cr} \xrightleftharpoons[54.9\text{ }^\circ\text{C}]{74.2\text{ }^\circ\text{C}} \text{IL}$ |
| C_{18} | $\text{Cr} \xrightleftharpoons[54.7\text{ }^\circ\text{C}]{68.3\text{ }^\circ\text{C}} \text{IL}$ |

Table 1: Transition temperature of Compounds as observed under polarizing microscope.

Liquid Crystal Behaviour

The synthesized compounds were examined under optical microscope for their liquid crystal properties and the results are collected in table 1. It shows that presence of an single alkyloxy group at the 4-position of the ester *ie* the single chain esters does support the formation of liq-

uid crystal phase while the presence of two (at the 3,5-position) alkyloxy groups or three (at the 3,5-position) alkyloxy groups does not support the mesogenic properties of the compounds. Molecular shape and anisotropy in molecular interactions *ie*. polarity/polarisibility, has significant influence on the liquid crystal behavior of a com-

ound. The single chain derivatives having only one alkoxy chain results relatively linear rod shape molecular structure (figure 2) and thus exhibit liquid crystal phase. Introduction of two or three alkoxy chains considerably

increase the width of the molecules and thus prevents the molecules to come in close contact to form an ordered fluid phase.

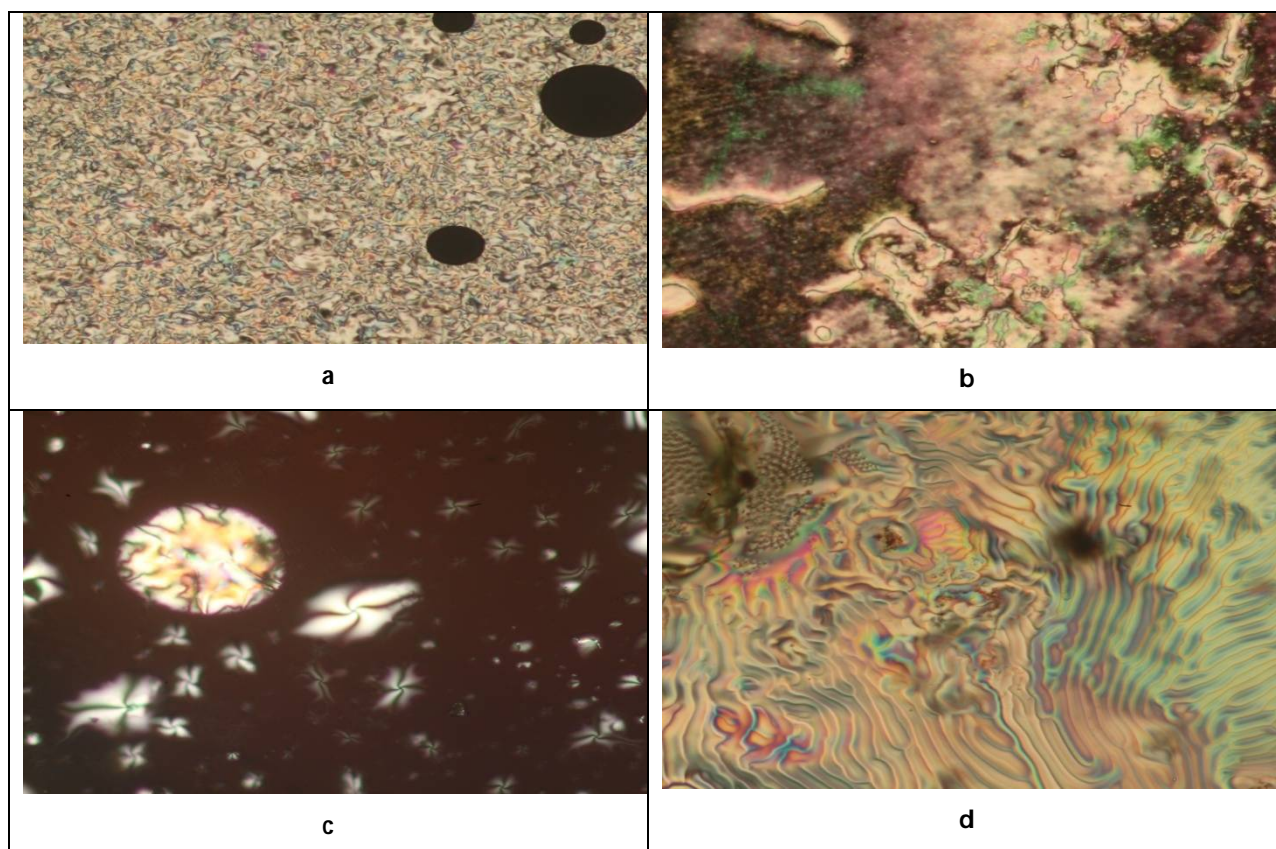


Fig. 1: Texture of the single chain alkoxy-4,4'-biphenyl esters (100 x) observed in the cooling cycle (a) C-6 ester at 145°C (b) C-8 ester at 218°C, (c) C-10 ester at 227°C and (d) C-12 ester at 125°C Fig. 4.1-4.4 Optical Texture.

Experimental

Materials:

Ethyl 4-hydroxybenzoate, methyl 3,5-dihydroxybenzoate, ethyl 3,4,5- trihydroxybenzoate were used as purchased so as the other conventional reagents. For analytical thin layer chromatography (TLC) pre-coated silica gel aluminium plate (silica gel 60 F₂₅₄, Merck) and for separation column chromatography (silica gel Merck 60, 230-400mesh) were used. Ethanol, methanol and butanol were distilled over anhydrous calcium oxide. Dichloromethane was distilled over anhydrous P₂O₅.

Technique:

¹H NMR spectra were recorded on Bruker 500MHz Spectrophotometer from chloroform-D solution using TMS as internal standard. IR spectra were recorded on Shimadzu Spectrophotometer with KBr pellets. Olympus CX 40 Microscope (upgraded for polarizing microscopy) fitted with INSTEC Hot and Cold stage HCS 402 and computer operated temperature controller INSTEC STC 200 was used to identify the various mesophases. MOPAC energy mini-

mized molecular structure was generated by Chem 3D software.

4-n-hexyloxy-4,4'-biphenyl Ester

Yield: 66%

IR (KBr): ν cm⁻¹ 2950 (s), 2929(m), 2850, 1727 (s), 1605(m), 1576(m), 1509(m), 1492(m), 1469(m), 1419(w), 1274(m), 1257(m), 1202(s), 1165(s), 1072(m), 1037(w), 1004(m), 881(w), 846(w), 764(w).

¹H NMR(CDCl₃) δ ppm: δ 6.98 (4H,d, J= 9.0Hz), δ 8.17 (4H, d, J= 9.0Hz), δ 7.29 (4H, d, J= 8.6Hz), δ 7.68 (4H, d, J= 8.6Hz), δ 4.05, δ 1.85, δ 1.49, δ 0.93 δ 1.37-1.33.

4-n-octyloxy-4,4'-biphenyl Ester

Yield: 65%

IR (KBr): ν cm⁻¹ 2951 (s), 2920(m), 2872 (s), 2853(s), 1730 (s), 1609(m), 1510(m), 1494(m), 1474(w), 1466(w), 1292(s), 1257(m), 1216(m), 1175(m), 1167(W), 1088(m), 1005(m), 879(m), 841(m), 760(m).

¹H NMR(CDCl₃) δ ppm: δ 6.99 (4H,d, J= 9.0Hz), δ 8.18 (4H, d, J= 9.0Hz), δ 7.3 (4H, d, J= 8.6Hz), δ 7.64 (4H, d, J= 8.6Hz), δ 4.07, δ 1.83, δ 1.49, δ 0. δ 1.39-1.27.

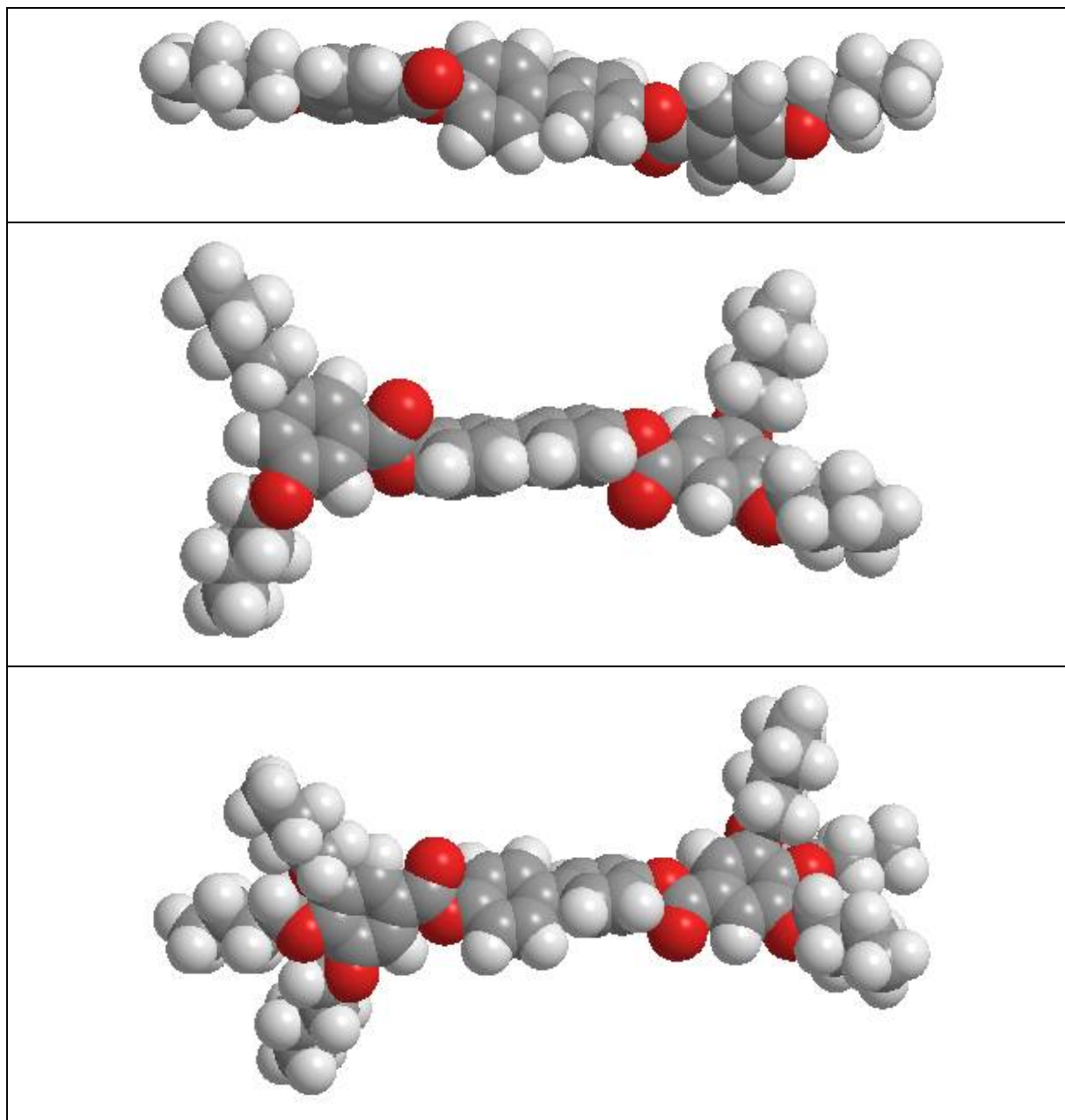


Fig. 2 Energy minimized molecular structure of C-10 homologue of single, double and triple chain biphenyl esters.

4-n-decyloxy-4,4'-biphenyl Ester

Yield: 62 %

IR (KBr): ν cm^{-1} 2955 (s), 2918(m), 2874 (s), 2850(s), 1730 (s), 1609(m), 1509(m), 1493(m), 1470(m), 1290(m), 1255(m), 1217(m), 1176(m), 1087(w), 1005(w), 880(w), 843 (m), 760(w), 744(w).

$^1\text{H NMR}(\text{CDCl}_3)$ δ ppm: 6.98 (4H,d, J= 9.0Hz), 8.16 (4H, d, J= 9.0Hz), 7.28 (4H, d, J= 8.6Hz), 7.63 (4H, d, J= 8.6Hz), δ 4.05, δ 1.84, δ 1.46, δ 0.89, δ 1.33-1.28.

4-n-dodecyloxy-4,4'-biphenyl Ester

Yield: 68%

IR (KBr): ν cm^{-1} 2955 (s), 2917(s), 2850 (s), 1731 (s), 1609(m), 1584(w), 1509(m), 1470(m), 1420(w), 1292(m), 1250(m), 1226(m), 1175(m), 1087(m), 1081(m), 1004(w), 881(w), 843(m), 808(w), 760(m), 718(w).

$^1\text{H NMR}(\text{CDCl}_3)$ δ ppm: δ 6.99 (4H,d, J= 9.0Hz), δ 8.17 (4H, d, J= 9.0Hz), δ 7.29 (4H, d, J= 8.6Hz), δ 7.63 (4H, d, J= 8.6Hz), δ 4.06, δ 1.86, δ 1.48, δ 0.87, δ 1.38-1.26.

3, 5-n-dihexadecyloxy-4,4'-biphenyl Ester

Yield: 58%

IR (KBr): ν cm^{-1} 2954 (s), 2917(s), 2850(s), 1740 (s)-1717(s), 1608(m), 1595(m), 1497(w), 1468(m), 1388(w), 1349(m),

1303(m), 1229(w), 1208(m), 1172(m), 1062(w), 1005(w), 757(w), 720(w).

¹H NMR(CDCl₃) δ ppm: 7.34 (4H, J_m = 2.3Hz), 7.29 (4H, d, J = 8.6Hz), 7.64 (4H, d, J = 8.6Hz), 6.73 (2H, J_m = 2.2Hz), δ 4.03, δ 1.82, δ 1.49, δ 0.90, δ 1.36-1.26.

3, 5-n-dioctadecyloxy-4,4'-biphenyl Ester

Yield: 61%

IR (KBr): ν cm⁻¹ 2918 (s), 2850(s), for aliphatic C-H, 1739 (s) for ester C=O, 1595(m), for aromatic C=C, 1468(m), 1354(w), 1357(w), 1207(m), 1202(m), 1194(m), 1173(m), 1051(m), 1011(m), 852(m), 843(m), 758(w), 741(w), 717(w).

¹H NMR(CDCl₃) δ ppm: δ 7.36 (4H, J_m = 2.6Hz), δ 7.3 (4H, d, J = 8.76Hz), δ 7.66 (4H, d, J = 8.75Hz), δ 6.71 (2H, J_m = 2.4Hz), δ 4.04, δ 1.85, δ 1.48, δ 0.89, δ 1.38-1.27.

3, 4, 5-n-tri decyloxy-4,4'-biphenyl Ester

Yield: 56%

IR (KBr): ν cm⁻¹ 2952 (s), 2917(s), 2850(s), 1735 (s), 1594(w), 1585(m), 1498(m), 1469(m), 1337(m), 1229(w), 1199(s), 1167(w), 1131(m), 1121(m), 1096(w).

¹H NMR(CDCl₃) δ ppm: δ 7.43 (4H, s), δ 7.28 (4H, d, J = 8.5Hz), δ 7.64 (4H, d, J = 8.5Hz) for the (2''/6'' + 2'/6'), δ 4.05, δ 1.85, δ 1.5, δ 0.90, δ 1.40-1.28.

3, 4, 5-n-tri-tetradecyloxy-4,4'-biphenyl Ester

Yield: 53%

IR (KBr): ν cm⁻¹ 2955 (s), 2917(s), 2872-2850(s), 1735 (s), 1661(m), 1641(m), 1585(m), 1499(m), 1468(m), 1429(m), 1385(w), 1340(s), 1200(w), 1166(w), 1121(m), 1098(m).

¹H NMR(CDCl₃) δ ppm: δ 7.36 (4H, s), δ 7.29 (4H, d, J = 8.5Hz), δ 7.62 (4H, d, J = 8.5Hz), δ 4.06, δ 1.82, δ 1.46, δ 0.85, δ 1.45-1.26.

3, 4, 5-n-trihexadecyloxy-4,4'-biphenyl Ester

Yield: 52%

IR (KBr): ν cm⁻¹ 2955 (s), 2917(s), 2872-2850(s), 1735 (s), 1661(m), 1641(m), 1585(m), 1499(m), 1468(m), 1429(m), 1385(w), 1340(s), 1200(w), 1166(w), 1121(m), 1098(m).

¹H NMR(CDCl₃) δ ppm: δ 7.36 (4H, s), δ 7.29 (4H, d, J = 8.5Hz), δ 7.62 (4H, d, J = 8.5Hz),

δ 4.06, δ 1.82, δ 1.46, δ 0.85, δ 1.45-1.26.

3, 4, 5-n-trioctadecyloxy-4,4'-biphenyl Ester(4.10)

Yield: 55%

IR (KBr): ν cm⁻¹ 2981 (s), 2949(s), 2876-2852(s), 1729 (s), 1667(m), 1629(m), 1571(m), 1503(m), 1468(m), 1422(m), 1376(w), 1276(m), 1208(w), 1121(m), 1098(m), 1009(w), 887(w), 763(w).

¹H NMR(CDCl₃) δ ppm: δ 7.43 (4H, s), at δ 7.27 (4H, d, J = 8.5Hz), δ 7.64 (4H, d, J = 8.5Hz), δ 4.09, δ 1.82, δ 1.49, δ 0.90, δ 1.43-1.25.

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