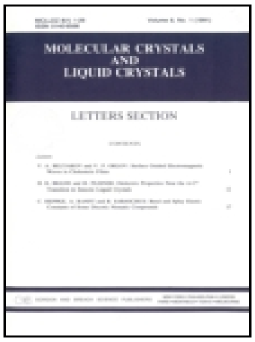


Taylor & Francis
Taylor & Francis Group

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Synthesis of Multiring Azo-Benzoic Acid Liquid Crystalline Molecules and Their Special Photosensitive Property

Min-Yan Zheng, Yong-Sheng Wei, Wei Geng, Nai-Ni Guo & Ping Zhang

To cite this article: Min-Yan Zheng, Yong-Sheng Wei, Wei Geng, Nai-Ni Guo & Ping Zhang (2015) Synthesis of Multiring Azo-Benzoic Acid Liquid Crystalline Molecules and Their Special Photosensitive Property, Molecular Crystals and Liquid Crystals, 608:1, 1-13, DOI: 10.1080/15421406.2014.949591

To link to this article: http://dx.doi.org/10.1080/15421406.2014.949591

Mol. Cryst. Liq. Cryst., Vol. 608: pp. 1–13, 2015

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.949591

Taylor & Francis
Taylor & Francis Group

Synthesis of Multiring Azo-Benzoic Acid Liquid Crystalline Molecules and Their Special Photosensitive Property

MIN-YAN ZHENG,* YONG-SHENG WEI, WEI GENG,
NAI-NI GUO, AND PING ZHANG

School of Chemistry and Chemical Engineering, Xianyang Normal University,
Xianyang, Shaanxi, China

10 new rod-like azo benzoic acid liquid crystals belonged to three series have been prepared, in which trans-*cyclohexyl benzene, biphenyl or bi*-trans-*cyclohexyl carboxylic acid mesogenic cores with ethyl,* n-*propyl,* n-*butyl or* n-*pentyl substituents were connected with azo benzoic acid. Meantime, a simple method was developed in synthesizing compounds bearing both ester and carboxyl groups in one-step reaction. All these compounds have been characterized on the basis of their spectral data, differential scanning calorimeter (DSC) and hot stage polarizing optical microscope (HS-POM). All these compounds have higher thermo-stability. 8 of these compounds have liquid crystalline properties. Their temperature ranges of mesophase have not been obtained, resulting from all the compounds decomposed before their clearing points. Although these compounds are photosensitive in solution under illumination of UV light (365nm), they can't do trans-cis isomerization in their mesophses, indicating the super stabilities of the* trans *isomer in mesophase.*

Keywords Azo compounds; benzoic acids; liquid crystals; photosensitivity

Introduction

The liquid crystal is one of the most convenient materials to operate optical properties due to it possesses a large anisotropy in dielectric and optical properties, which are controlled by change alignment of molecules with external stimuli such as heat and electric, electromagnetic or light fields [1–3]. Optical switching materials composed by liquid crystal molecules need at least two optically distinct states of an inherent one and a latent one. Especially, all optical switching materials, whose optical properties can be changed selectively and reversibly by light, have considerable potential use in photonics. These materials are operative by monitoring the change in the optical properties [4]. The wavelengths remote from these used for switching liquid crystalline azobenzene compound can display new properties related to the cis-trans photoisomerization of azobenzene on UV light exposure [5]. According to Rau [6], azo compounds are classified into three classes based on the

---

*Address correspondence to Min-Yan Zheng, School of Chemistry and Chemical Engineering, Xianyang Normal University, Xianyang, Shaanxi 712000, China. Tel.: +86-29-33720704; Fax: +86-29-33720371. E-mail: zmy71@126.com

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

relative energetic order of their (n, π^*) and (π, π^*) states: molecules of the azobenzene type, molecules of the amino azobenzene type, and molecules of pseudo-stilbenes type. The azobenzene type molecules are characterized spectroscopically by a low-intensity n-π^* band in the visible region of the spectrum and a high intensity π-π^* band in the UV light [7]. Azo functionalized materials are of great interest due to their photo-sensitive nature, which can be exploited for optical and optoelectronic devices[8]. Many researches focused on synthesizing of liquid crystal with core of azo group, most of them involved the synthesis of such kind of liquid crystal of polymers [9, 10] or preparation of other compounds [11, 12], but little report about design such kind of liquid crystal with smaller molecular weight, especially with terminal groups of strong polarity.

Liquid crystals with azo group were always designed with terminal longer alkoxy chain [13, 14], which is easier to be formed by terminal hydroxy reacting with different haloalkanes. Although being more stable than alkoxy chain, the terminal alkyl chains located in liquid crystalline structure is difficult to form and hence seldom use in constructing liquid crystalline molecules. Some literature involved the effect of some polar end groups on the mesomorphic property [15], but few of them took carboxyl acid as an end group. Our former publication has synthesized liquid crystalline molecules with terminal alkyls and a polar end group of carboxyl acid, which exhibited mesophase and thermostability [16]. Beside properties of mesophase, aromatic acids are often used as intermediates of other reactions. As a kind of new compounds, it is worth to obtaining their properties of photosensitivity and liquid crystalline. Based on the idea above, we have synthesized here 10 rod-like liquid crystalline molecules of terminal alkyl chain and COOH with azo bridge bonding, by changing the terminal double rings to cyclohexyl benzene or biphenyl or bicyclohexane in order to research the effect of these variations on their liquid crystalline property and their photosensitivities.

Experimental Section

Materials

All initial intermediates used in the synthesis were prepared in our laboratory with purity higher than 99%, and characterized by IR, GC-MS and ^{1}H NMR methods. Other reagents from commercial sources and used without further purification. 4-(4-Hydroxyphenylazo) benzoic acid was prepared using the method reported elsewhere [17].

Instruments and Conditions

The purities of compounds were detected by LC-10A (Shimadzu) instrument with methanol as eluent and flowing rate was 1 mL/min. Elemental analyses were conducted by PE-2400 analyzer (Perkin Elmer). UV spectra were determined by Agilent 8453 Spectrometer (Agilent Technologies). IR (KBr) spectra were recorded on a Vertex 70 spectrophotometer (BRUKER). The irradiation of samples was carried out by hand-held UV lamp ZF-7A (Shanghai Jiapeng Technology Co. Ltd.). Mass data were recorded on a GCMS-QP2010 (Shimadzu) and IE was 70 ev. ^{1}H NMR spectra were obtained on a BRUKER Avance 500 spectrometer (500 MHz, solvent $CDCl_3$). The DSC experiments were carried out on MDSC Q100 instrument (TA) and the determination conditions were: the sample mass less than 5 mg; heating rate, 10°C/min and samples were protected by nitrogen. All images of textures were taken on a LV100POL Polarizing Optical Microscopy (Nikon) with LTS E350 hot-stage (Linkam) and heating rate 1°C/min.

Synthesis

Synthesis of Compound 2

2a was prepared by heating and stirring a mixture of 4-ethyl(4-*trans*-cyclohexyl) benzoic acid(**1a)** (1.16 g, 5 mmol) and $SOCl_2$ (0.60 g, 5 mmol) and several drops of DMF in toluene (25 mL) at ambient temperature for 5 hr. The solvent was then removed under vaccum condition. A brown liquid (**2a**) was obtained and used to next step without further purifying.

Synthesis of Compound 3

3a was obtained by dissolving **2a** into CH_2Cl_2 (20 mL) and the mixture was dropped into a solution of 4'-hydroxylazo-4-benzoic acid (1.21 g, 5 mmol) and triethylamine (0.9 mL, 5 mmol) in CH_2Cl_2 (50 mL) and stirred at ambient temperature for 12 hr. The reacting solvent was removed under vacuum condition. Some orange solid was obtained, washed by 5% (mass fraction) NaOH and water. The residue was dried and recystalized with THF. An orange powder (**3a**, 1.82 g) was obtained in yield of 80% (two steps). The **3b**, **3c**, **3d**, **3e, 3f, 3g, 3h, 3i** and **3j** were also prepared by the same way, and their yields were 85%, 84%, 80%, 81%, 85%, 82%, 81%, 85%, 82%, 81%, 79% and 83%, respectively.

4-(4-(4-(4-ethylcyclohexyl)benzoyloxy)phenyldiazenyl) benzoic acid (**3a**), Relative molecular mass: 456.53, the mass fraction detected by LC is 98.5%, yield: 80%, orange powder, m.p.181-182°C. Anal. Calcd for $C_{28}H_{28}N_2O_4$: C 73.66, H 6.18, N 6.14, found: C 73.54, H 6.02, N 5.97; IR(KBr)ν: 3100-2500(m, OH), 2960, 2914, 2848(s, C—H), 1734(vs,C=O), 1683(vs, C=O), 1608(m, N=N), 1594, 1506(m, ArH), 1406, 1315, 1284, 1180, 1128, 1016(vs, C—O—C), 880(s, *trans* —H—N=N—R), 807(w, 1,4-Ar), 776(w, $(CH_2)n$)cm^{-1}; MS(70 ev)m/z(%): 456(M+, 14), 388(0.62), 360(0.66), 274(0.70), 257(18.17), 242(6.74), 229(0.96), 215(100), 185(0.74), 147(17.86), 119(28.99), 105(10.44), 91(22.12), 81(4.91), 77(11.84), 69(14.30), 66(29.72), 55(10.79), 44(12.35), 41(8.08). ^{1}H NMR: 0.925(t, 3H, J = 6.4Hz, CH_3), 1.062–1.117(m, 2H, CH_2), 1.276–2.618(m, 10H, the proton of cyclohexane), 7.378, 7.412, 8.048, 8.118, 8.149, 8.317(d, J = 8.0 Hz, 8.8 Hz, 8.0 Hz, 8.0 Hz, 8.0 Hz, 8.4 Hz, 2H of each), 12.79(s, 1H, COOH).

4-(4-(4-(4-*n*-propylcyclohexyl)benzoyloxy)phenyldiazenyl) benzoic acid (**3b**), Relative molecular mass:470.56, the mass fraction detected by LC is 98.0%, yield: 85%, orange powder, m.p. 223-224°C, Anal. Calcd for $C_{29}H_{30}N_2O_4$: C 74.02, H 6.43, N 5.95; found C 73.86, H 6.23, N 6.05; IR(KBr)ν: 3100-2500(m, C—H), 2955, 2921, 2849(s, C—H), 1734(vs, C=O), 1687(vs, C=O), 1602(m, N=N), 1597, 1502, 1495(m, ArH), 1424, 1266, 1221, 1140, 1065(vs, C—O—C), 881(s, *trans*-R—N=N—R), 866, 817(w, 1, 4-Ar), 764, 736(w, $(CH_2)n$)cm^{-1}; MS(70ev) m/z(%): 470(M, 3.5), 456(1.48), 388(0.34), 360(1.14), 346(0.29), 274(0.33), 257(24.46), 229(100), 215(38.15), 147(4.09), 131(14.02), 119(17.31), 105(9.46), 91(16.97), 481(4.76), 77(11.34), 69(7.88), 65(23.20), 55(7.81), 51(2.11), 41(5.89). ^{1}H NMR: 0.907(t, 3H, J = 7.2 Hz, CH_3), 1.017-1.102(m, 2H, CH_2), 1.211–1.248(m, 2H, CH_2), 1.310–2.554(m, 10H, the proton of cyclohexane), 7.308, 7.344, 8.020, 8.061, 8.147, 8.316(d, J = 8.0 Hz, 8.2 Hz, 8.0 Hz, 8.2 Hz, 8.2 Hz, 8.2 Hz, 2H of each), 12.83(s, 1H, COOH).

4-(4-(4-(4-*n*-butylcyclohexyl)benzoyloxy)phenyldiazenyl) benzoic acid(**3c**), Relative molecular mass:484.59; the mass fraction detected by LC is 98.0%, yield: 84%, orange powder, m.p. undetected; Anal. Calcd for $C_{30}H_{32}N_2O_4$: C 74.36, H 6.66, N 5.78; found C 74.54, H 6.49, N 5.57; IR(KBr)ν: 3000–2500(—OH), 2921, 2850(s, C—H), 1735(vs, C=O), 1684(vs, C=O), 1595, 1495(m, ArH), 1414(m), 1267, 1223, 1198, 1178, 1141(vs, C—O—C), 880(s, *trans*-R—N=N—R), 815(w, 1, 4-Ar), 719(w, $(CH_2)n$)cm^{-1}; MS(70 ev)m/z(%): 484(M’, 2.66), 470(0.52), 456(0.78), 360(0.73), 274(0.35), 257(25.09), 243(200), 229(22.45), 215(17.53), 185(0.98), 157(1.28), 147(12.16), 135(4.01), 131(12.63), 119(11.39), 105(9.22), 91(15.60), 81(4.72), 77(2.12), 69(5.11), 65(2.11), 55(7.11), 51(1.86), 41(6.20). ^1H NMR: 0.899(t, 3H, J = 4.8 Hz, CH_3), 1.041-1.094(m, 2H, CH_2), 1.216-1.249(m, 4H, CH_2CH_2), 1.251–2.565(m, 12H, the proton of cyclohexane), 7.366, 7.516, 8.000, 8.048, 8.139, 8.250(d, J = 8.4 Hz, 8.0 Hz, 8.0 Hz, 8.4 Hz, 8.0 Hz, 8.0 Hz, 2H of each), 12.03(s, 1H, COOH).

4-(4-(4-(4-*n*-pentylcyclohexyl)benzoyloxy)phenyldiazenyl) benzoic acid (**3d**), Relative molecular mass: 498.61, mass fraction detected by LC is 98.5%, yield: 80%, orange powder, m.p. 195-196°C; Anal. Calcd for $C_{31}H_{34}N_2O_4$: C 74.67, H 6.87, N 5.62; found C 74.57, H 6.78, N 5.53; IR(KBr)ν: 3100–2500(s,OH), 2954, 2922, 2850(s, C—Hstretching vibration), 1743(vs, C=O), 1687(vs, C=O), 1595, 1506(m, ArH), 1264, 1177, 1059(vs, C—O—C), 880(s, trans—H—N=N—R), 838, 812(w, 1,4-Ar), 719(w, $(CH_2)n$)cm^{-1}; MS(70ev)m/z(%): 498(M+, 2.89), 484(0.46), 70(0.18), 456(0.20), 388(0.15), 360(0.18), 346(0.10), 274(0.89), 257(100), 243(17.24), 229(6.32), 215(6.61), 199(0.21), 185(0.90), 147(5.48), 131(10.92), 121(7.00), 105(6.39), 91(10.67), 77(6.88), 69(0.94), 65(12.23), 55(5.48), 41(4.19). ^1H NMR: 0.898(t, 3H, J = 7.2 Hz, CH_3), 1.075(m, 2H, CH_2), 1.256-1.311(m, 6H, $CH_2CH_2CH_2$), 1.458–2.610(m, 10H, the proton of cyclohexane), 7.378,7.481, 8.011, 8.061, 8.136, 8.398(d, J = 8.4 Hz, 8 Hz, 8.4 Hz, 8.0 Hz, 8.4 Hz, 8.4 Hz, 2H of each), 11.02(s, 1H, COOH).

4-(4-(4-(4-ethylphenyl)benzoyloxy)phenyldiazenyl)benzoic acid (**3e**), Relative molecular mass: 450.49, mass fraction detected by LC is 98.1%, yield: 81%, orange powder, m.p. undetected; Anal. Calcd for $C_{28}H_{22}N_2O_4$: C 74.65, H 4.92, N 6.22; found C 74.49, H 4.77, N 6.32; IR(KBr)ν: 3100-2500(—OH), 2966, 2931 (s, C—H), 1732, 1687(vs, C=O), 1603(m, N=N), 1559, 1541, 1495(m, ArH), 1400, 1110, 1071, 1007 (vs, C—O—C), 883(s, *trans*—H—N=N—R—), 827(w, 1,4-Ar), 776(w, $(CH_2)n$) cm^{-1}; MS(70ev)m/z(%): 450(M+, 0.20), 429(0.08), 414(0.35), 396(0.19), 382(0.09), 369(0.05), 355(0.20), 341(0.09), 329(0.14), 317(0.31), 270(0.92), 254(5.96), 239(2.87), 226(72.54), 211(100), 198(1.81), 181(10.69), 165(38.55), 152(28.08), 139(5.91), 115(7.35), 105(3.01), 97(1.65), 86(8.85), 65(6.99), 44(6.72), 32(8.60). ^1H NMR: 1.243(t, 3H, J = 7.6 Hz, CH_3), 2.673(q, 2H, J = 7.6 Hz, CH_2), 7.287, 7.402, 7.639, 7.636, 8.001, 8.106, 8.234, 8.297(d, J = 8.0 Hz, 8.4 Hz, 8.0 Hz, 8.0 Hz, 8.4 Hz, 8.0 Hz, 8.4 Hz, 8.4 Hz, 2H of each), 12.780(s, 1H, COOH).

4-(4-(4-(4-*n*-propylphenyl)benzoyloxy)phenyldiazenyl)benzoic acid (**3f**), Relative molecular mass: 464.51; the mass fraction detected by LC is 98.2%, yield: 85%, orange powder, m.p. 190–191 °C; Anal. Calcd for $C_{29}H_{24}N_2O_4$: C 74.98, H 5.21, N 6.03; found C 74.88, H 5.16, N 6.08; IR(KBr)ν: 3000–2500(—OH), 2956, 2928, 2869(s, C—H), 1737, 1686(vs, C=O), 1604(m, N=N), 1496, 1429(m, ArH), 1401, 1272, 1222, 1139, 1070, 1003(vs, C—O—C), 881(s, *trans*—H—N=N—R—), 838, 814(w, 1, 4-Ar), 741(w, $(CH_2)n$), 691, 549 cm^{-1}; MS(70ev)m/z(%): 464(M+, 2.06), 450(3.24), 435(0.06), 422(0.10), 405(0.03), 388(0.11), 360(0.16), 43(0.05), 331(0.29), 317(0.61), 301(0.09), 286(0.16), 268(1.38), 255(0.37), 251(8.40), 240(10.98), 223(76.54), 209(100), 194(1.69), 181(5.58), 165(36.46), 152(39.70), 139(5.54), 121(13.72), 119(3.82), 115(8.38), 93(9.07), 77(5.60), 65(27.36), 39(8.89), 29(10.5). ^1H NMR: 0.979(t, 3H, J = 7.2Hz, CH_3), 1.662–1.728(m, 2H, CH_2), 2.662(t, 2H, J = 7.2 Hz, CH_2), 7.260, 7.313, 7.451, 7.759, 8.048, 8.160, 8.282, 8.345(d, J = 8.0 Hz, 8.4 Hz, 8.0 Hz, 8.0 Hz, 8.0 Hz, 8.0 Hz, 8.4 Hz, 8.4 Hz, 2H of each), 12.972(s, 1H, COOH).

4-(4-(4-(4-*n*-butylphenyl)benzoyloxy)phenyldiazenyl)benzoic acid (**3g**), Relative molecular mass: 478.54; the mass fraction detected by LC is 98.0%, yield: 82%, orange powder, m.p. 226–227°C; Anal. Calcd for $C_{30}H_{26}N_2O_4$: C 74.98, H 5.21, N 6.03; found C 74.81, H 5.16, N 6.18; IR(KBr)ν: 3000-2500(−OH), 2958, 2926, 2856(s, C−H), 1779, 1737, 1688(vs, C=O), 1604(m, N=N), 1495, 1463(m, ArH), 1400, 1272, 1222, 1140, 1070, 1003(vs, C−O−C), 882(s, *trans*−H−N=N−R−), 821(w, 1, 4-Ar), 712(w, $(CH_2)n$), 691, 547 cm^{-1}; MS(70 ev)m/z(%): 478(M+, 0.11), 450(0.04), 429(0.07), 403(0.04), 355(0.11), 331(0.08), 317(0.03), 301(0.09), 272(0.39), 254(42.94), 237(4.52), 224(1.02), 211(100), 191(0.17), 178(3.67), 165(3.18), 152(17.21), 139(4.27), 128(2.74), 115(5.81), 93(2.62), 86(10.33), 77(3.32), 65(4.27), 51(1.93), 41(5.93), 29(7.57), ^{1}H NMR: 0.958(t, 3H, J = 7.2 Hz, CH_3), 1.375-1.672(m, 4H, CH_2CH_2), 2.678(t, 2H, J = 7.2 Hz, CH_2), 7.317, 7.455, 7.563, 7.759, 8.092, 8.148, 8.237, 8.349(d, J = 8.0 Hz, 8.8 Hz, 8.0 Hz, 8.0 Hz, 8.4 Hz, 8.4 Hz, 8.4 Hz, 8.4 Hz, 2H of each), 12.079(s, 1H, COOH).

4-(4-(4-(4-*n*-pentylphenyl)benzoyloxy)phenyldiazenyl)benzoic acid (**3h**), Relative molecular mass: 492.57; the mass fraction detected by LC is 98.5%, yield: 81%, orange powder, m.p. 220–221°C; Anal. Calcd for $C_{31}H_{28}N_2O_4$: C 75.59, H 5.73, N 5.69; found C 75.32, H 5.66, N 5.57; IR(KBr)ν: 3000-2500(−OH), 2954, 2923, 2854(s, C−H), 1738, 1687(vs, C=O), 1642, 1631, 1603(m, N=N), 1593, 1495,(m, ArH), 1428, 1271, 1225, 1198, 1178, 1142, 1072, 1009(vs, C−O−C), 881(s, *trans*−H−N=N−R−), 812(w, 1, 4-Ar), 713(w, $(CH_2)n$), 690, 549 cm^{-1} MS(70ev)m/z(%): 492(M, 0.11), 470(0.14), 456(0.28), 435(0.18), 388(0.10), 360(0.23), 346(0.04), 329(0.07), 315(0.12), 286(0.10), 268(0.89), 257(45.93), 251(100), 243(12.51), 229(4.14), 215(6.7), 211(2.21), 194(1.27), 178(0.11), 165(6.25), 152(5.9), 121(9.86), 105(3.85), 91(.86), 77(5.41), 65(17.27), 55(3.66), 43(7.16), 32(1.31). ^{1}H NMR: 0.910(t, 3H, J = 7.4 Hz, CH_3), 1.256-1.658(m, 6H, $CH_2CH_2CH_2$), 2.660(t, 2H, J = 7.2 Hz, CH_2), 7.458, 7.562, 7.687, 7.761, 8.148, 8.238, 8.403(d, J = 8.0 Hz, 8.0 Hz, 8.0 Hz, 8.0 Hz, 8.0 Hz, 8.0 Hz, 8.0 Hz, 8.4 Hz, 8.0 Hz, 8.4 Hz, 2H of each), 12.069(s, 1H, COOH).

4-(4-(4-(4-*n*-propylcyclohexyl)cyclohexylacyloxy)phenyldiazenyl)benzoic acid (**3i**), Relative molecular mass: 476.61; the mass fraction detected by LC is 98.3%, yield: 79%, orange powder, m.p. 200–201°C; Anal. Calcd for $C_{29}H_{36}N_2O_4$: C 73.08 H 7.61, N 5.88; found C 73.02, H 7.56, N 5.97; IR(KBr)ν: 2913, 2851, 2853(s, C−H), 1744, 1684(vs, C=O), 1541,1507,1457(m, ArH), 1308, 1291, 1262, 1125, 1064, 1010(vs, C−O−C), 988, 948, 867, 849, 806(w, 1, 4-Ar), 765(w, $(CH_2)n)cm^{-1}$. MS(70ev)m/z(%): 476(M, 3.26), 464(0.41), 450(1.19), 435(0.16), 404(0.03), 388(0.06), 371(0.09), 345(0.41), 331(0.09), 317(0.21), 301(0.13), 251(6.19), 242(94.90), 237(78.42), 223(16.43), 209(37.37), 194(1.73), 178(3.01), 165(14.45), 152(23.63), 137(20.27), 125(29.54), 121(66.83), 111(45.04), 109(39.13), 93(38.12), 83(69.41), 69(100), 65(49.67), 55(80.78), 43(15.98), 41(36.55). ^{1}H NMR: 0.868(t, 3H, J = 7.8 Hz, CH_3), 0.944-1.148(m, 4H, CH_2CH_2), 1.256-2.525(m, 20H, the proton of cyclohexane), 7.319, 7.461, 8.087, 8.384(d, J = 8.0 Hz, 8.4 Hz, 8.4 Hz, 8.4 Hz 2H of each), 12.41(s, 1H, COOH).

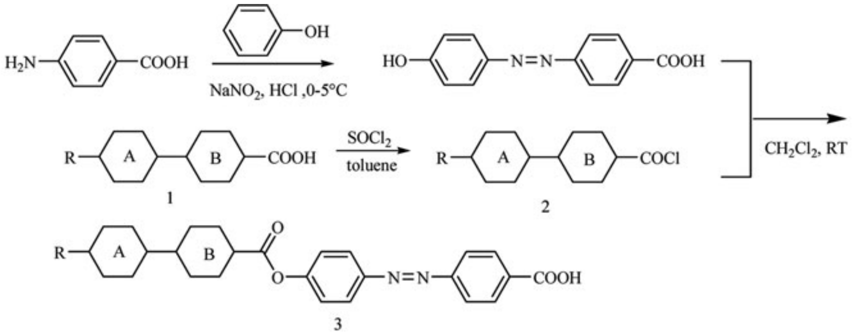
4-(4-(4-(4-*n*-pentylcyclohexyl)cyclohexylacyloxy)phenyldiazenyl)benzoic acid (**3j**), Relative molecular mass: 504.66; the mass fraction detected by LC is 98.2%, yield: 83%, orange powder, m.p 208–209°C; Anal. Calcd for $C_{31}H_{40}N_2O_4$: C 73.78, H 7.99, N 5.55; found C 73.62, H 8.04, N 5.44; IR(KBr)ν: 2953, 2921, 2850 (s, C−H), 1734, 1685 (vs, C=O), 1605(m, N=N), 1507, 1457, 1494(m, ArH), 1418, 1267, 1221, 1197, 1141, 1066, 1010(vs, C−O−C), 951, 883, 810(w, 1, 4-Ar), 776, 719((w, $(CH_2)n$), 670, 547, 531cm^{-1}; MS(70ev)m/z(%):504(M, 0.11), 478(0.15), 460(0.10), 371(0.22), 327(0.10), 280(0.36), 269(1.11), 262(4.64), 251(3.56), 242(100), 235(9.93), 224(3.37), 211(7.02), 198(1.48), 179(2.58), 165(4.44), 153(11.61), 139(26.72), 121(37.26), 109(35.37), 97(44.84), 83(47.85), 69(15.66), 55(9.78), 44(8.44), 29(1.85). ^{1}H NMR:

0.828(t, 3H, J = 7.2 Hz, CH_3), 0.895-0.001(m, 4H, CH_2CH_2), 1.076–1.101(m, 4H, CH_2CH_2), 1.076-2.197(m, 20H, the proton of cyclohexane), 7.3884, 7.971, 8.162, 8.332(d, J = 9.2 Hz, 8.8 Hz, 8.4 Hz, 8.4 Hz 2H of each), 12.725(s, 1H, COOH).

Results and Discussion

The Pathway of Synthesis of Target Products

4-(4-Hydroxyphenylazo)benzoic acid, as an initial material with double functional groups, is used to synthesize different photo-sensitive materials. It is usually applied to form an ester of carboxyl acid and an ether of the hydroxyl group [17, 18], or sometimes esterify the carboxyl acid with the hydroxyl unchanged [19], or etherify hydroxyl with the carboxyl acid group keeping constant [20–21]. There is little report of a method to esterify the hydroxyl of the molecule with the carboxyl acid unchanged in one-step reaction. Generally speaking, both carboxyl acid and hydroxyl groups can be easily transformed into the corresponding ester groups so that it is difficult to only esterify hydroxyl in molecules containing carboxyl acid unit in one-step reaction. Through a great deal of attempts, we found esterification of hydroxyl can be done at room temperature, while esterification of carboxyl can be carried out at heated condition. Accordingly, the reaction we expected can be done selectively between both carboxyl acid and hydroxyl groups with triethylamine and CH_2Cl_2 as reactants at room temperature with yields more than 79%. Furthermore, there was no other byproduct found in the reaction solution. The pathway gives us a chance to obtain compounds bearing both ester and carboxyl acid in one-step reaction and further to synthesize compounds of asymmetrical bi-ester with other hydroxy benzoic acids.



Series 1: a: R=*eth*yl, A=*trans*-cyclohexyl, B=phenyl; **b**: R=*n*-propyl, A=*trans*-cyclohexyl, B=phenyl; **c**: R=*n*-butyl, A= *trans*-cyclohexyl, B=phenyl; **d**: R=*n*-pentyl, A=*trans*-cyclohexyl, B=phenyl;

Series 2: **e**: R=*eth*yl, A=phenyl, B=phenyl;.**f**: R=*n*-propyl, A=phenyl, B=phenyl; **g**: R=*n*-butyl, A= phenyl, B=phenyl; **h**: R=*n*-pentyl, A=phenyl, B=phenyl;

Series 3: **i**: R=*n*-propyl, A=*trans*-cyclohexyl, B= *trans*-cyclohexyl; **j:** R=*n*-pentyl, A=*trans*-cyclohexyl, B= *trans*-cyclohexyl.

Scheme 1. The synthesis process of resulting compounds.

Determination of Photo-sensitivities in Solution

Target compounds were synthesized according to Scheme 1, their structural data were shown above. The spectral values are in accordance with the assigned structure. Generally speaking, the azo functional group may be isomerized from the more stable *trans* isomer to the *cis* one under illumination of UV light. The respective solutions utilized were kept in the dark for 2 days in order to we can infer that the compounds were almost in the *trans* form. The UV spectra were recorded over the same time interval until photostationary states were reached. The maximum time of photoisomerization were obtained at photostationary states. Under exposure on UV-light, the optical absorbances of all target compounds and the maximum time of isomerization in methanol solution are summarized in Table 1 and the change of UV spectrum of **3b** is shown in Fig. 1. The result shows that these compounds can do cis-trans isomerization in a solution of methanol. The highest photoisomerization of target compounds is reached between 40 and 80 min. for illumination intensities of 105 μWcm^{-2}. The observation of two isosbestic points at nearby 300 nm and 400 nm in Fig. 1 indicate the existence of only two compounds, the *trans* and *cis* isomer[22]. Table 1 tells us that, before irradiation, the maximum absorption wavelength (λ_{max}) of **3a**, **3b**, **3c** and **3d**(with structure of terminal cyclohexyl benzene ring) recorded at 237, 331; 241, 334; 239, 338; 239, 341nm, and λ_{max} of **3e**, **3f**, **3g** and **3h** (with structures of terminal double benzoic rings) at 296, 325; 298, 320; 296, 324; 299, 323 nm and **3i**, **3g**(with structures of terminal double trans cyclohexane rings) at 230, 333; 230, 333 nm; respectively, while after irradiation, all maximum absorption wavelength (λ_{max}) change their previous positions, indicating all the compounds are photosensitive in solution. Figure 1 is the absorption spectral change of **3b** (its concentration is 5×10^{-5} mol/L) in methanol by irradiation with 365 nm light for the same time interval of 10min. Every peak in UV spectra has a relationship with molecular structure. From the sample of **3b** in solution (Fig. 1), we observe that the small shoulder at ~430 nm is assigned to n-π^* transition and the maximum of the absorbance in the range of 334 nm corresponds to a strong π-π^* electronic transition of azo-moiety, while the peak at 241nm is caused by aromatic ring system. We can see from Table 1 that, before irradiation by UV-light, these compounds all have two main absorption

Table 1. The UV spectral data of target compounds

		Trans isomer λ_{max}(nm)		Cis isomer λ_{max}(nm)		
Series	Compd.	I	II	I	II	Time(min) of cis-trans isomerization ($5\times10^{-}5$ mol/L)
1	**3a**	237	331	240	328	50
	3b	241	334	246	328	60
	3c	239	338	244	335	70
	3d	239	341	241	337	40
2	**3e**	296	325	293	327	40
	3f	298	320	294	325	60
	3g	296	324	293	326	40
	3h	299	323	295	326	40
3	**3i**	230	333	232	330	80
	3g	230	333	232	327	80

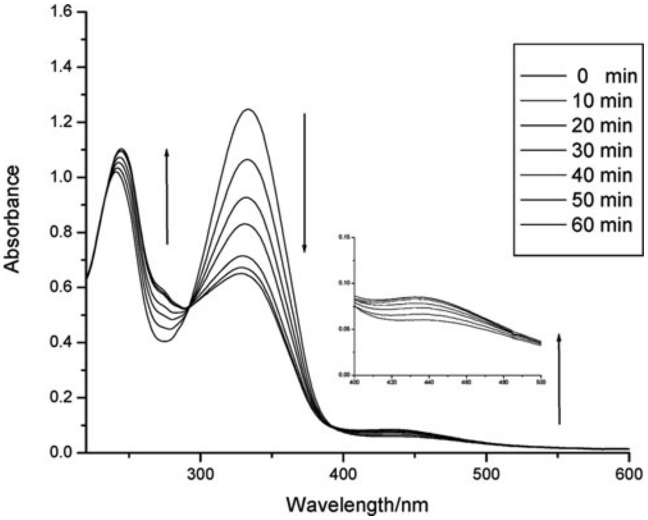


Figure 1. The UV-Visible absorption spectrum of **3b** in methanol during cis-trans isomerization. The inset illustrates the small increase of absorption in 430 nm.

peaks. After irradiation by UV-light, the compounds with terminal double benzene rings just have one peak left in the UV spectra, while the other two series still had two peaks for each compound. According to the data presented in Table 1, we find that terminal ring system promote two effects on the λ_{max} of the compounds. The first is a shift of the absorption bands, having the same effect on the azo band and on the aromatic ring. Under exposure to UV light, the first peaks of compounds in the series 1 promotes a small bathochromic shift in the range of 2∼5 nm, while the second peak of benzene absorption band produces a small hypsochromic shift between 3 and 6 nm. The first peak of compounds in the series 2 promotes a small hypsohromic shift in the range of 3∼4 nm, while the second peak produces a small bathochromic shift between 2 and 5 nm. The first peak of the compounds in the series 3 yields a small bathochromic shift of 2 nm, while the second peak of them presents a small hypsochromic shift of 2 nm. The second effect is that, after irradiation, compounds with terminal double benzene rings make the first peak a small hypsochromic shift and the second one a bathochromic shift, while compounds with one or two terminal cyclohexane rings make the first peak a small bathochromic shift and the second one a small hypsochromic shift, suggesting the terminal rings have effects on the λ_{max} of peaks of these compounds during cis-trans isomerization process. Compared the period of each compound need to change their structure from *trans* to *cis* isomer, compounds with terminal double benzene rings are easiest to transfer their structures, while those with terminal double cyclohexane rings are the most difficult to change.

Liquid Crystal Properties

The transition temperatures, associated enthalpy values obtained from DSC studies and the ranges of decomposing from TG for the target compounds are summarized in Table 2. DSC thermograms were measured at the rate of 10 °C/min for heating process. Among them, 8 compounds exhibit the appearance of textures should belong to nematic. The mesophase of these molecules were observed by POM. The POM micrographs are shown in Fig. 2.

Table 2. The results of DSC measurement

Compd.	**3a**	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**	**3h**	**3i**	**3j**
M.p/(°C)	181.2	225.3	undetected	195.7	undetected	190.9	227.2	220.8	200.7	208.1
ΔH of M.p./(J/g)	11.97	17.62	—	9.342	—	9.196	6.836	8.132	6.869	18.12
D.p./(°C)	305–404	293–409	292–402	323–385	309–376	318–373	320–399	319–396	291–402	257–428

*m.p. is melting point, c.p. is clearing point, d.p is decomposing point

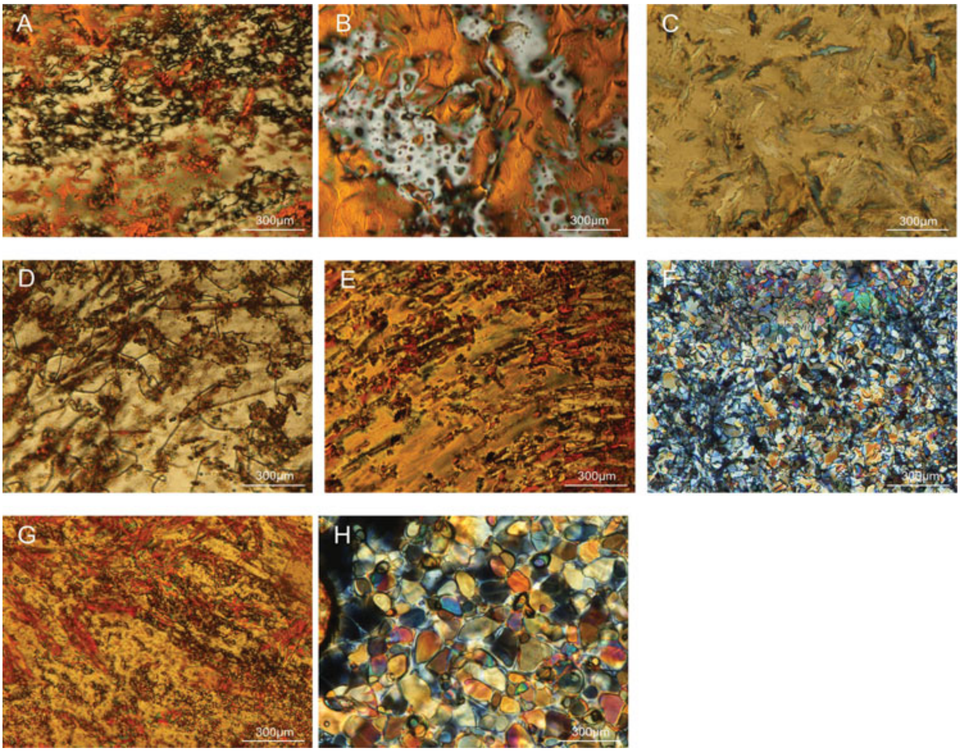


Figure 2. The textures of resulting compounds observed under polarizing optic microscope during heating process. (a) The schlieren texture of **3a** taken at 281°C; (b) the schlieren texture of **3b** taken at 240°C; (c) the schlieren texture of **3d** taken at 254°C; (d) the schlieren texture of **3f** taken at 270°C; (e) the schlieren texture of **3g** taken at 310°C; (f) the schlieren texture of **3h** taken at 275°C; (g) the schlieren texture of **3i** taken at 289°C; (h) the schlieren texture of **3j** taken at 238°C.

Except **3c** and **3e**, which decompose before melt, the melting points of other compounds are detected. the 8 compounds have higher decomposing point from 257°C to 323°C, while melting points from 181°C to 227°C, indicating these compounds have thermostablity.

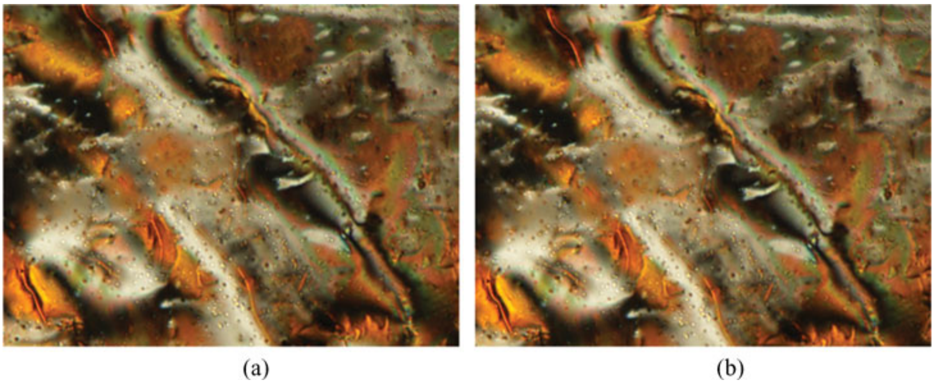

(a) (b)

Figure 3. The texture change during UV radiation of 3b at 260°C. (a) The texture taken after 10 min UV radiation; (b) the texture taken after 180 min UV radiation.

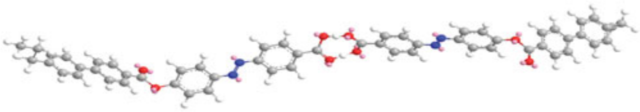


Figure 4. Dimers of one of the target compounds in mesophase (drawn by chembioDraw 3D ultra 12.0 and minized molecular energy).

The **3j**(with terminal pentyl bicyclohexane rings) is the least thermostable one, while the **3d**(with terminal pentyl cyclohexyl phenyl rings) is the most thermostable. There has no clear trend of change of their melting point, indicating melting points of these compounds has great relationship with the carboxyl acid group other than terminal alkyls and terminal rings in other compounds [23]. Although the 8 compounds show no any clear point during determination of DSC, the mesophases of them are still observed. Unlike azo benzaldehyde compounds we have prepared [24], their mesophases remained unchanged under radiation of UV light, suggesting these compounds are difficult to change their structures form *trans* isomer to *cis* one in mesophase under the radiation of UV light. The maximum absorpotion wavelengths of π-π^* electronic transition of azo-moiety in *cis* isomer of 3i and 3j calculated by Gaussian 3.0 at 332 nm and 328 nm are in good agreement with determining results of these *cis* isomers, showing these *trans* compounds almost convert into cis isomer after enough radiation of UV light.

Determination of Photo Sensitivities in Liquid Crystal Phase

After radiating under UV light of 365 nm from 10 min to 180 min, the textures of all compounds were observed by POM (represent compound **3b** shown as Fig. 3). Figure 3 shows that the textures kept unchanged as the increasing time of UV light radiation, indicating although at higher temperature, these azo benzoic acids do not change their shapes in mesophase by the radiation of UV light. As it is known to all, conventional azobenzenes can do cis-trans isomerization at higher temperature. But these azo compounds in the paper remain their *trans* structures in mesophase, suggesting they must have formed some stable structures in mesophase to resist transferring their structures by radiation of UV-light under heating condition. It is because the carboxyl acid group is easy to form a dimer in solid and liquid crystalline phase (as Fig. 4 shown)

Conclusions

We have discussed the synthesis, mesomorphic properties, and photo sensitive property of asymmetric azo benzoic acid liquid crystals. 10 target molecules synthesized are consisted by asymmetric four-ring molecule with variation terminal alkyl chains ($n = 2$, 3, 4 and 5) on one end and the carboxyl acid group on the other end. A simple one-step reaction was applied to synthesize the target compound bearing both groups of ester and carboxyl acid. 8 compounds appear the mesophase before their decomposing points. The existence of phase is confirmed by POM investigation. The mesophase of them belongs to nematic. The photo-switching properties of these compounds were investigated by using UV–Vis spectroscopy under illumination with UV light (365 nm). Photoisomerization processes in solution revealed all compounds exhibited cis-trans isomerization occurs around 40 to 80 min. The compound with terminal double hexane rings took the longest average time to transfer from *trans* isomer to *cis* one, while the compounds with terminal double benzene rings took the least mean time to change their configuration. All the compounds can not do cis-trans isomerization in mesophase, suggesting these compounds form some stable structure to resist the change of configuration, such as dimmer.

Funding

We gratefully acknowledge the financial support from the National Natural Science Foundation of China (No. 21102121), Natural Science Foundation of Shaanxi Province (No. 2010JM2009) and Natural Science Foundation of Shaanxi Province Educational Department (No. 2010JK902).

References

[1] Yang, D.-K., Chien, L.-C., & Doane, J. W. (1992). Cholesteric liquid crystal/polymer dispersion for haze-free light shutters. *Appl. Phys. Lett.*, *60*, 3102–3014.
[2] Ikeda, T., & Tsutsumi, O. (1995). Optical switching and image storage by means of azobezene liquid crystal film. *Science*, *268*, 1873–1875.
[3] Eich, M., & Wendorff, J. H. (1987). Erasable holograms in polymeric liquid crystals. *Makromol. Chem. Rapid Commun.*, *8*, 467–471.
[4] Lee, H.-K., Doi, K., Harada, H., Tsutsumi, O., Kanazawa, A., *et al.* (2000). Photochemical modulation of color and transmittance in chiral nematic liquid crystal containing an czobenzene as a photosensitive chromophore. *J. Phys. Chem. B*, *104*, 7023–7028.
[5] Tong, X., & Zhao, Y. (2009). Multiple photochemical processes in liquid crystalline azo dye-doped liquid crystals. *Chem. Mater.*, *21*, 4047–4054.
[6] Rau, H. (1990). *Photochemistry and Photophysics*, Rabek, J. F. (Eds.), Vol. II, Chapter 4, CRC Press: Boca Raton, FL.
[7] Xie, S., Natansohn, A., & Rochoni, P. (1993). Recent developments in aromatic azo polymers research. *Chem. Mater.*, *5*, 403–411.
[8] de Silva, A. P., Gunarane, H. Q. N., Gunnlaugsson T., Huxley A. J. M., McCoy P., *et al.* (1997). Signaling recognition events with fluorescent sensors and switches. *Chem. Rev.*, *97*, 1515–1566.
[9] Zhou, D.-W, Liang, L.-Y., & Lu, M.-G. (2011). Dimeric liquid crystalline thermosets from azo-containing diglycidyl ether cured by anhydride. *Polym. Bull.*, *66*, 1111–1123.
[10] Wu, L., Tuo, X., Cheng, H., Chen, Z., & Wang, X. (2001). Synthesis, photoresponsive behavior, and self-assembly of poly(acrylic acid)-based azo polyelectrolytes. *Macromolecules*, *34*, 8005–8013.
[11] Krohn, K., John, M., & Demikhov, E. I. (2001). New aromatic compounds: syntheses and liquid-crystalline properties. *Russ. Chem. Bull. (international edition)*, *50*, 1248–1254.
[12] Hernandez-Ainsa, S., Alcal, R., Barbera, J., Marcos, M., Sanchez, C., *et al.* (2010). Ionic photoresponsive azo-codendrimer with room temperature mesomorphism and high photoinduced optical anisotropy. *Macromolecules*, *43*, 2660–2663.
[13] Yao, J., You, Y., Liu, H., Dong, L., & Xiong, C. (2011). Liquid–crystal azopolyamides with high thermal stability and inherent viscosity. *J. Mater. Sci.*, *46*, 3343–3348.
[14] Circu, V., Mocanu, A. S., Ros, C., Manaila-Maximean, D., & Dumitrascu, F. Thermal behaviour and electro-optical properties of a series of liquid crystals based on palladium complexes with mixed ligands Schiff bases and N-benzoyl thioureas. *J. Therm Anal. Calorim.*, *107*, 877–886.
[15] Kašpar, M., Novotná, V., Hamplová, V., Podoliak, N., Nonnenmacher D., *et al.* (2011). Anti-ferroelectric phase in liquid crystalline compounds containing an azo groups containing an azo group in their molecular core. *Liq. Cryst.*, *38*, 309–315.
[16] Zheng, M.-Y., Wei, Y.-S., & An, Z.-W. (2008). Synthesis of multi-ring (p-Alkyl benzoyloxy)benzoic acids by selective oxidation, *Chinese J. Org. Chem.*, *28*, 1948–1953.
[17] Leclair, S., Mathew, L., Giguere, M., Motallebi, S., & Zhao, Y. (2003). *Macromolecules*, *36*, 9024.

[18] Sevigny, S., Bouchard, L., Motallebi, S., & Zhao, Y. (2003). Photoinduced alignment of ferroelectric liquid crystals using azobenzene polymer networks of polyethers and polyepoxides. *Macromolecules*, *36*, 9033–9041.

[19] Yu, Y., Maeda, T., Mamiya, J.-I., & Ikeda, T. (2007). Photomechanical effects of ferroelectric liquid-crystalline elastomers containing azobenzene chromophores. *Angwandte Chemie, international edition*, *46*, 881–883.

[20] Hunter, C. A., & Sarson, L. D. (1996). Azobenzene-porphyrins. *Tetrahedron Lett.*, *37*, 699–702

[21] Cevasco, G., & Thea, S. (1999). Mechanism of alkaline hydrolysis of some HO-p-COOAr acyl derivatives. *J. Org. Chem.*, *64*, 5422–5426.

[22] Arias, J., Bardaj, M., Espinet, P., Folcia, C. L., Ortega, J., *et al.* (2009). Azo isocyanide gold(I) liquid crystals, highly birefringent and photosensitive in the mesophase. *Inorg. Chem.*, *48*, 6205–6210.

[23] Srinivasan, M. V., & Roy, P. K. A. (2013). Investigations on photo and electrically switchable asymmetric bent-core liquid crystals. *New J. Chem.*, *37*, 1584–1590.

[24] Zheng, M.-Y., Wei, Y.-S., Gu, Y.-Z., & Wang, S. (2014). Multi-rings aromatic aldehyde liquid crystal with azo linkage and their photosensitivity in mesophase. *Mol. Cryst. Liq. Cryst.*, *593*, 151–164