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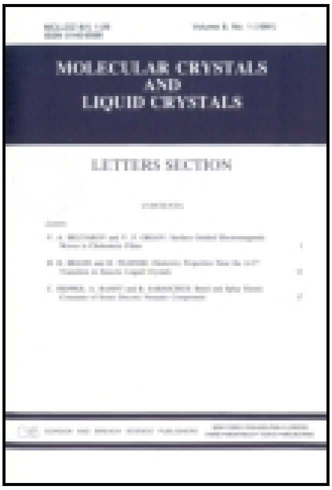

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# Multirings Aromatic Aldehyde Liquid Crystal with Azo Linkage and Their Photosensitivity in Mesophase

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# Multirings Aromatic Aldehyde Liquid Crystal with Azo Linkage and Their Photosensitivity in Mesophase

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*Ten new rod-like aromatic aldehyde liquid crystalline molecules with azo linkage were synthesized, in which bi(*trans*-cyclohexyl), cyclohexyl phenyl, and biphenyl carboxylic acid mesogenic cores with terminal ethyl,* n*-propyl,* n*-butyl, and* n*-pentyl substituents were esterified with azo benzoic aldehyde. These molecules were designed in an attempt to construct a series of new azo liquid crystalline molecules to investigate the influence of ultraviolet (UV) light on their mesophase. All 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 exhibited liquid crystalline phase that belonged to nematic and photosensitive properties. Their temperature ranges of mesophase are from 101 °C to 150 °C. Under irradiated 365 nm UV light, they showed photosensitivity in the solvent of methanol. Observed under HS-POM, the UV light also did change the textures of these compounds. The result showed that terminal ethyl is enough for these molecules to exhibit wider temperature range of mesophase, and these new molecules have photosensitivities observed under illumination of UV light not only in solution but also in mesophase due to the change of their structures from trans isomer to cis one.*

**Keywords** Aromatic aldehyde; azo group; liquid crystals; photosensitivity

## 1. Introduction

To investigate the relationship between molecular structures and properties is a major task of material chemistry. Modification of molecular structures to make them response to outer stimuli such as magnetism, thermal, and light is an important way to innovate specific materials [1]. Some aromatic azo compounds are always key raw materials widely used in industry as organic dyes [2, 3], food additives [4], radical reaction initiators [5], and therapeutic agents [6]. Recently, a great interest is attracted to molecules that have access to two or more forms, the interconversion of which can be triggered by external stimulus [7–9]. Among them, azo-functionalized materials are of great interest due to their photosensitive nature, which can be exploited for optical and optoelectronic devices [10]. There were a lot of functional azo compounds that have been designed and synthesized in recent years

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[11, 12]. Some of them are produced by connecting azo group with liquid crystalline cores [13, 14]. Even an article focused on studying the effect of UV light on solid state of azo compounds [15]. But there is little report involved in studying the influence of UV light on mesophase of azo liquid crystal molecules.

As it is known to all, the molecular architecture is an important factor which governs the liquid crystalline properties of any compound. Liquid crystalline molecules normally consist of an aromatic molecular core and two terminal chains. Azo liquid crystals reported were always designed with terminal-longer alkoxy ($n \geq 12$ or $n \geq 14$) groups [16 , 17], which are easy to be synthesized by converting hydroxy into different ethers in one-step reaction. In spite of being more stable than alkoxy, terminal alkyls always formed by multistep reactions are complicated to prepare so that they are seldomly used in constructing molecules of liquid crystals. Although some papers studied the effect of polar end groups on the mesomorphic property [18], few of them involved aldehyde as an end group. Our former work has designed some liquid crystals with terminal short-chain alkyls ($n \geq 2$) and a polar end group of CHO [19], which has mid polarity, thermostability, and wider temperature range of mesophase than other common functional groups with similar structure, for example alkyls, alkoxys, or cyano group. In addition, molecules with structures of aromatic aldehyde are also easier to be converted into other groups, such as aromatic acid [20], Schiff base [21], or other functional molecules [22]. Sometimes liquid crystals with aldehyde are able to be used as stationary phases to separate special mixtures [23]. From this point of view, we have designed and synthesized here 10 rod-like liquid crystalline molecules consisted by terminal short-chain alkyls ($n \geq 2$), aldehyde, and azo linkage. By changing the terminal double rings from cyclohexyl benzene to biphenyl or bicyclohexane, the effect of these variations on their liquid crystalline properties and their photosensitivity was also studied.

## 2. Experimental Section

### 2.1 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 were obtained from commercial sources and used without further purification.

### 2.2 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$^{-1}$. Elemental analyses were conducted by PE-2400 (Perkin Elmer). Irradiation of every sample was carried out by hand-held UV lamp ZF-7A (Shanghai Jiapeng Technology Co. Ltd.). UV spectra were determined by Agilent 8453 (Agilent Technologies). IR (KBr) spectra were recorded on a Vertex 70 (Bruker). 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, 1 °C·min$^{-1}$; and samples were protected by nitrogen. All images of textures were taken on a LV100POL Polarizing Optical Microscopy (Nikon) with LTS E350 thermal plate (Linkam) and heating rate 1 °C·min$^{-1}$.

### *2.3 Synthesis*

*2.3.1 Synthesis of 4-aminobezaldehyde.* A typical procedure for synthesis of $Na_2S_x$ is as follows. Twelve grams of $Na_2S$ (0.15 mol) was mixed with a solution of 12 g of NaOH and 200 mL of water at 65 °C. 5.4 g of sulphur (0.16 mol) was then added into the mixture, keeping the temperature of the solution, and stirring about 25 min. A dark red solution of $Na_2S_x$ was then obtained. 27.4 g of *p*-nitrotoluene (0.2 mol) and a few drops of DMF were dissolved in ethanol (100 mL, 95%) and then heated at 80 °C. $Na_2S_x$ solution was dropped into the mixture and heated at 90 °C for 3.5 hr. The extra reactant was removed by wet distillation until there is no oily liquid in the distilled solution. The reaction solution was then filtered. The remainder was dried and recystallized by ether. A yellow crystal was obtained with a yield of 80%.

4-aminobezaldehyde m.p. 71–72 °C

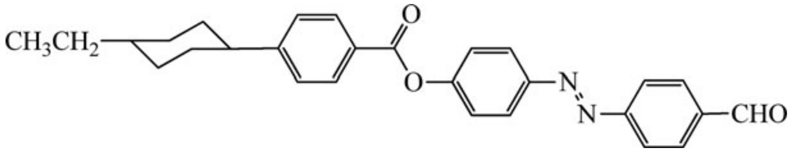
*2.3.2 Synthesis of 4′-Hydroxybenzene-azo-4-benzadehyde(1a).* 12.12 g of *p*-aminobezaldehyde (0.1 mol) and 250 mL of hydrogen chloric acid (2 mol·$L^{-1}$) were added into a flask. 7.72 g of $NaNO_2$ (0.102 mol) dissolved in 25 mL of water was then added dropwise to the solution with constant stirring for 6 hr under ice bath. 9.40 g of phenol (0.1 mol) mixed with 4 g of NaOH and 200 mL of water was added into the flask and the pH value of the solution was regulated to 8. The reaction mixture was stirred vigorously in a ice bath for 4 hr. The reaction solution was then filtered. The remainder was dried and recrystallised by ethnol. Finally, 18.88 g of 4′-hydroxy-azo-4-benzaldehyde was obtained as orange crystal with the yield of 84%.

$^1$H NMR (500 MHz, $CDCl_3$, ppm): 9.874 (s, H), 6.003 (s, H), 8.124 (d, 2H, $J = 9.0$), 7.763–8.012 (m, 4H), 6.937 (d, 2H, $J = 9.0$).

IR (KBr, pellet, $cm^{-1}$): 3421, 1671, 1599, 1588, 1559, 1542, 1466, 1398, 1355, 1205, 1138, 1102, 936, 851, 840, 660

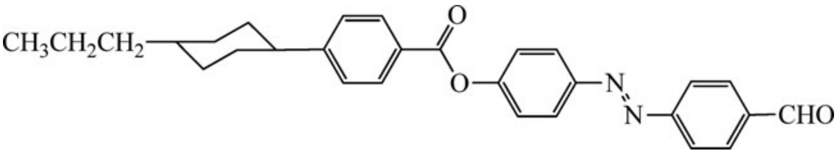
*2.3.3 Synthesis of Compound **2a**.* was prepared by stirring a mixture of **1a** (1.16 g, 5 mmol), $SOCl_2$ (0.59 g, 5 mmol), and several drops of DMF in toluene (30 mL) at ambient temperature for 5 hr. The solvent was removed under vacuum. A brown liquid (**2a**) was obtained and used to next step without further purifying.

*2.3.4 Synthesis of Compounds **3a**.* was obtained by adding a solution of **2a** and $CH_2Cl_2$ (20 mL) into a mixture of 4-(4-hydroxyphenylazo) benzaldehyde (1.13 g, 5 mmol) and triethylamide (0.9 mL, 5 mmol) in $CH_2Cl_2$ (40 mL) and stirring at ambient temperature for 12 hr. The reacting solvent was removed under vacuum. The residue was washed by 5% (mass fraction) NaOH and water to get an orange-colored product. The crude product was dried and recystalized with THF. An orange powder (**3a**, 1.82 g) was obtained with a yield of 85% (two steps). The **3b**, **3c**, **3d**, **3e, 3f, 3g, 3h, 3i,** and **3j** were also prepared by using similar procedure, and their yields were 86%, 84%, 80%, 83%, 81%, 85%, 82%, 80%, and 82% respectively.



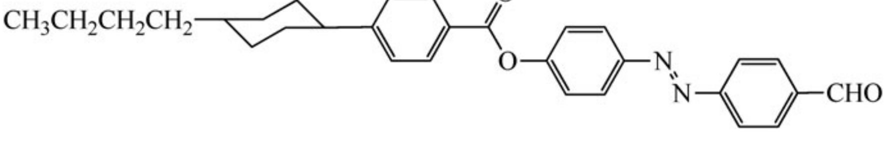
**Structural formula of 3a**

4-(4-(4-(4-ethylcyclohexyl) benzoyloxy) phenyldiazenyl) benzaldehyde (**3a**), Relative molecular mass: 440.53; the mass fraction detected by LC is 99.1%, yield: 85%, orange powder, m.p 128–129 °C; Anal. Calcd. for $C_{28}H_{28}N_2O_3$: C 76.34, H 6.41, N 6.36, found: C 76.23, H 6.55, N 6.23; IR (KBr) $\nu$: 2957, 2917 (s, C–H), 2849, 2729 (s, H of aldehyde), 2361, 2342, 1741 (vs, C=O), 1703 (vs, C = O), 1648, 1636 (N = N), 1598, 1559, 1541, 1508, 1495, 1458 (m, ArH), 1418, 1375, 1308, 1272, 1223, 1198, 1178, 1139, 1099, 1063, 1009 (vs, C–O–C), 985, 924, 884 (s, *trans*-R–N=N–R), 837, 819 (w, 1,4-Ar), 775 (w, $(CH_2)n$), 761, 699, 684 $cm^{-1}$; MS (70 ev) *m/z* (%): 440($M^+$, 1.60), 426 (0.14), 364 (0.05), 323 (0.11), 293 (0.02), 243 (0.40), 217 (1.55), 215 (100), 199 (0.05), 187 (0.16), 171 (0.05), 157 (0.14), 145 (0.30), 131 (1.14), 121 (1.20), 105 (3.30), 91 (2.23), 79 (0.55), 69 (0.69), 55 (0.52), 43 (0.31), 32 (0.32); $^1H$ NMR: 0.927 (t, 3H, $J = 7.2$ Hz, $CH_3$), 1.253–2.623 (m, 2H, $CH_2$), 1.253–2.633 (m, 10H, the proton of cyclohexane), 7.372, 7.404, 8.140 (d, $J = 8.4$ Hz, 8.8 Hz, 8.4 Hz, 2H of each), 8.046–8.066 (m, 6H), 10.114 (s,1H, CHO)



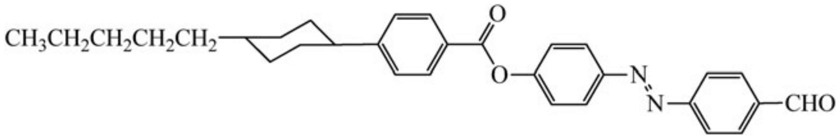
**Structural formula of 3b**

4-(4-(4-(4-*n-propyl*cyclohexyl) benzoyloxy) phenyldiazenyl) benzaldehyde (**3b**), Relative molecular mass: 454.56, the mass fraction detected by LC is 98.9%, yield: 86%, orange powder, m.p. 140–141 °C; Anal. Calcd. for $C_{29}H_{30}N_2O_3$: C 76.63, H 6.65, N 6.16 found: C 76.44, H 6.87, N 6.01; IR (KBr) $\nu$: 2953, 2921 (s, C–H), 2843, 2736 (s, H of aldehyde), 2361, 2343, 1734 (vs,C=O), 1696 (vs, C=O), 1654, 1637 (N=N), 1589, 1559, 1542, 1494 (m, ArH), 1448, 1418, 1376, 1309, 1266, 1223, 1198, 1176, 1137, 1099, 1060, 1010 (vs, C–O–C), 968, 924, 882 (s, *trans*-H—N=N—R), 847, 815 (w, 1,4-Ar), 761 (w, $(CH_2)n$), 727, 698 $cm^{-1}$; MS (70 ev) *m/z* (%): 454($M^+$, 1.48), 440 (0.10), 337 (0.12), 321 (0.02), 307 (0.08), 257 (0.81), 243 (0.20), 229 (100), 227 (2.26), 209 (1.11), 199 (0.03), 187 (0.32), 171 (0.08), 157 (0.17), 145 (0.29), 131 (1.31), 117 (1.01), 105 (3.52), 91 (2.22), 81 (0.54), 67 (0.66), 55 (0.62), 43 (0.24), 32 (0.23); $^1H$ NMR: 0.904 (t, 3H, $J = 7.5$ Hz, $CH_3$), 1.120–1.158 (m, 2H, $CH_2$), 1.304–1.408 (m, 2H, $CH_2$), 1.433–2. 638 (m, 10H, the proton of cyclohexane), 7.375, 7.445, 8.154 (d, $J = 8.0$ Hz, 8.0 Hz, 8.0 Hz, 2H of each), 8.137 (b, 6H), 10.104 (s,1H, CHO).



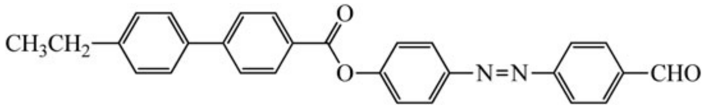
**Structural formula of 3c**

4-(4-(4-(4-*n-butyl*cyclohexyl) benzoyloxy) phenyldiazenyl) benzaldehyde (**3c**), Relative molecular mass: 468.59, the mass fraction detected by LC is 98.7%, yield: 84%, orange powder, m.p.141–142; Anal. Calcd. for $C_{30}H_{32}N_2O_3$: C 76.90, H 6.88, N 5.98; found C 76.77, H 6.92, N 5.73; IR (KBr) $\nu$: 2957, 2917 (s, C–H), 2872, 2861, 2712 (C–H of aldehyde), 2360, 2342, 1745 (vs, C=O), 1699 (vs, C=O), 1653, 1636 (N=N), 1587, 1559, 1541, 1495 (m, ArH), 1445, 1418, 1375, 1339, 1300, 1296, 1262, 1223, 1203, 1180, 1138, 1099, 1061, 1008 (vs, C—O—C), 879 (s, *trans*-R—N=N—R), 840, 814 (w, 1,4-Ar), 779, 760, 726 (w, $(CH_2)n$), 698, 682, 659, 633 cm$^{-1}$; MS (70 ev) *m/z* (%): 468 (M$^+$, 1.85), 454 (0.09), 351 (0.18), 321 (0.02), 299 (0.03), 277 (0.19), 257 (0.24), 243 (100), 225 (0.41), 199 (0.07), 185 (0.15), 171 (0.06), 157 (0.17), 145 (0.30), 131 (1.22), 117 (0.83), 105 (0.12), 91 (2.84), 81 (0.62), 67 (0.74), 55 (1.05), 43 (0.30), 32 (0.25); $^1$H NMR: 0.910–1.080 (m, 5H, $CH_3CH_2$), 1.252–1.270 (m, 2H, $CH_2$), 1.414 (t, 2H, $J$ = 7.2 Hz, $CH_2$), 1.433–2.542 (m, 10H, the proton of cyclohexane), 7.999 (d, $J$ = 8.8 Hz, 2H), 7.25 (d, $J$ = 8 Hz, 4H), 8.036 (b, 6H), 10.107 (s, 1H, CHO)



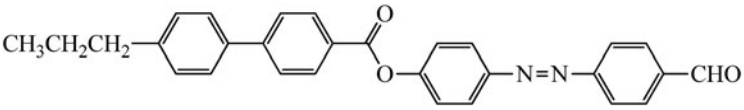
**Structural formula of 3d**

4-(4-(4-(4-*n-pentyl*cyclohexyl) benzoyloxy) phenyldiazenyl) benzaldehyde (**3d**), Relative molecular mass: 482.61; the mass fraction detected by LC is 98.8%, yield: 80%, orange powder, m.p.161–162 °C; Anal. Calcd. for $C_{31}H_{34}N_2O_3$: C 77.15, H 7.10, N 5.80; found C 77.02, H 7.25, N 5.69; IR (KBr) $\nu$: 2950, 2916 (s, C–H), 2847, 2741 (C–H of aldehyde), 1736 (vs, C=O), 1699 (vs, C=O), 1638 (N=N), 1588, 1493, 1485 (m, ArH), 1448, 1418, 1264, 1196, 1177, 1137, 1064, 1014 (vs, C—O—C), 884 (s, *trans*-R—N=N—R), 839, 816 (w, 1, 4-Ar), 763, 727 (w, $(CH_2)n$), 699, 683, 659, 549 cm$^{-1}$, MS (70 ev) *m/z* (%): 482 (1.150), 274 (6.98), 257 (100), 255 (1.410), 229 (2.70), 226 (19.92), 211 (2.45), 185 (2.72), 169 (3.59), 162 (8.77), 150 (19.59), 148 (39.67), 141 (5.22), 131 (10.94), 126 (4.27), 121 (69.69), 117 (15.61), 115 (8.68), 105 (33.64), 93 (90.63), 91 (28.95), 81 (13.68), 77 (19.38), 69 (12.64), 55 (10.50), 44 (11.44), 36 (11.42), 32 (21.05); $^1$H NMR: 0.904 (t, 3H, $J$ = 7.2 Hz, $CH_3$), 1.25–1.29 (m, 4H, $CH_2CH_2$), 1.33 (m, 2H, $CH_2$), 1.40–2.96 (m, 10H, the proton of cyclohexane), 7.367, 7.402, 8.130 (d, $J$ = 8.0 Hz, 8.0 Hz, 8.0 Hz, 2H of each), 8.130 (b, 6H), 10.111 (s,1H, CHO)



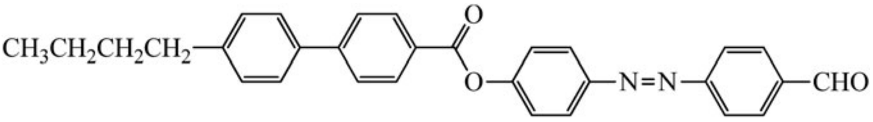
**Structural formula of 3e**

4-(4-(4-(4-*n*-ethylphenyl) benzoyloxy) phenyldiazenyl) benzaldehyde (**3e**), Relative molecular mass: 434.49, mass fraction detected by LC is 98.9%, yield: 83%, orange powder, m.p.171–172 °C; Anal. Calcd. for $C_{28}H_{22}N_2O_3$: C 77.40, H 5.10, N 6.45; found C 77.27, H 5.28, N 6.26; IR (KBr) $\nu$: 2967, 2918, 2874 (s, C-Hstretching vibration), 2849, 2734 (s, H of aldehyde), 2361, 2342, 1730 (vs, C=O), 1699 (vs, C=O), 1654, 1637 (N=N), 1598, 1495, 1458 (m, ArH), 1418, 1399, 1280, 1203, 1137, 1081, 1007 (vs, C—O—C), 891 (s, *trans*-H—N=N—R), 830 (w, 1,4-Ar), 779 (w, $(CH_2)n$), 760, 696 cm$^{-1}$; MS (70 ev) *m/z* (%): 434 (M$^+$, 3.16), 420 (0.22), 406 (0.12), 329 (0.02), 317 (0.11), 300 (0.03), 285 (0.02), 243 (0.14), 226 (0.77), 209 (100), 207 (0.88), 194 (0.10), 181 (3.30), 166 (3.36), 152 (6.83), 141 (0.43), 121 (0.93), 105 (0.70), 93 (1.05), 77 (0.48), 65 (0.68), 57 (0.23), 44 (0.54), 32 (0.40); $^1$H NMR: 1.230 (t, 3H, $J$ = 7.6 Hz, $CH_3$), 2.659 (q, 2H, $J$ = 7.6 Hz, $CH_2$), 7.266, 7.372, 7.534, 7.608, 8.208 (d, $J$ = 8.0 Hz, 8.8 Hz, 8.0 Hz, 8.4 Hz, 8.4 Hz, 2H of each), 7.985 (b, 6H), 11.02 (s, 1H, COOH)



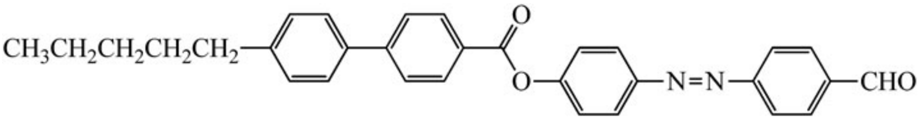
**Structural formula of 3f**

4-(4-(4-(4-*n*-propylphenyl) benzoyloxy) phenyldiazenyl) benzaldehyde (**3f**), Relative molecular mass: 448.51, mass fraction detected by LC is 98.5%, yield: 81%, orange powder, m.p.174–175 °C; Anal. Calcd. for $C_{29}H_{24}N_2O_3$: C 77.66, H 5.39, N6.25; found C 77.73, H 5.43, N 6.19; IR (KBr) $\nu$: 2958, 2928 (s, C—H), 2869, 2728, 2676, 2552, 2360, 2341, 1732 (vs, C=O), 1689 (vs, C=O), 1588, 1558, 1507, 1466 (m, ArH), 1428, 1398, 1284, 1206, 1139, 1103, 1006 (vs, C—O—C), 948, 838, 823 (w, 1, 4-Ar), 773, 730 (w, $(CH_2)$n), 660, 544 $cm^{-1}$; MS (70 ev) *m/z* (%): 448 ($M^+$, 5.64), 371 (0.07), 359 (0.06), 344 (0.03), 284 (0.02), 268 (0.04), 259 (0.06), 237 (0.81), 224 (0.35), 211 (0.23), 193 (0.03), 181 (0.19), 164 (0.20), 147 (100), 131 (0.66), 121 (1.30), 119 (3.92), 104 (0.51), 93 (1.64), 91 (7.77), 65 (1.82), 44 (1.37), 32 (0.32), $^1$H NMR: 0.981 (t, 3H, $J = 7.2$ Hz, $CH_3$), 1.646–1.738 (m, 2H, $CH_2$), 2.649 (t, 2H, $J = 7.2$, $CH_2$), 7.293 (d, 4H, $J = 8.0$ Hz), 7.569, 7.695, 7.932, 8.167, 8.281 (d, $J = 8.4$ Hz, 8.8 Hz, 8.4 Hz, 8.0 Hz, 8.0 Hz, 2H of each), 10.095 (s,1H, CHO)



**Structural formula of 3g**

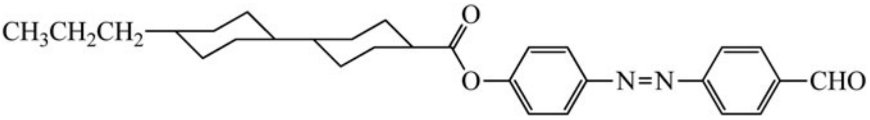
4-4-(4-(4-(4-*n*-butylphenyl) benzoyloxy) phenyldiazenyl) benzaldehyde (**3g**), Relative molecular mass: 462.54; the mass fraction detected by LC is 98.6%, yield: 85%, orange powder, m.p. 126–127 °C; Anal. Calcd. for $C_{30}H_{26}N_2O_3$: C 77.90, H 5.67, N 6.06; found C 78.01, H 5.79, N 5.97; IR (KBr) $\nu$: 2958, 2927 (s, C–H), 2855, 2728 (s, H of aldehyde), 2361, 1732 (vs, C = O), 1697 (vs, C = O), 1654, 1637 (m, N = N), 1600, 1559, 1541, 1495, 1458 (m, ArH), 1541, 1495, 1458, 1397, 1289, 1202, 1137, 1079, 1006 (vs, C–O–C), 891, 825 (w, 1, 4-Ar), 762, 737 (w, $(CH_2)$n), 694 $cm^{-1}$ MS (70 ev) *m/z* (%): 462 ($M^+$, 1.02), 448 (0.02), 419 (0.08), 357 (0.05), 345 (0.06), 330 (0.02), 304 (0.04), 271 (0.36), 251 (0.30), 237 (100), 235 (0.80), 226 (5.24), 223 (0.34), 211 (0.44), 194 (0.56), 180 (0.25), 167 (1.61), 153 (2.02), 141 (0.38), 121 (5.66), 115 (0.49), 105 (1.88), 93 (8.44), 92 (0.34), 77 (1.58), 65 (3.88), 57 (0.56), 39 (0.80), 32 (0.36); $^1$H NMR: 0.961 (t, 3H, $J = 7.2$ Hz, $CH_3$), 1.349–1.432 (m, 2H, $CH_2$), 1.619–1.695 (m, 2H, $CH_2$), 2.689 (t, 2H, $J = 7.6$ Hz, 7.315, 7.444, 7.596, 7.754, 8.279 (d, $J = 8.4$ Hz, 8.8 Hz, 8.0 Hz, 8.4 Hz, 8.4 Hz, 2H of each), 8.053 (b, 6H), 10.119 (s, 1H, CHO).



**Structural formula of 3h**

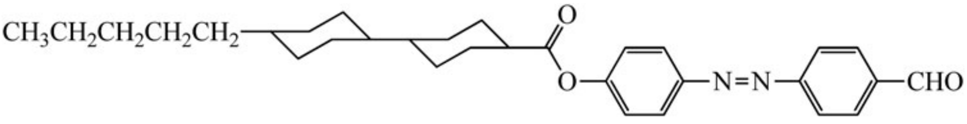
4-(4-(4-(4-*n*-pentylphenyl) benzoyloxy) phenyldiazenyl) benzaldehyde (**3h**), Relative molecular mass: 476.57; the mass fraction detected by LC is 98.8%, yield: 82%, orange powder, m.p.140–141 °C; Anal. Calcd. for $C_{31}H_{28}N_2O_3$: C 78.13, H 5.92, N 5.88; found

C 78.00, H 6.09, N 5.67; IR (KBr) $\nu$: 2954, 2922, 2871 (s, C–H), 2854, 2734 (s, H of aldehyde), 2361, 1729 (vs, C=O), 1704 (vs, C=O), 1654, 1637 (m, N=N), 1602, 1581, 1496, 1457 (m, ArH), 1437, 1399, 1273, 1200, 1175, 1138, 1073, 1008 (vs, C—O—C), 891, 843, 817 (w, 1, 4-Ar), 782, 763, 719 (w, $(CH_2)n$), 693, 664, 629, 553 $cm^{-1}$, MS (70 ev) *m/z* (%): 476 ($M^+$, 1.49), 419 (0.10), 359 (0.11), 331 (0.07), 285 (0.12), 268 (0.20), 253 (2.07), 251 (100), 237 (0.17), 226 (0.60), 211 (0.50), 194 (0.82), 181 (0.22), 167 (2.05), 153 (2.69), 133 (0.43), 121 (1.86), 105 (0.74), 93 (1.51), 77 (0.34), 65 (0.63), 57 (0.30), 44 (1.90), 32 (1.47); $^1$H NMR: 0.915 (t, 3H, $J = 6.8$ Hz, $CH_3$), 1.341–1.377 (m, 4H, $CH_2CH_2$), 1.654–1.687 (m, 2H, $CH_2$), 2.672 (t, 2H, $J = 7.8$ Hz, $CH_2$), 7.308, 7.436, 7.590, 7.746, 8.272 (d, $J = 8.0$ Hz, 8.8 Hz, 8.0 Hz, 8.4 Hz, 8.0 Hz, 2H of each), 8.049–8.079 (m, 6H), 10.110 (s,1H, CHO).



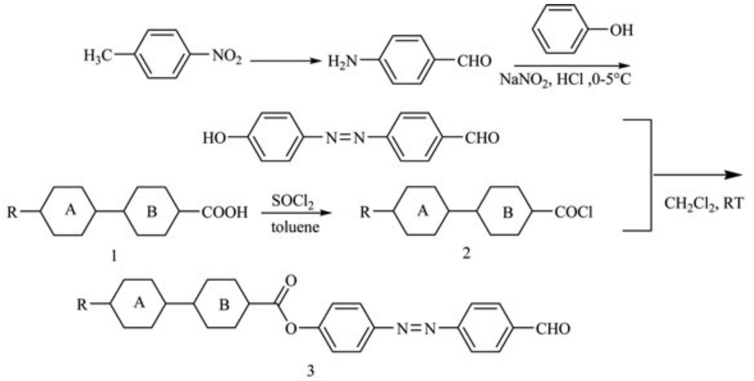
**Structural formula of 3i**

4-(4-(4-(4-*n*-propylcyclohexyl) cyclohexylacyloxy) phenyldiazenyl) benzaldehyde (**3i**), Relative molecular mass: 460.61; the mass fraction detected by LC is 99.1%, yield: 80%, orange powder, m.p.128–129 °C; Anal. Calcd. for $C_{29}H_{36}N_2O_3$: C 75.62, H 7.88, N 6.08; found C 75.52, H 7.97, N 5.91; IR (KBr) $\nu$: 2926(s, C–H), 2849, 2731 (s, H of aldehyde), 1755 (vs, C=O), 1692 (vs, C=O), 1655, 1638 (m, N=N), 1559, 1494, 1458 (m, ArH), 1376, 1326, 1202, 1161, 1123 (vs, C—O—C), 988, 926, 880, 856, 837 (w, 1, 4-Ar), 801, 763, 727 (w, $(CH_2)n$), 548 $cm^{-1}$, MS (70 ev) *m/z* (%): 460 ($M^+$, 4.41), 432 (0.08), 343 (0.11), 325 (0.05), 299 (0.21), 269 (0.05), 251 (0.18), 237 (2.03), 235 (14.42), 226 (100), 217 (2.04), 207 (23.19), 188 (0.31), 175 (0.20), 165 (1.57), 151 (9.37), 137 (15.50), 135 (1.28), 125 (29.89), 120 (1.65), 111 (47.81), 105 (2.96), 97 (29.42), 95 (14.23), 92 (0.98), 85 (1.24), 83 (38.62), 77 (1.78), 69 (40.78), 67 (7.06), 64 (0.59), 55 (9.65), 51 (0.45), 43 (1.12), 32 (1.11). $^1$H NMR: 0.914 (t, 3H, $J = 7.2$ Hz, $CH_3$), 1.037–1.132 (m, 4H, $CH_2CH_2$), 1.208–2.612 (m, 20H, the proton of cyclohexane), 7.368, 7.402, 8.047, 8.141 (d, $J = 8.4$ Hz, 8.8 Hz, 8.4 Hz, 8.8 Hz, 2H of each), 10.111 (s, 1H, CHO).



**Structural formula of 3j**

4-(4-(4-(4-*n*-pentylcyclohexyl) cyclohexylacyloxy) phenyldiazenyl) benzaldehyde (**3j**), Relative molecular mass: 488.66; the mass fraction detected by LC is 99.2%, yield: 82%, orange powder, m.p. 125–126 °C; Anal. Calcd. for $C_{31}H_{40}N_2O_3$: C 76.19, H 8.25, N 5.73; found C 76.01, H 8.31, N 5.64; IR (KBr) $\nu$: 2954, 2922 (s, C–H), 2854, 2734 (s, H of aldehyde), 2361, 2343, 1729, 1704, 1654, 1637 (m, N=N), 1602, 1581, 1496, 1457 (m, ArH), 1399, 1386, 1273, 1200, 1175, 1138, 1096, 1073, 1008 (vs, C–O–C), 891, 843, 817, 782, 763, 726, (w, $(CH_2)n$), 693, 664, 553 $cm^{-1}$; MS (70 ev) *m/z* (%): 488 ($M^+$, 3.29), 262 (12.37), 245 (2.43), 235 (14.78), 226 (100), 212 (1.96), 179 (2.84), 165 (3.57), 153 (10.73), 139 (23.22), 135 (2.73), 125 (10.21), 121 (32.07), 120 (3.70), 109 (41.20), 105 (5.57), 97 (49.66), 95 (19.59), 92 (2.29), 83 (54.23), 79 (2.47), 69 (24.60), 67 (10.15), 57 (12.76), 55



**a**: R = ethyl, 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.; **e**: R = ethyl, A = *phen*yl, B = phenyl; **f**: R = *n*-propyl, A = phenyl, B = phenyl; **c**: R = *n*-butyl, A = phenyl, B = phenyl; **g**: R = *n*-pentyl, A = phenyl, B = phenyl; **h**: R = *n*-pentyl, A = phenyl, B = phenyl; **i**: R = *n*-propyl, A = *trans*-cyclohexyl, B = *trans*-cyclohexyl; **j**: R = *n*-pentyl, A = *trans*-cyclohexyl, B = phenyl.

**Scheme 1.** The synthesis process of resulting compounds,

(16.71), 45 (10.58), 44 (27.56), 40 (5.01), 32 (52.37); $^1$H NMR: 0.96 (t, 3H, $J = 6.5$ Hz, CH$_3$), 1.25–1.33 (m, 6H, CH$_2$CH$_2$CH$_2$), 1.60 (m, 2H, CH$_2$), 1.21–1.60 (m, 20H, the proton of cyclohexane), 7.251, 7.992 (d, $J = 8.4$ Hz, 8.4 Hz,2H of each), 8.030 (b, 4H), 10.101 (s,1H, CHO).

## 3. Results and Discussion

### 3.1 Photosensitivity of Target Molecules in Solution

All compounds were synthesized according to Scheme 1 and their structural data are shown. The spectral values are in accordance with the assigned structure. Under illumination of UV light, the azo functional group can do isomerization from the more stable *trans*-isomer to the *cis* one as stated earlier. As the expose time increases, concentration of trans isomer decreases and conversely, concentration of *cis*-isomer increases. The UV spectra of all target compounds were recorded over the same time intervals until photostationary states were reached. The spectrum variations verified the *trans*-to-*cis* isomerization of the azo chromophores. The $\lambda_{\max}$ in UV spectra of all compounds before and after irradiation are shown in Table 1. Figures 1 to 3 show changes in absorption intensities of compound **3b**, **3f**, and **3i** in methanol under irradiation of 365 nm UV light with time interval of every 10 min. These peaks have a relationship with the structure of each molecule. For example, the *trans*-isomer of **3a** shows a maximum absorbance at 332 nm associated with an azo $\pi$–$\pi^*$ transition, while the other peak at 242 nm is related to an aromatic $\pi$–$\pi^*$ transition (Table 1). Before irradiation, the $\lambda_{\max}$ were recorded at 241, 334 for **3b**, 327 for **3f**, and 230, 333 nm for **3i**, respectively. After irradiation, the $\lambda_{\max}$ were recorded at 245, 328 for **3b**, 293 for **3f**, and 232, 330 nm for **3i**, respectively. The highest photoisomerization of every compound is achieved within 70 min for illumination intensities of 105 $\mu$W.cm$^{-2}$ (365 nm). The observation of two isosbestic points, located at 291 nm and 394 nm in Fig. 1, 300 nm and 382 nm in Fig. 2, and 291 nm and 391 nm in Fig. 3, confirms the existence of only two compounds in each figure, the *cis* and *trans* isomers [24]. Upon irradiation with 365 nm UV light, the absorption peaks of **3b** at 241 nm and 334 nm decrease, while the other two at

**Table 1.** The $\lambda_{max}$ of target molecules before and after irradiation.

| | Before isomerization $\lambda_{max}\cdot$nm | | After isomerization $\lambda_{max}\cdot$nm | |
|---|---|---|---|---|
| Compd. | I | II | I | II |
| **3a** | 242 | 332 | 245 | 329 |
| **3b** | 241 | 334 | 245 | 328 |
| **3c** | 241 | 333 | 245 | 328 |
| **3d** | 241 | 333 | 245 | 329 |
| **3e** | — | 331 | — | 294 |
| **3f** | — | 327 | — | 293 |
| **3g** | — | 337 | — | 293 |
| **3h** | — | 329 | — | 294 |
| **3i** | 230 | 333 | 232 | 330 |
| **3j** | 230 | 333 | 232 | 326 |

245 and 328 nm increase. Finally, the peaks at 241 and 334 nm almost disappear. The peak of **3f** at 362 nm also disappears gradually, while the other at 293 nm emerges as the time of irradiation increases. The peaks of **3i** at 230 nm and 333 nm gradually transfer to 232 nm and 326 nm. The process indicates the transfer of molecular configurations from *trans* to *cis* isomer. We can see from Table 1 that before or after irradiation of UV light, **3a**, **3b**, **3c**, and **3d** with terminal cyclohexane benzene rings have all two main absorption peaks, **3e**, **3f**, **3g**, and **3h** with terminal double benzene rings have all one peak, while **3i** and **3j** with terminal double cyclohexane rings have two peaks. This tells us that the compounds with similar terminal structures have similar absorptions before or after they transfer their structures. But the longer rod-like structure of liquid crystals makes it difficult to convert from one isomer to the other. It almost takes 60 to 70 min for these target compounds to reach their photostationary states (shown in Table 2).

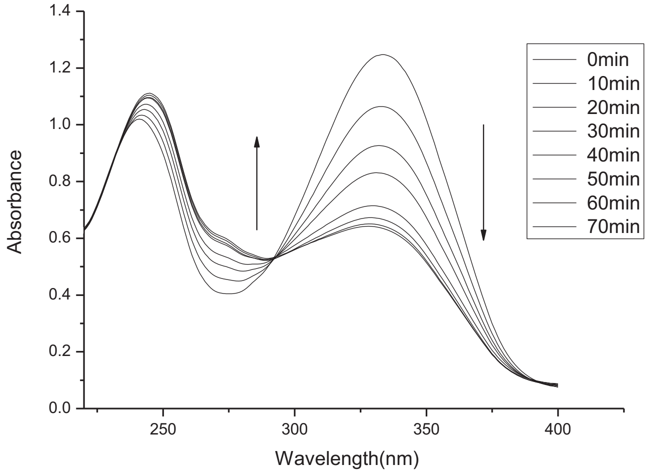


**Figure 1.** The change in the UV spectrum of **3a** caused by photoisomerization (in methanol).

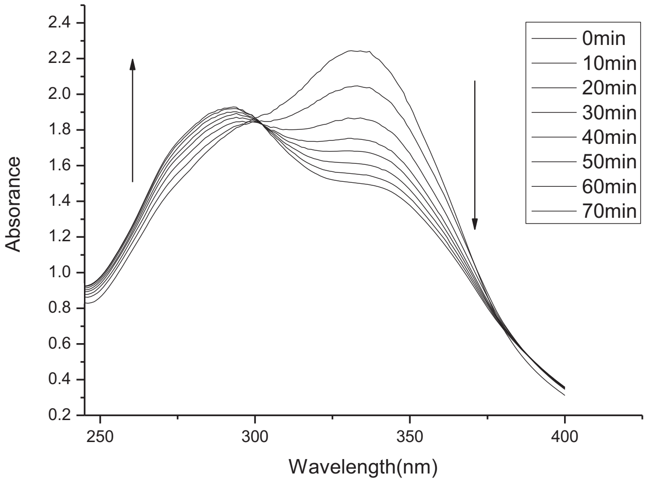


**Figure 2.** The change in the UV spectrum of **3f** caused by photoisomerization (in methanol).

### *3.2 Liquid Crystalline Properties and Photo-Sensitivity in Mesophase*

The mesophases of all these molecules were observed by the DSC and the mesogenic behaviors were studied by POM. The POM micrographs are shown in Figure 4. All the target compounds even the one with terminal ethyl chain exhibit the appearance of textures that belong to nematic. The temperature ranges of mesophase of these compounds are more than 101 °C. Although **3g** has not found any clear point during the determination of DSC, its mesophase is still observed under POM. Except **3g**, all the other compounds exhibit clear points before they decompose as shown Table 3. Among them, **3i** and **3g** whose A and B rings are both cyclohexanes have widest temperature range of mesophase. Compared with other liquid crystals had aldehyde group [19], these azo aromatic aldehydes have higher

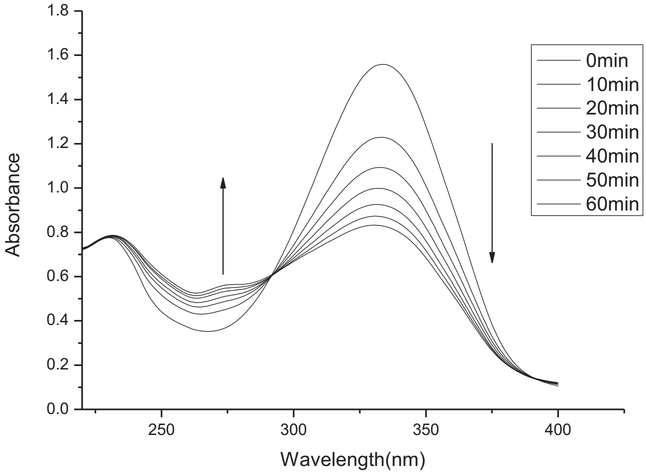


**Figure 3.** The change in the UV spectrum of **3a** caused by photoisomerization (in methanol).

**Table 2.** The maximum time of *trans*-to-*cis* isomerization in solution and mesophase (min)

| Sample | 3a | 3b | 3c | 3d | 3e | 3f | 3g | 3h | 3i | 3j |
|---|---|---|---|---|---|---|---|---|---|---|
| Time/min (in solution) | 60 | 60 | 60 | 70 | 60 | 70 | 70 | 70 | 60 | 70 |
| Time/min (in mesophase) | 70 | 70 | 80 | 90 | 70 | 80 | 90 | 90 | 70 | 80 |

thermostability and wider temperature range of mesophase. They also have wider range of mesophase than other polymers with azo group [25].

Since the compounds display photosensitivity in solution, it is also interesting to check this behavior in their mesophase. The main feature of azo liquid crystals, in which the azo moiety plays both roles as a mesogen moiety and a photosensitive moiety, is that they show a liquid crystal phase only if the azo moiety is in the *trans*-form while they never show any liquid crystal phase after melting when azo moiety is in the *cis*-form. If azo liquid crystals can do isomerization from trans to cis in mesophase, the textures will disappears. We chose **3d** as the first sample to study this property due to its melting point not being the highest or lowest one. After exposing the texture of **3d** under UV light of illumination intensities of 105 $\mu$W.cm$^{-2}$ (365 nm) with time interval of every 10 min, the changes were observed by POM (shown as Figure 5). From these pictures, we can see that the bright area in the texture decreases as the expose time increases, i.e., the texture gradually disappears with the increasing of expose time under UV light, indicating the trans to cis isomerization

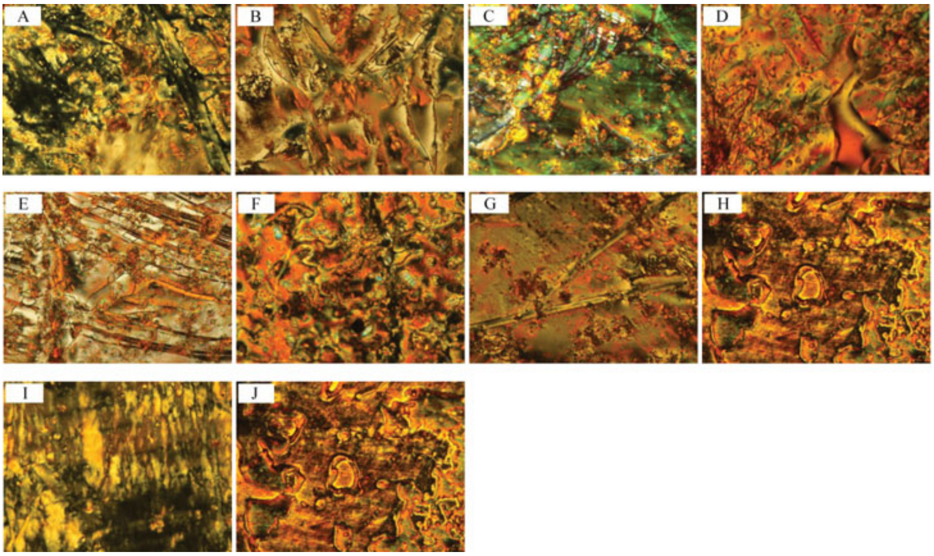


**Figure 4.** The textures of resulting compounds observed under polarizing optic microscope during heating process. (a): The schlieren texture of **3a** taken at 182 °C ×300; (b): The schlieren texture of **3b** taken at 170 °C ×300; (c): The schlieren texture of **3c** taken at 170 °C ×300; (d): The schlieren texture of **3d** taken at 179 °C ×300; (e): The schlieren texture of **3e** taken at 190 °C ×300; (f): The schlieren texture of **3f** taken at 196 °C ×300; (g): The schlieren texture of **3g** taken at 178 °C ×300; (h): The schlieren e texture of **3h** taken at 180 °C ×300; (i): The schlieren texture of **3i** taken at 153 °C ×300; (j): The schlieren texture of **3j** taken at 150 °C ×300.

**Table 3.** The results of DSC measurement of all compounds

| Compd. | 3a | 3b | 3c | 3d | 3e | 3f | 3g | 3h | 3i | 3j |
|---|---|---|---|---|---|---|---|---|---|---|
| m.p. (°C) | 128.5 | 140.9 | 141.3 | 161.8 | 170.1 | 174.5 | 140.8 | 139.3 | 128.19 | 124.7 |
| ΔH of m.p. ($J{\cdot}g^{-1}$) | 62.17 | 42.44 | 35.56 | 28.74 | 23.17 | 40.36 | 11.89 | 41.47 | 21.61 | 52.74 |
| c.p. (°C) | 268.9 | 241.1 | 280.7 | 282.1 | 275.2 | 276.5 | — | 260.5 | 277.2 | 280.1 |
| ΔH of c.p. ($J{\cdot}g^{-1}$) | 2.777 | 1.3838 | 1.140 | 0.5710 | 1.890 | 1.788 | — | 0.5067 | 1.050 | 0.925 |
| Range of mesophase (°C) | 140.4 | 101.2 | 139.4 | 120.3 | 105.1 | 102.0 | — | 121.2 | 146.0 | 155.4 |
| d.p. (°C) | 291.8–333.2 | 290.6–340.1 | 292.8—411.63 | 281.22–404.20 | 285.1–392.5 | 283.1–305.8 | 245.7–350.8 | 300.1–399.1 | 280.5–410.3 | 298.1–402.1 |

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

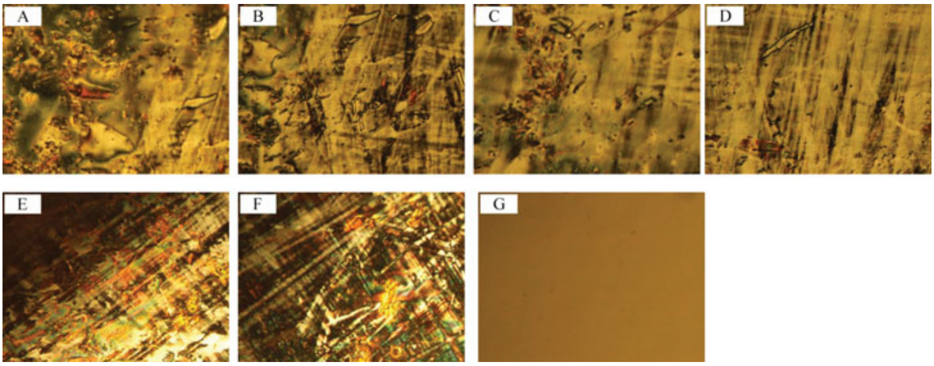


**Figure 5.** The texture change during UV radiation of **3d** at 185 °C ×300. A: texture after 10 min radiation; B: texture after 20 min radiation; C: texture after 30 min radiation; D: texture after 40 min radiation; E: texture after 50 min radiation; F: texture after 60 min radiation; G: texture after 70 min radiation

happens in mesophase. As shown in Table 2, the expose time for the other compounds reached their photostationary states are also obtained. The phenomena demonstrate that these azo liquid crystalline molecules can also do photoisomerization in mesophase. The maximum time used to do this (Table 2) suggests that it is more difficult to do isomerization in mesophase than in solution. It is because these molecules in mesophase still have higher intermolecular forces than in solution. We can see from Table 2 that molecules with longer structure are not easy to change their shape as they need more exposure time. Compared with other molecules with the same alkyl group, molecules with double terminal benzene rings need the longest time to change their shape.

## 4. Conclusion

In this paper, 10 new azo aromatic liquid crystal molecules with three different terminal double rings are successfully synthesized by a combination of long-rigid core involved in azo linkage and different terminal rings system with polar CHO and short-chain alkyls ($5 \geq n \geq 2$) as terminal units. Compared with rod-like azo liquid crystals in other publications [24 , 26 , 27], the structures we designed have wider temperature range of liquid crystalline phase even with a shorter alkyl chain ($n = 2$). The molecular structure allows these compounds to exhibit phase behaviors belonging to the nematic phase, providing us an opportunity to investigate their photosensitivity not only in solution but also in mesophase. All these compounds in a solution of methanol can gradually change their shape under exposure of UV light (365 nm). We also performed photoinduce studies on mesophase of compounds, which is seldomly reported until now. Results have shown that under exposure of UV light, the molecules are able to change their shapes even in mesophase, which are observed by gradually disappearing of mesogenic texture under POM. But owe to their longer rigid core, these compounds need longer exposure time of UV light to do isomerization in solution than other azo molecules without mesophase [28, 29].

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