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Title: "Synthesis and Physical Properties of Novel Liquid Crystals Containing Pyranobenzopyrans as a Core Structure**"**

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Details of material preparations

Diethyl 2-pentyl-2-propynylmalonate (10)

Compound **8** (10.0 g, 43.0 mmol) was added to a solution of sodium ethoxide (prepared from sodium (1.09 g, 47.0 mmol) in ethanol (70 ml)), and the whole mixture was warmed up to 50 °C and stirred for 1 h. To this warmed mixture compound **9** (13.5 g, 64.0 mmol) was added slowly, and the reaction mixture was refluxed for 1 h. After being cooled to room temperature, it was poured into cold sat. NH_4Cl and H_2O (1 : 1) solution (50 ml). The whole mixture was neutralized, and extracted with ethyl acetate (50 ml × 3). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was distilled at 146-147 °C / 4-5 Torr. Yield 9.90 g (85%), colorless oil; IR (neat) 3286, 2960, 2933, 2868, 1736, 1464, 1371, 1194, 1130, 1039, 860, 667 cm^{-1}; ^1H NMR δ 0.88 (t, 3H, J = 6.9 Hz), 1.25 (t, 6H, J = 6.9 Hz), 1.14-1.34 (m, 6H), 1.99 (t, 1H, J = 2.6 Hz), 1.97-2.06 (m, 2H), 2.82 (d, 2H, J = 2.6 Hz), 4.20 (q, 4H, J = 6.9 Hz).

Ethyl 2-pentyl-4-pentynoate (11)

A solution of **10** (9.00 g, 33.5 mmol) and lithium chloride (2.84 g, 67.0 mmol) in dimethyl sulfoxide (60 ml) containing water (0.6 ml) was heated at 185 °C for 12 h. The cooled reaction mixture was diluted with water (60 ml) and the organic layer was separated. The aqueous phase was extracted with ether (50 ml × 4). The organic layer and extracts were combined, washed with water (200 ml) and brine (200 ml), dried over $MgSO_4$, filtered, and concentrated. The residue was distilled at 82-85 °C / 2-3 Torr. Yield 4.60 g (70%), colorless oil; IR (neat) 3312, 2957, 2933, 2861, 1736,

1465, 1377, 1177, 1039, 857, 639 cm^{-1}; ^1H NMR δ 0.88 (t, 3H, *J* = 6.6 Hz), 1.27 (t, 3H, *J* = 6.9 Hz), 1.22-1.34 (m, 6H), 1.58-1.67 (m, 2H), 1.97 (t, 1H, *J* = 2.3 Hz), 2.35-2.58 (m, 3H), 4.17 (q, 2H, *J* = 6.9 Hz).

Ethyl 2-pentyl-5-(phenylthio)-4-pentenoate (12)

AIBN (2, 2'-azobisisobutyronitrile) (1.05 g, 6.51 mmol) was added to a stirred solution of **11** (4.25 g, 21.7 mmol) and thiophenol (2.35 g, 21.7 mmol) in benzene (50 ml) under nitrogen at room temperature. The reaction mixture was refluxed for 1 h, and quenched with 10% NaOH solution (30 ml). The organic layer was separated and the aqueous layer was extracted with ether (50 ml × 2). The combined organic layer was washed with water (150 ml), dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography with hexane / ethyl acetate (9 : 1) as an eluent. Yield 3.98 g (60%), a mixture of two stereoisomers (*E* / *Z* = 1 : 1 by ^1H NMR) (yellow oil). The isomers could not be separated at all by silica gel column chromatography; IR (neat) 3059, 2956, 2931, 2859, 1733, 1584, 1479, 1440, 1377, 1160, 1026, 951, 740, 691 cm^{-1}; ^1H NMR δ 0.88 (t, 3H, *J* = 6.6 Hz), 1.25 (t, 3H, *J* = 6.9 Hz), 1.18-1.32 (m, 6H), 1.42-1.63 (m, 2H), 2.29 (t, 1H, *J* = 7.6 Hz), 2.34-2.51 (m, 2H), 4.15 (q, 2H, *J* = 6.9 Hz), 5.76 (dt, *J* = 9.2, 7.3 Hz) and 5.84 (dt, *J* = 14.8, 6.9 Hz) for (*Z*) and (*E*) isomer, respectively, total 1H, 6.18 (dt, *J* = 14.8, 1.3 Hz) and 6.26 (dt, *J* = 9.2, 1.3 Hz) for (*E*) and (*Z*) isomer, respectively, total 1H, 7.16-7.40 (m, 5H).

2-Pentyl-5-(phenylthio)-4-penten-1-ol (13)

A solution of **12** (3.75 g, 12.2 mmol) in dry ether (50 ml) was added dropwise to a mixture of lithium aluminium hydride (0.90 g, 24.5 mmol) in dry ether (35 ml) with vigorous stirring at 0 °C and the mixture was stirred at room temperature for 2 h. After cooling to 0 °C, it was quenched by 4N NaOH solution (10 ml), and the mixture was stirred until the solution color turned to white. Then it was filtered *in vacuo* and washed with ether (50 ml). The filtrate was concentrated, and purified by silica gel column chromatography with hexane / ethyl acetate (9 : 1) as an eluent. Yield 3.30 g (quantitative), a mixture of two stereoisomers (*E* / *Z* = 1 : 1 by ^1H NMR) (yellow oil); IR (neat) 3357, 3060, 2927, 2858, 1584, 1478, 1440, 1026, 954, 902, 739, 691 cm^{-1}; ^1H

NMR δ 0.89 (t, 3H, *J* = 6.9 Hz), 1.28-1.33 (m, 8H), 1.47-1.70 (m, 1H), 2.21-2.35 (m, 2H), 3.53-3.63 (m, 2H), 5.76 (dt, *J* = 9.2, 7.6 Hz) and 5.88 (dt, *J* = 14.9, 7.3 Hz) for (*Z*) and (*E*) isomer, respectively, total 1H, 6.11 (dt, *J* = 14.9, 1.3 Hz) and 6.19 (dt, *J* = 9.2, 1.3 Hz) for (*E*) and (*Z*) isomer, respectively, total 1H, 7.10-7.29 (m, 5H).

4-Hexyloxysalicylaldehyde (15c)

A round bottomed flask was charged with **14** (5.00 g, 36.2 mmol), potassium carbonate (5.70 g, 41.3 mmol), potassium iodide (0.60 g, 3.62 mmol) under nitrogen atmosphere, and *N,N*-dimethylformamide (100 ml) was added. The mixture was stirred for 30 min at room temperature, and 1-bromohexane (8.95 g, 54.3 mmol) was added slowly, then it was stirred for 18 h at room temperature. The reaction mixture was treated under stirring with 10% NaOH solution (100 ml) and ether (250 ml), and the organic layer was separated. The aqueous layer was neutralized by 1N HCl solution (70 ml), and it was extracted with ether (200 ml) and washed with brine (200 ml). The organic layer was dried over $MgSO_4$, and filtered. The filtrate was evaporated *in vacuo* to give a crude product, which was purified by silica gel chromatography using hexane / ethyl acetate (9 : 1) as an eluent. Yield 3.30 g (41%), colorless oil; IR (neat) 2933, 2859, 2746, 1651, 1574, 1506, 1372, 1336, 1299, 1225, 1136, 1117, 1017, 839, 805, 716, 659, 636 cm^{-1}; ^1H NMR δ 0.89 (t, 3H, *J* = 6.9 Hz), 1.31-1.46 (m, 6H), 1.64-1.84 (m, 2H), 3.99 (t, 2H, *J* = 6.6 Hz), 6.41 (d, 1H, *J* = 2.3 Hz), 6.50 (dd, 1H, *J* = 8.9, 2.3 Hz), 7.39 (d, 1H, *J* = 8.9 Hz), 9.70 (s, 1H), 11.49 (s, 1H).

***trans*-3-Pentyl-5-phenylthio-3,4,4a,10b-tetrahydro-2*H*,5*H*-pyrano[3,2-*c*][1] benzopyran (21)**

The experimental procedure was the same as that for the preparation of **1c**. The following quantities were used; compound **13** (3.00 g, 11.3 mmol), **18** (1.66 g, 13.6 mmol), trimethyl orthoformate (1.44 g, 13.6 mmol), and *p*-toluenesulfonic acid (0.43 g, 2.27 mmol) in benzene (70 ml). Yield 2.55 g (61%), colorless oil; IR (neat) 3061, 2954, 2920, 2853, 1611, 1584, 1483, 1457, 1364, 1222, 1111, 1086, 978, 818, 752, 692 cm^{-1}; ^1H NMR δ 0.90 (t, 3H, *J* = 6.9 Hz), 0.85-1.04 (m, 1H), 1.22-1.36 (m, 8H), 1.69-1.99 (m, 2H), 2.31-2.35 (m, 1H), 3.22 (t, 1H, *J* = 11.2 Hz), 4.08-4.13 (m, 1H), 4.19

(d, 1H, *J* = 10.2 Hz), 5.30 (d, 1H, *J* = 10.9 Hz), 6.90 (d, 1H, *J* = 8.3 Hz), 6.95 (dd, 1H, *J* = 7.6, 7.3 Hz), 7.15 (dd, 1H, *J* = 8.3, 7.3 Hz), 7.25-7.33 (m, 3H), 7.36 (d, 1H, *J* = 7.6 Hz), 7.60 (dd, 2H, *J* = 7.9, 1.7 Hz).

trans-8-Hexyloxy-3-pentyl-5-phenylthio-3,4,4a,10b-tetrahydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran (22c)

The experimental procedure was the same as that for the preparation of **1c**. The following quantities were used; compound **15c** (3.00 g, 13.5 mmol), **13** (2.97 g, 11.2 mmol), trimethyl orthoformate (1.19 g, 11.2 mmol), and *p*-toluenesulfonic acid (0.39 g, 2.25 mmol) in benzene (70 ml). Yield 3.32 g (63%), colorless crystal, mp. 72.8-76.3 °C; IR (KBr) 3074, 2953, 2925, 2841, 1600, 1573, 1479, 1409, 1284, 1215, 1083, 970, 794, 746, 690 cm^{-1}; ^1H NMR δ 0.96 (t, 6H, *J* = 6.9 Hz), 0.87-1.02 (m, 1H), 1.18-1.43 (m, 16H), 1.71-1.82 (m, 2H), 2.27-2.32 (m, 1H), 3.20 (t, 1H, *J* = 11.2 Hz), 3.90 (t, 2H, *J* = 6.6 Hz), 4.05-4.11 (m, 1H), 4.14 (d, 1H, *J* = 9.9 Hz), 5.30 (d, 1H, *J* =10.9 Hz), 6.44 (d, 1H, *J* = 2.3 Hz), 6.50 (dd, 1H, *J* = 8.6, 2.3 Hz), 7.23 (d, 1H, *J* = 8.6 Hz), 7.27-7.37 (m, 3H), 7.59 (dd, 2H, *J* = 7.9, 1.7 Hz).

trans-8-Methoxycarbonyl-3-pentyl-5-phenylthio-3,4,4a,10b-tetrahydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran (23)

The experimental procedure was the same as that for the preparation of **1c**. The following quantities were used; compound **18** (2.50 g, 13.9 mmol), **13** (3.31 g, 12.6 mmol), trimethyl orthoformate (1.34 g, 12.6 mmol), and *p*-toluenesulfonic acid (0.48 g, 2.77 mmol) in benzene (150 ml). Yield 3.10 g (58%), colorless crystal, mp. 92.1-94.8 °C; IR (KBr) 2926, 2855, 1732, 1575, 1431, 1300, 1097, 983, 947, 911, 893, 869, 844, 815, 764, 623 cm^{-1}; ^1H NMR δ 0.90 (t, 3H, *J* = 6.9 Hz), 0.95-1.04 (m, 1H), 1.23-1.37 (m, 8H), 1.72-1.86 (m, 2H), 2.33-2.38 (m, 1H), 3.22 (t, 1H, *J* = 11.2 Hz), 3.89 (s, 3H), 4.09-4.14 (m, 1H), 4.19 (d, 1H, *J* = 9.9 Hz), 5.32 (d, 1H, *J* = 10.6 Hz), 7.29-7.33 (m, 3H), 7.43 (d, 1H, *J* = 7.9 Hz), 7.56 (d, 1H, *J* = 2.0 Hz), 7.60 (dd, 3H, *J* = 7.9, 2.0 Hz).

trans-8-Methoxycarbonyl-3-pentyl-3,4,4a,10b-tetrahydro-2_H_,5_H_-pyrano[3,2-_c_][1] benzopyran (24)

The experimental procedure was the same as that for the preparation of compound **2**. The following quantities were used; compound **23** (3.00 g, 7.03 mmol), tributyltin hydride (6.14 g, 21.1 mmol), and AIBN (0.11 g, 0.70 mmol) in benzene (50 ml). Yield 1.34 g (60%), colorless crystal, mp. 85.9-89.9 °C; IR (KBr) 2915, 1730, 1713, 1618, 1574, 1503, 1469, 1416, 1389, 1366, 1351, 1126, 983, 947, 911, 893, 869, 844, 815, 785, 760, 725, 694 cm^{-1}; ^1H NMR δ 0.89 (t, 3H, J = 6.9 Hz), 0.83-0.94 (m, 1H), 1.22-1.36 (m, 8H), 1.67-2.03 (m, 3H), 3.27 (t, 1H, J = 11.2 Hz), 3.88 (s, 3H), 3.89 (t, 1H, J = 11.2 Hz), 4.12 (d, 1H, J = 9.9 Hz), 4.16-4.22 (m, 2H), 7.43 (d, 1H, J = 1.3 Hz), 7.45 (d, 1H, J = 7.9 Hz), 7.56 (dd, 1H, J = 7.9, 1.3 Hz).

trans-8-Carboxy-3-pentyl-3,4,4a,10b-tetrahydro-2_H_,5_H_-pyrano[3,2-_c_][1] benzopyran (25)

Compound **24** (1.18 g, 3.70 mmol) was treated with sodium hydroxide (0.42 g, 10.0 mmol) in methanol (40 ml) and water (4 ml) under reflux for 3 h. The solvent was removed *in vacuo* and water (80 ml) was added to residue, which was then adjusted to pH 1 by adding 2N HCl. The precipitated white solid was filtered off and dried *in vacuo*, then it was recrystallized from hexane / ethyl acetate (95: 5). Yield 1.02 g (90%), colorless crystal, mp. 179.5-183.5 °C; IR (KBr) 3442, 3416, 3360, 3178, 2957, 2923, 2850, 1702, 1650, 1614, 1567, 1504, 1468, 1428, 1389, 1321, 1298, 1232, 1208, 1154, 1097, 1024, 917, 893, 802, 736 cm^{-1}; ^1H NMR δ 0.89 (t, 3H, J = 6.6 Hz), 0.80-0.92 (m, 1H), 1.20-1.41 (m, 8H), 1.68-2.05 (m, 3H), 3.29 (t, 1H, J = 11.2 Hz), 3.90 (t, 1H, J = 11.2 Hz), 4.15 (d, 1H, J = 9.9 Hz), 4.17-4.25 (m, 2H), 7.49 (d, 1H, J = 7.9 Hz), 7.51 (d, 1H, J = 1.3 Hz), 7.64 (dd, 1H, J = 7.9, 1.3 Hz).

trans-8-Carbamoyl-3-pentyl-3,4,4a,10b-tetrahydro-2_H_,5_H_-pyrano[3,2-_c_][1] benzopyran (26)

A mixture of compound **25** (0.95 g, 3.12 mmol) and thionyl chloride (1.11 g, 9.36 mmol) in dry benzene (15 ml) was heated under reflux (2 h) with exclusion of moisture.

The solvent was removed *in vacuo*, and crude acid chloride was dissolved in dry THF (10 ml). Ammonia solution (28%, 1.4 ml) was added with stirring. The mixture was stirred for further 1 h, cold water (40 ml) was added, the precipitate was filtered off and washed with cold water, then it was recrystallized from ethanol. Yield 0.67 g (71%), colorless crystal, mp. 204.8-209.2 °C; IR (KBr) 2916, 2352, 2326, 2050, 1913, 1864, 1814, 1727, 1703, 1667, 1650, 1619, 1573, 1505, 1470, 1433, 1416, 1385, 1349, 1226, 1207, 1096, 1029, 983, 920, 892, 845, 815, 765, 691, 648, 608, 533 cm^{-1}; ^1H NMR δ 0.89 (t, 3H, *J* = 6.6 Hz), 0.80-0.91 (m, 1H), 1.20-1.40 (m, 8H), 1.68-2.03 (m, 3H), 3.28 (t, 1H, *J* = 11.2 Hz), 3.91 (t, 1H, *J* = 11.2 Hz), 4.14 (d, 1H, *J* = 9.2 Hz), 4.18-4.24 (m, 2H), 5.60 (s, 1H), 6.00 (s, 1H), 7.22 (d, 1H, *J* = 2.0 Hz), 7.31 (dd, 1H, *J* = 7.9, 2.0 Hz), 7.47 (d, 1H, *J* = 7.9 Hz).

trans-8-Bromo-3-pentyl-5-phenylthio-3,4,4a,10b-tetrahydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran (27)

The experimental procedure was the same as that for the preparation of **1c**. The following quantities were used; compound **13** (3.27 g, 12.3 mmol), **20** (3.00 g, 14.8 mmol), trimethylorthoformate (1.56 g, 14.8 mmol), and *p*-toluenesulfonic acid (0.47 g, 2.48 mmol) in benzene (75 ml). Yield 3.26 g (59%), colorless crystal, mp. 70.2-73.8 °C; IR (KBr) 3074, 2953, 2925, 2841, 1600, 1573, 1479, 1409, 1284, 1215, 1083, 970, 794, 746, 690 cm^{-1}; ^1H NMR δ 0.90 (t, 3H, *J* = 6.9 Hz), 0.95-1.04 (m, 1H),1.15-1.38 (m, 8H), 1.64-1.83 (m, 2H), 2.28-2.36 (m, 1H), 3.19 (t, 1H, *J* = 11.2 Hz), 4.07-4.13 (m, 1H), 4.10 (d, 1H, *J* = 10.6 Hz), 5.27 (d, 1H, *J* = 10.9 Hz), 7.05 (dd, 1H, *J* = 8.6, 2.0 Hz), 7.07 (d, 1H, *J* = 2.0 Hz), 7.23 (d, 1H, *J* = 8.6 Hz), 7.26-7.37 (m, 3H), 7.59 (dd, 2H, *J* = 7.9, 2.0 Hz).

trans-3-Pentyl-5-phenylthio-8-(4-trifluoromethoxyphenyl)-3,4,4a,10b-tetrahydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran (29c)

A round bottomed flask was charged with Pd $(PPh_3)_4$ (0.20 g, 0.174 mmol), benzene (30 ml), compound **27** (2.60 g, 5.82 mmol), and aqueous K_2CO_3 (10 ml of a 2M solution) under nitrogen atmosphere, and compound **28c** (1.32 g, 6.40 mmol) in ethanol (12 ml) was added. The mixture was refluxed for 12 h. After cooling to room temperature, it

was extracted with ether (100 ml). The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by silica gel chromatography using hexane / ethyl acetate (98 : 2) as an eluent to give a crude product, which was purified by recrystallization from hexane / toluene (95 : 5). Yield 1.69 g (55%), colorless crystal, mp. 85.2-95.2 °C; IR (KBr) 3062, 2928, 2856, 1618, 1558, 1523, 1491, 1432, 1397, 1263, 1219, 1163, 1086, 981, 802, 750, 691 cm^{-1}; ^1H NMR δ 0.91 (t, 3H, *J* = 6.9 Hz), 0.99-1.04 (m, 1H), 1.24-1.34 (m, 8H), 1.72-1.88 (m, 2H), 2.34-2.38 (m, 1H), 3.25 (t, 1H, *J* =11.2 Hz), 4.08-4.16 (m, 1H), 4.22 (d, 1H, *J* = 10.2 Hz), 5.35 (d, 1H, *J* = 10.9 Hz), 7.10 (d, 1H, *J* = 1.7Hz), 7.14 (dd, 1H, *J* = 7.9, 2.0 Hz), 7.25 (dd, 2H, *J* = 8.9, 2.0 Hz), 7.28-7.36 (m, 3H), 7.43 (d, 1H, *J* = 7.9 Hz), 7.56 (dd, 2H, *J* = 8.9, 2.3 Hz), 7.62 (dd, 2H, *J* = 7.9, 1.6 Hz).