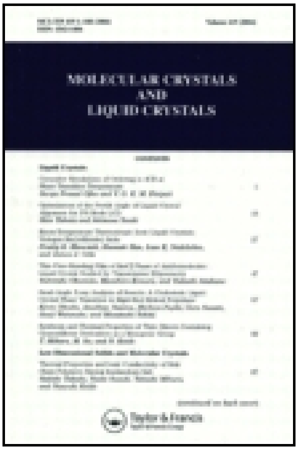


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Facile Synthesis of 4-alkylphenyl 4-(4-Nitrobenzoyloxy)Benzoate (DBXNO$_2$) and its Cyano Analog (DBXCN)

Long Y. Chiang [a]
[a] Corporate Research Science Laboratory, Exxon Research and Engineering Company, Annandale, NJ, 08801

Version of record first published: 13 Dec 2006.

To cite this article: Long Y. Chiang (1987): Facile Synthesis of 4-alkylphenyl 4-(4-Nitrobenzoyloxy)Benzoate (DBXNO$_2$) and its Cyano Analog (DBXCN), Molecular Crystals and Liquid Crystals, 146:1, 137-142

To link to this article: http://dx.doi.org/10.1080/00268948708071809

Mol. Cryst. Liq. Cryst., 1987, Vol. 146, pp. 137–142
Photocopying permitted by license only

Printed in the United States of America

Facile Synthesis of 4-alkylphenyl 4-(4-Nitrobenzoyloxy)Benzoate (DBXNO$_2$) and its Cyano Analog (DBXCN)

LONG Y. CHIANG

Corporate Research Science Laboratory, Exxon Research and Engineering Company, Annandale, NJ 08801

(*Received November 15, 1986; in final form November 26, 1986*)

Two series of unsymmetrical phenylbenzoate analogs of thermotropic liquid crystals, namely, 4-alkylphenyl 4-(4-nitrobenzoyloxy) benzoate (DBXNO$_2$) and its cyano analogy (DBXCN) are synthesized by a new route from benzyloxybenzoic acid. The first ester linkage of these phenylbenzoates is made by a condensation reaction between benzyloxybenzoic acid and an alkylphenol in the presence of carbodiimide and a base to give compound **6**. A benzyl deprotection reaction of **6** is carried out by catalytical hydrogenation to yield compound **7**. The second ester connection is performed by a condensation reaction between **7** and *p*-cyano or *p*-nitrobenzoyl chloride. This reaction sequence leads to the final products, DBXNO$_2$ or DBXCN, in an overall yield of 50% or 37%, respectively.

Keywords: synthesis of phenyl benzoate liquid crystals

INTRODUCTION

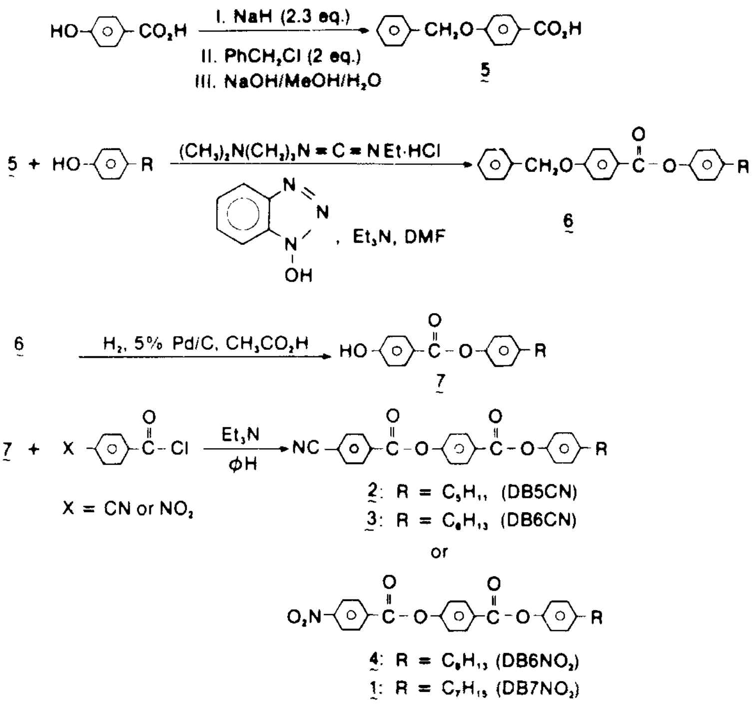
The understanding of the temperature dependent ordering and phase transition behavior in liquid crystalline materials has been an active area of interest for decades. To date, numerous thermotropic liquid crystal materials with nematic and smectic phases have been synthesized.[1] Among them, the smectic-A phases have been differentiated into at least three distinguishable forms,[2,3] namely, the monolayer S_{A1} phase, the bilayer S_{A2} phase, and the partial bilayer $S_{\tilde{A}}$ antiphase. Recently 4-heptylphenyl 4-(4-nitrobenzoyloxy)benzoate (DB7NO$_2$, **1**), one of the most interesting members of the phenyl benzoate liquid crystals, was found[4] to exhibit an unusual transition between a smectic-A phase (S_{A1}) and a smectic-A antiphase ($S_{\tilde{A}}$) around 93°C in a pure material. This was the first observation of the S_{A1}-$S_{\tilde{A}}$ transition in the nitro derivatives of a linear phenyl benzoate liquid crystal analog. A similar type of phase transition was also found in the pure cyano comound of 4-heptylphenyl 4-(4-cyanobenzoyloxy)benzoate (DB7CN),[5,6] and in the binary mixture of DB5CN (**2**) or DB6CN (**3**) with another cyano liquid crystal exhibiting a monomolecular S_A phase.[3]

To understand the structure of smectic-A antiphase and the nature of ordering in the S_{A1}-$S_{\tilde{A}}$ transition experimentally,[7,8] we have synthesized a series of 4-alkylphenyl 4-(4-nitrobenzoyloxy)benzoate (DBXNO_2) and its cyano analog (DBXCN). Using x-ray scattering techniques,[7] we have studied the smectic-A_1 to smectic-A antiphase transition in the pure compound of DB7NO_2. The x-ray results will be published separately.

RESULTS AND DISCUSSIONS

The previous synthesis[9] of the DBXNO_2 and DBXCN series involved a condensation reaction between *p*-hydroxybenzoic acid and *p*-alkylphenol in the presence of a catalytic mixture of boric acid and sulfuric acid as a key step.[10,11] However, this procedure was accompanied by a competitive ester condensation of *p*-hydroxybenzoic acid between *p*-alkylphenol and the second molecule of *p*-hydroxybenzoic acid. The latter reaction resulted in a polymer formation. The problem is eliminated by following the alternative procedure as illustrated in the Scheme below.

Upon treatment of *p*-hydroxybenzoic acid with 2.3 equivalents of sodium hydride in DMF, the initially formed disodium salt was allowed to react with benzyl chloride to afford benzyl 4-benzyloxybenzoate as an intermediate. Hydrolysis of this benzoate in alkaline solution gave 4-benzyloxybenzoic acid (**5**)[12] in an overall yield of 92%. The ester condensation reaction was carried out between benzoic acid (**5**) and *p*-alkylphenol with *N*-(N,N′-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride[13] in the presence of 1-hydroxybenzotriazole and triethylamine in DMF solution. The coupled product (**6**, *R* = alkyl group) was isolated in 69% yield. In this step, dicyclohexylcarbodiimide (DCC) could also be used as a coupling reagent. However, it gave a slightly lower yield of 44%. Catalytic hydrogenation of **6** in the presence of 5% Pd/C in acetic acid gave a 90% yield of 4-alkylphenyl 4-hydroxybenzoate (**7**). Treatment of compound **7**



Scheme 1

with *p*-nitrobenzoyl chloride or *p*-cyanobenzoyl chloride in the presence of triethylamine afforded DBXNO$_2$ (**1** or **4**) or DBXCN (**2** or **3**) in a yield of 88% or 65%, respectively.

EXPERIMENTAL

Synthesis of 4-alkylphenyl 4-benzyloxybenzoate (*6*) To a stirred solution of benzyloxybenzoic acid (**5**)[14] (27.8 g, 0.12 mol), *p*-alkylphenol (0.12 mol), and 1-hydroxybenzotriazole hydrate (33.8 g, 0.25 mol) in DMF (350 ml) was added *N*-(N,N'-dimethylaminopropyl)-*N*-'ethylcarbodiimide hydrochloride (23 g, 0.12 mol) followed by triethylamine (12 g, 0.12 mol). The reaction mixture was stirred at room temperature for 2 days and then at 50°C for 3 h. After being cooled to room temperature, the mixture was poured into water (2.8 l) and extracted with ethyl acetate (4 × 400 ml). The organic solution was then washed with 1 N NaOH (100 ml), 1 N HCl (100 ml), H_2O (200 ml), dried ($MgSO_4$), filtered, and concentrated. Recrystallization (diethyl ether-hexane/1:2) of the resulting crude product gave a 69% yield of 4-alkylphenyl 4-benzyloxybenzoate (**6**). The physical properties of compound **6** are as follows: 4-Pentylphenyl 4-benzyloxybenzoate (**6**, $R = n-C_5H_{11}$): mp 124°C; IR(KBr) 1732 cm^{-1}; MS m/e 374 (m^+, 1), 212 (13), 211 (100), 92 (6), 91 (87); ^{1}H-NMR δ 0.92 (t, 3 H), 1.14–1.82 (m, 6 H), 2.63 (t, 2 H), 5.15 (s, 2 H), 7.04 (d, J = 9 Hz, 2 H), 7.10–7.56 (m, 9 H), 8.18 (d, J = 9 Hz, 2 H). Anal. Calcd for $C_{25}H_{26}O_3$: C, 80.21; H, 6.95; 0, 12.83. Found: C, 80.13; H, 7.05; 0, 13.06. 4-Hexylphenyl 4-benzyloxybenzoate (**6**, $R = n-C_6H_{13}$): mp 115°C. Anal. Calcd for $C_{26}H_{28}O_3$: C, 80.41; H, 7.22; 0, 12.37. Found: C, 80.63; H, 7.50; 0, 12.12. IR, ^{1}H-NMR, and MS data were similar to those of **6** ($R = n-C_5H_{11}$). 4-Heptylphenyl 4-benzyloxybenzoate (**6**, $R = n-C_7H_{15}$): mp 117°C. Anal. Calcd for $C_{27}H_{30}O_3$: C, 80.56: H, 7.51; 0, 11.98. Found: C, 80.28; H, 7.72; 0, 12.12. IR, ^{1}H-NMR, and MS data were similar to those of **6** ($R = n-C_5H_{11}$).

Synthesis of 4-alkylphenyl 4-hydroxybenzoate (**7**). A stirred suspension 4-alkylphenyl 4-benzyloxybenzoate (**6**, 10 mmol) and 5% palladium on carbon (0.4 g) in acetic acid (50 ml) was hydrogenated at 50 psi at room temperature. After no starting material was detected by TLC (SiO_2, EtOAc-hexane/1:2 as eluent), the catalyst was filtered and washed with ethanol (100 ml). The solvent was then evaporated to dryness. The resulting residue was extracted into ether (200 ml). The ether solution was washed with water (400 ml), dried ($MgSO_4$), and concentrated. Chromatography (SiO_2, EtOAc-hexane/1:1) of the crude product yielded 90% of 4-alkylphenyl 4-hydroxybenzoate (**7**). The physical properties of compound **7** was described as follows. 4-Pentylphenyl 4-hydroxybenzoate (**7**, $R = n-C_5H_{11}$): mp 142°C; IR(KBr) 3405, 2945, 1705 cm^{-1}; MS m/e 284 (m^+, 3), 122 (9), 121 (100); ^{1}H-NMR δ 0.90 (t, 3 H), 1.12–1.90 (m, 6 H), 2.63 (t, 2 H), 6.29 (s, 1 H), 6.86 (d, J = 8.5 Hz, 2 H), 7.10–7.35 (m, 4 H), 8.11 (d, J = 8.5 Hz, 2 H). Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.06; H, 7.04; 0, 16.90. Found: C, 76.27; H, 7.15; O, 16.24. 4-Hexylphenyl 4-hydroxybenzoate (**7**, $R = n-C_6H_{13}$): mp 136°C. Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.51; H, 7.38; O, 16.11. Found: C, 76.64; H, 7.53; O, 16.06. IR, ^{1}H-NMR, and MS data were similar to those of **7** ($R = n-C_5H_{11}$). 4-Heptylphenyl 4-hydroxybenzoate (**7**, $R = n-C_7H_{15}$): mp 136°C. Anal. Calcd for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74; O, 15.36. Found: C, 76.79; H, 7.75; O, 15.42. IR, ^{1}H-NMR, and MS data were similar to those of **7** ($R = n-C_5H_{11}$).

Synthesis of 4-Pentylphenyl 4-(4-cyanobenzoyloxy)benzoate (*DB5CN*, **2**). To a stirred solution of 4-pentylphenyl 4-hydroxybenzoate (**7**, $R = n - C_5H_{11}$) (11 g, 37 mmol) and triethylamine (5.5 ml, 39 mmol) in benzene (300 ml) was added a solution of *p*-cyanobenzoyl chloride (7.5 g, 45 mmol) in benzene (170 ml) dropwisely over a period of 30 min. The stirring was continued at room temperature for 2 h. The resulting mixture was washed with dilute hydrochloric acid (100 ml), H_2O (200 ml), brine (200 ml), and dried ($MgSO_4$). After the solvent was evaporated, the crude product was recrystallized from isopropyl alcohol (300 ml) to afford 10.6 g (65% yield) of 4-pentylphenyl 4-(4-cyanobenzoyloxy)benzoate (**2**): mp 137–139°C; IR(KBr) 1745, 1615, 1520, 1416, 1320, 1287, 1220, 1206, 1173, 1082, 1023, 887, 859, 765 cm^{-1}; MS m/e 413 (m^+, 4), 251 (16), 250 (100), 130 (67), 102 (12); ^1H NMR δ 0.9 (t, 3 H), 1.15 – 1.80 (m, 6 H), 2.63 (t, 2 H), 7.17 – 8.40 (m, 12 H). Anal. Calcd for $C_{26}H_{23}O_4N$: C, 75.53; H, 5.60; 0, 15.47; N, 3.39. Found: C, 75.28; H. 5.77; O, 15.65; N, 3.35.

Synthesis of 4-hexylphenyl 4-(4-cyanobenzoyloxy)benzoate (*DB6CN*, **3**). The condensation reaction of 4-hexylphenyl 4-hydroxybenzoate with *p*-cyanobenzoyl chloride in the presence of triethylamine was conducted as described for DB5CN (**2**). The physical properties of DB6CN (**3**) are as follows: mp 115 – 118°C. Anal. Calcd for $C_{27}H_{25}O_4N$: C, 75.88, H, 5.85; O, 14.99; N, 3.28. Found: C, 75.87; H, 6.01; O, 15.10; N, 3.19. IR, ^1H-NMR, and MS data were similar to those of **2**.

Synthesis of 4-hexylphenyl 4-(4-nitrobenzoyloxy)benozoate (*DB6NO*$_2$, **4**). The condensation reaction of 4-hexylphenyl 4-hydroxybenzoate (**7**) with *p*-nitrobenzoyl chloride was carried out as the method described for DB5CN (**2**) in 88% yield. The physical properties of compound **4** are as follows: mp 106 – 108°C; IR(KBr) 1742, 1614, 1536, 1515, 1420, 1370, 1324, 1270, 1203, 1165, 1070, 1020, 900, 863, 718 cm^{-1}; MS m/e 447 (m^+, 4), 271 (19), 270 (100), 151 (8), 159 (95), 121 (15), 120 (29), 92 (14); ^1H-NMR δ 0.9 (t, 3 H), 1.15 – 1.70 (m, 8 H), 2.62 (t, 2 H), 7.16 – 8.40 (m, 12 H). Anal. Calcd for $C_{26}H_{25}O_6N$: C, 69.80; H, 5.59; O, 21.48; N, 3.13. Found: C, 70.01; H, 5.60; O, 21.44; N, 3.06.

Synthesis of 4-heptylphenyl 4-(4-nitrobenzoyloxy)benzoate (*DB7NO*$_2$, **1**). The preparation method was the same as that for $DB6NO_2$, except 4-heptylphenyl 4-hydroxybenzoate was used. The physical properties of compound **1** are as follows: mp 101–103°C. Anal. Calcd for $C_{27}H_{27}O_6N$: C, 70.35; H, 5.90; O, 20.82; N, 3.04. Found: C, 70.41; H, 6.02; O, 20.47; N, 2.99. IR, ^{1}H-NMR, and MS data were similar to those of **4**.

Acknowledgment

I thank C. R. Safinya of Exxon Research and Engineering Company for the encouragement of this work.

References

1. G. H. Brown, ed., "*Advances in Liquid Crystals*," Volume 1, 2, 3, 4, and 5, Academic Press, New York, 1975, 1976, 1978, 1979, and 1982.
2. A. M. Levelut, R. J. Tarento, F. Hardouin, M. F. Achard and G. Sigaud, *Phys. Rev.*, **A24**, 2180 (1981).
3. G. Sigaud, F. Hardouin, M. F. Achard and A. M. Levelut, *J. Physique*, **42**, 107 (1981).
4. F. Hardouin, G. Sigaud, H. T. Nguyen and M. F. Achard, *J. Physique*, **42(3)**, 63-6 (1981).
5. F. Hardouin, A. M. Levelut and G. Sigaud, *J. Physique*, **42**, 71-7 (1981).
6. A. M. Levelut, B. Zaghloul and F. Hardouin, *J. Physique*, **43**, 83-7 (1982).
7. C. R. Safinya, L. Y. Chiang, W. A. Varady, and P. Dimon, *Phys. Rev. Lett.*, **57**, 432-5 (1986); B. M. Ocko, P. S. Pershan, C. R. Safinya and L. Y. Chiang, submitted to *Phys. Rev. Lett. Rapid Commun.* (1986).
8. C. C. Huang, S. C. Lien, S. Dumrongrattana and L. Y. Chiang, *Phys. Rev. A*, **30**, 965 (1984).
9. G. Sigaud and H. T. Nguyen, private communication.
10. W. W. Lawrence, *Tetrahedron Lett.*, 3453–54 (1971).
11. J. P. VanMeter and B. H. Klanderman, *J. Amer. Chem. Soc.*, **95**, 626-27 (1973); *J. Mol. Cryst. Liq. Cryst.*, **22**, 285–99 (1973).
12. This type of benzyl protecting group has also been used in the preparation of other phenyl benzoates: see B. K. Sadashiva, *Liq. Cryst., Proc. Int. Conf.*, 165–6 (1979).
13. J. C. Sheehan, P. A. Cruickshank and G. L. Boshart, *J. Org. Chem.*, **26**, 2525 (1961); F. Sweet and N. K. Adair, *Biochem. Biophys. Res. Commun.*, **63**, 99 (1975).
14. S. M. McElvain and T. P. Carney, *J. Amer. Chem. Soc.*, **68**, 2592–2600 (1946).