from ethanol, affording colorless needles: mp 188–189° (94%); ir (KBr) 3045, 3010, 2960 (CH), 1720, 1690 cm$^{-1}$ (CO); $\lambda_{max}^{CH_3OH}$ 235 nm sh (log $\epsilon$ 3.00), 2.00 (4.69); nmr (CDCl$_3$) $\tau$ 8.82 (s, 3, C$_1$ CH$_3$), 6.11 (s, 3, C$_6$ COOCH$_3$), 6.09 (s, 3, C$_5$ COOCH$_3$), 5.02 (s, 1, H$_4$), 3.0–2.4 (m, 10, aromatic); mass spectrum, identical with that of **4** (R$^1$ = Ph; R$^2$ = CH$_3$).

*Anal.* Calcd for $C_{23}H_{20}N_2O_6$: C, 65.70; H, 4.80; N, 6.66. Found: C, 65.62; H, 4.78; N, 6.62.

**Thermal Elimination of Phenyl Isocyanate from 3 (R$^1$ = Ph; R$^2$ = CH$_3$).**—The primary adduct **3** (R$^1$ = Ph; R$^2$ = CH$_3$) (0.42 g, 0.001 mol) was heated for 20 min above its melting point at about 0.5 mm. After cooling and trituration with ether, the product crystallized from benzene–cyclohexane as colorless prisms of dimethyl 6-methyl-2-oxo-1-phenylpyridine-4,5-dicarboxylate (**4**, R$^1$ = Ph; R$^2$ = CH$_3$): 90%; mp 155–158°; ir (KBr) 3001, 2950 (CH), 1740, 1725, 1660 cm$^{-1}$ (CO); $\lambda_{max}^{CH_3OH}$ 328 nm (log $\epsilon$ 3.74), 251 (4.08), 203 (4.68); nmr (CDCl$_3$) $\tau$ 7.90 (s, 3, C$_6$ CH$_3$), 6.17 (s, 3, C$_4$ COOCH$_3$), 6.10 (s, 3, C$_5$ COOCH$_3$), 3.09 (s, 1, H$_3$), 2.32–2.90 (m, 10, aromatic); mass spectrum, $M^{+\cdot}$, $m/e$ (rel intensity) 301 (100).

*Anal.* Calcd for $C_{16}H_{15}NO_5$: C, 63.78; H, 5.02; N, 4.65. Found: C, 63.50; H, 4.98; N, 4.52.

**Registry No.**—**2** (R$^1$ = R$^2$ = Ph), 33821-84-0; **2** (R$^1$ = CH$_3$; R$^2$ = Ph), 33821-85-1; **2** (R$^1$ = Ph; R$^2$ = H), 33821-86-2; **2** (R$^1$ = Ph; R$^2$ = CH$_3$), 33821-87-3; **3** (R$^1$ = Ph; R$^2$ = CH$_3$), 33821-88-4; **4** (R$^1$ = CH$_3$; R$^2$ = Ph), 33821-89-5; **4** (R$^1$ = Ph; R$^2$ = CH$_3$), 33821-90-8; **5a** (R$^1$ = Ph), 33821-91-9; **5b** (R = H), 33821-92-0.

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# Liquid Crystals. II. Unsymmetrical *p*-Phenylene Di-*p*-*n*-alkoxybenzoates[1]

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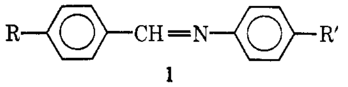
Nematic mesophases that exist at low temperatures are desirable in several applications, but compounds which exhibit nematic mesomorphism tend also to have high melting points. Schiff bases (**1**), the best materials for these applications until recently, are relatively unstable chemically. Esters are more stable and the symmetrical *p*-phenylene di-*p*-*n*-alkoxybenzoates (**2**, R = R′) are nematogenic. However, no compound in this series melts to a nematic mesophase below 122°. The possibility of obtaining lower melting nematic esters by introducing molecular dissymmetry was explored. Twenty-eight unsymmetrical esters (**2**, R $\neq$ R′), providing all possible combinations of terminal *n*-alkyl groups from methyl through *n*-octyl, were synthesized and their phase transition temperatures determined. The nematic–isotropic transition point is high, even for the most unsymmetrical esters, while the melting point is depressed. The lowest melting products are the hexyl-octyl and pentyl-heptyl esters, which are nematic at 107–202 and 108–210°, respectively. The high nematic–isotropic transition temperatures of these compounds suggest that much lower melting points can be achieved in this system, without losing nematic mesomorphism, by introducing even more molecular dissymmetry. In addition to the 28 unsymmetrical esters of type **2**, seven new *p*-hydroxyphenyl *p*-*n*-alkoxybenzoates (**3**) and the previously unreported **2** (R = R′ = *n*-$C_5H_{11}$) were also prepared. Similar studies of other chemically stable nematic compounds are reviewed briefly.

Nematic liquid crystallinity (mesomorphism)[2,3] is exhibited by certain compounds with relatively rigid, polar, rod-shaped molecules that tend to be oriented with their long axes parallel because of mutual attractive forces. When such a compound is heated, the crystalline solid melts to a birefringent, anisotropic liquid (nematic mesophase) in which adjoining molecules lie parallel to one another. At a higher temperature, the mesophase undergoes transition to isotropic liquid.

For practical applications, such as optical and display devices[4] and gas–liquid chromatography,[5] nematic mesophases which exist at or near room temperature are desirable. This is a difficult criterion to meet because the molecular characteristics that are necessary for nematic mesomorphism also produce stable crystalline lattices. Accordingly, nematic compounds generally have high melting points. Success in meeting the requirement has been achieved with nematic substances having a relatively high degree of molecular dissymmetry and their mixtures. The dissymmetry and the mixing depress the solid–nematic melting point without necessarily lowering the nematic–isotopic transition temperature. Accordingly, by proper selection of compounds, low melting points are obtainable with retention of nematic mesomorphism.



**1**

At the time our investigation was begun, the outstanding examples of these successes involved Schiff bases (**1**). A ternary mixture of **1** (R = CH$_3$O; R′ = *n*-C$_3$H$_7$COO), **1** (R = *n* -C$_4$H$_9$O; R′ = CH$_3$COO), and **1** (R = CH$_3$O; R′ = CH$_3$COO) has a nematic range[6] of 22–105°.[7] The compound **1** (R = CH$_3$O; R′ = *n*-C$_4$H$_9$) is nematic at 22–48°.[8] The trouble with Schiff bases is their hydrolytic, oxidative, and thermal instability. Aromatic esters are much more stable, and symmetrical *p*-phenylene di-*p*-*n*-alkoxybenzoates (**2**, R = R′) are known to have long nematic ranges.[9,10] However, no compound in the series undergoes transi-

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(1) (a) Presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971. (b) From the M.S. thesis of S. A. H., The University of North Carolina at Greensboro, 1971. (c) This work was supported in part by a grant-in-aid from The University of North Carolina at Greensboro Research Council. (d) Previous paper in this series: J. P. Schroeder and Dorothy C. Schroeder, *J. Org. Chem.*, **33**, 591 (1968).

(2) G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, New York, N. Y., 1962.

(3) G. H. Brown and W. G. Shaw, *Chem. Rev.*, **57**, 1049 (1957).

(4) T. Kallard, Ed., "Liquid Crystals and Their Applications," Optosonic Press, New York, N. Y., 1970.

(5) H. Kelker and E. Von-Schivizhoffen, *Advan. Chromatog.*, **6**, 247 (1968).

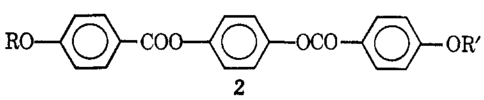
(6) Temperature range over which the nematic mesophase exists.

(7) J. E. Goldmacher and J. A. Castellano (to Radio Corporation of America), British Patent 1,170,486 (Nov. 12, 1969).

(8) (a) H. Kelker and B. Scheurle, *Angew. Chem., Int. Ed. Engl.*, **8**, 884 (1969); (b) H. Kelker, B. Scheurle, R. Hatz, and W. Bartsch, *ibid.*, **9**, 962 (1970).

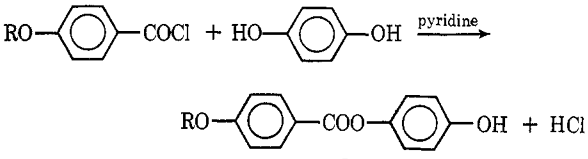
(9) M. J. S. Dewar and J. P. Schroeder, *J. Org. Chem.*, **30**, 2296 (1965).

(10) S. L. Arora, J. L. Fergason, and T. R. Taylor, *ibid.*, **35**, 4055 (1970).



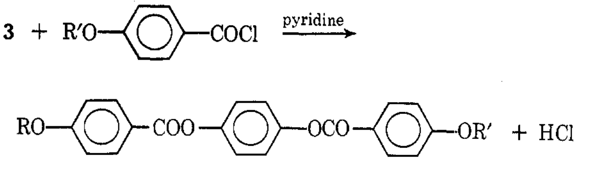
**2**

tion to the nematic mesophase below 122°. This paper describes an exploration of the molecular dissymmetry approach to low melting nematic compounds based on this chemically more stable system. Twenty-eight esters of type **2** (R ≠ R′) were synthesized, encompassing all combinations of the terminal *n*-alkoxy groups $CH_3O$ through *n*-$C_8H_{17}O$. The experimental procedure was to prepare a *p*-hydroxyphenyl *p*-*n*-alkoxybenzoate (**3**) from a *p*-alkoxybenzoyl chloride and an excess of hydroquinone in pyridine solution (eq 1). This was converted to the desired unsymmetrical diester by reaction with a different *p*-alkoxybenzoyl chloride, again in pyridine (eq 2). In the course of the study, 7 new compounds of type **3** and the previously unreported **2** (R = R′ = *n*-$C_5H_{11}$) were also prepared. The phase transition temperatures of these materials were determined using a hot stage polarizing microscope.



(1)

**3**



(2)

While this study was in progress, several reports of similar approaches were published. It was shown[10] that molecular dissymmetry in esters of type **2** (R = R′) resulting from introduction of a methyl substituent on the central phenylene group shifts the nematic range downward significantly. *E.g.*, the methyl-substituted ester with R = R′ = *n*-$C_8H_{17}$ is nematic at 72–156° as compared with 126–195° for **2** (R = R′ = *n*-$C_8H_{17}$). Another unsymmetrical ester system that has been studied is the homologous series of *p*-alkoxyphenyl *p*-alkylcarbonatobenzoates.[11] Mixtures of these compounds have solid–nematic transition temperatures as low as 24°. Additional chemically stable systems that exhibit nematic mesophases at low temperatures are unsymmetrically substituted azoxybenzenes,[8b,12,13] stilbenes,[14] and tolanes.[15]

## Experimental Section

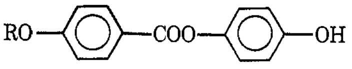
***p*-*n*-Alkoxybenzoic Acids.**—The ethoxy, butyloxy, and octyloxy acids were commercial products. The others were obtained by reaction of ethyl *p*-hydroxybenzoate with the appropriate *n*-alkyl bromides and saponification of the resulting ethyl *p*-alkoxybenzoates in ethanolic KOH solution.[9] The products had the following phase transitions: *p*-*n*-propyloxybenzoic acid, solid–nematic at 145°, nematic–isotropic at 156° (lit.[16] 145, 154°); *p*-*n*-hexyloxybenzoic acid, solid–nematic at 109°, nematic–isotropic at 155° (lit.[16] 105, 153°); *p*-*n*-heptyloxybenzoic acid, solid–smectic at 94°, smectic–nematic at 99°, nematic–isotropic at 146° (lit.[16] 92, 98, 146°).

***p*-*n*-Alkoxybenzoyl Chlorides.**—The methoxy and pentyloxy compounds were purchased. The others were prepared from the corresponding acids by treatment with thionyl chloride in the presence of pyridine as catalyst. Excess thionyl chloride was distilled to give the acid chlorides as residue products.

***p*-Hydroxyphenyl *p*-*n*-Alkoxybenzoates (3).**—Typically, 0.10 mol of the appropriate *p*-*n*-alkoxybenzoyl chloride was added with stirring to a saturated solution of hydroquinone (0.50 mol) in dry pyridine. After stirring for 20–24 hr, the mixture was poured into 1.1 l. of 2.2 *N* hydrochloric acid. The precipitated solid was collected by filtration, washed with water, and stirred for 1 hr in 1 l. of saturated aqueous $NaHCO_3$ solution to remove any *p*-alkoxybenzoic acid from unreacted acid chloride. The slurry was filtered to recover the desired hydroxyphenyl ester.[17] After this was washed with water, the solid was dried at 100° and used in the next step without further purification.[18] The crude yields and the melting points and analyses of the materials after recrystallization from ethanol–water are listed in Table I.

TABLE I

*p*-HYDROXYPHENYL *p*-*n*-ALKOXYBENZOATES[a]



| R | Registry no. | Yield, % | Mp, °C | % C Calcd | % C Found | % H Calcd | % H Found |
|---|---|---|---|---|---|---|---|
| $CH_3$ | | 84 | 156[b] | | | | |
| $C_2H_5$ | 33905-60-1 | 89 | 164 | 69.8 | 69.75 | 5.5 | 5.1 |
| *n*-$C_3H_7$ | 33905-61-2 | 90 | 136 | 70.6 | 70.75 | 5.9 | 6.1 |
| *n*-$C_4H_9$ | 33905-62-3 | 88 | 144 | 71.3 | 71.55 | 6.3 | 6.6 |
| *n*-$C_5H_{11}$ | 33905-63-4 | 80 | 120 | 72.0 | 71.7 | 6.7 | 6.5 |
| *n*-$C_6H_{13}$ | 33905-64-5 | 66 | 116 | 72.6 | 72.5 | 7.05 | 6.9 |
| *n*-$C_7H_{15}$ | 33905-65-6 | 86 | 113 | 73.15 | 73.2 | 7.4 | 7.4 |
| *n*-$C_8H_{17}$ | 33905-66-7 | 85 | 111 | 73.7 | 73.3 | 7.65 | 7.3 |

[a] Satisfactory analytical data (±0.4% for C and H) were reported for all new compounds listed in the table: Ed. [b] Literature mp 152°: M. J. S. Dewar and R. S. Goldberg, *J. Amer. Chem. Soc.*, **92**, 1582 (1970).

***p*-Phenylene Di-*p*-*n*-alkoxybenzoates (2).**—The unsymmetrical esters were synthesized from the appropriate *p*-*n*-alkoxybenzoyl chloride and hydroxyphenyl *p*-*n*-alkoxybenzoate by essentially the same procedure used to prepare the latter except that, at the start, a solution of the phenol was added to a solution of the acid chloride (3 mol/mol of phenol), both in anhydrous pyridine. The dried product was dissolved in a suitable solvent, treated with Norit, and recrystallized twice from that solvent and then repeatedly from a mixture of the same solvent and hexane until the phase transition temperatures remained constant. *p*-Phenylene di-*p*-*n*-pentyloxybenzoate was prepared by the reaction of excess *p*-*n*-pentyloxybenzoyl chloride and hydroquinone in dry pyridine.[9]

The results are summarized in Table II along with the transition temperatures of symmetrical esters from the literature for comparison.

**Transition Temperatures.**—These were determined with a Reichert "Thermopan" polarizing microscope equipped with a Kofler micro hot stage. The instrument was calibrated against pure compounds of known melting points.

**Analyses.**—The elemental microanalyses were performed by Dr. Kurt Eder, Laboratoire Microchimique, Ecole de Chimie, Geneva, Switzerland.

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[11] M. T. McCaffrey, J. E. Goldmacher, and J. A. Castellano, *Mol. Cryst. Liq. Cryst.*, **12**, 345 (1971).

[12] R. Steinsträsser and L. Pohl, *Tetrahedron Lett.*, 1921 (1971).

[13] M. T. McCaffrey and J. A. Castellano, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, PHYS Paper No. 148.

[14] W. R. Young, A. Aviram, and R. J. Cox, *Angew. Chem., Int. Ed. Engl.*, **10**, 410 (1971); Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, PHYS Paper No. 147.

[15] J. Malthete, M. Leclercq, J. Gabard, J. Billard, and J. Jacques, *C. R. Acad. Sci., Paris, Ser. C*, **273**, 265 (1971).

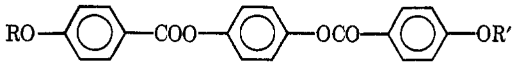
[16] G. W. Gray and B. Jones, *J. Chem. Soc.*, 4179 (1953).

[17] The heptyloxy and octyloxy products required hot filtration because of the low water solubility of the sodium *p*-alkoxybenzoate at room temperature.

[18] Recrystallization of the intermediate before the next step is recommended. Despite the large excess of hydroquinone in the reaction, some symmetrical ester was usually produced and this was troublesome to remove from the unsymmetrical ester.

TABLE II

*p*-PHENYLENE DI-*p*-*n*-ALKOXYBENZOATES[a]



| R | R′ | Registry no.. | Recrystn solvent | Yield, % | Nematic range, °C | % C | | % H | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Calcd | Found | Calcd | Found |
| $CH_3$ | $CH_3$ | | | | 222–300[b] | | | | |
| $CH_3$ | $C_2H_5$ | 33905-67-8 | Dioxane | 81 | 213–295 | 70.4 | 70.1 | 5.1 | 5.3 |
| $CH_3$ | $n$-$C_3H_7$ | 33905-68-9 | Dioxane | 67 | 167–277 | 70.9 | 70.7 | 5.5 | 5.25 |
| $CH_3$ | $n$-$C_4H_9$ | 33905-69-0 | EtOAc | 75 | 134–266 | 71.4 | 71.8 | 5.75 | 5.8 |
| $CH_3$ | $n$-$C_5H_{11}$ | 33905-70-3 | Dioxane | 56 | 137–253 | 71.9 | 72.1 | 6.0 | 6.0 |
| $CH_3$ | $n$-$C_6H_{13}$ | 33905-71-4 | EtOAc | 54 | 125–244 | 72.3 | 72.4 | 6.3 | 6.3 |
| $CH_3$ | $n$-$C_7H_{15}$ | 33905-72-5 | EtOAc | 66 | 127–234 | 72.7 | 72.5 | 6.5 | 6.4 |
| $CH_3$ | $n$-$C_8H_{17}$ | 33905-73-6 | EtOAc | 62 | 125–229 | 73.1 | 73.25 | 6.8 | 6.5 |
| $C_2H_5$ | $C_2H_5$ | | | | 226–287[c] | | | | |
| $C_2H_5$ | $n$-$C_3H_7$ | 33905-74-7 | Dioxane | 81 | 198–278 | 71.4 | 70.9 | 5.75 | 5.8 |
| $C_2H_5$ | $n$-$C_4H_9$ | 33905-75-8 | Dioxane | 77 | 150–270 | 71.9 | 71.6 | 6.0 | 6.2 |
| $C_2H_5$ | $n$-$C_5H_{11}$ | 33905-76-9 | Dioxane | 69 | 150–251 | 72.3 | 72.5 | 6.3 | 6.3 |
| $C_2H_5$ | $n$-$C_6H_{13}$ | 33905-77-0 | EtOAc | 81 | 134–248 | 72.7 | 72.1 | 6.5 | 6.2 |
| $C_2H_5$ | $n$-$C_7H_{15}$ | 33905-78-1 | EtOAc | 84 | 130–235 | 73.1 | 73.5 | 6.8 | 6.7 |
| $C_2H_5$ | $n$-$C_8H_{17}$ | 33905-79-2 | EtOAc | 74 | 124–235 | 73.45 | 73.5 | 7.0 | 6.8 |
| $n$-$C_3H_7$ | $n$-$C_3H_7$ | | | | 175–249[c] | | | | |
| $n$-$C_3H_7$ | $n$-$C_4H_9$ | 33905-80-5 | EtOAc | 82 | 151–248 | 72.3 | 72.2 | 6.3 | 6.5 |
| $n$-$C_3H_7$ | $n$-$C_5H_{11}$ | 33905-81-6 | EtOAc | 59 | 126–236 | 72.7 | 72.8 | 6.5 | 6.9 |
| $n$-$C_3H_7$ | $n$-$C_6H_{13}$ | 33905-82-7 | EtOAc | 78 | 114–230 | 73.1 | 73.2 | 6.8 | 7.0 |
| $n$-$C_3H_7$ | $n$-$C_7H_{15}$ | 33905-83-8 | EtOAc | 67 | 120–222 | 73.45 | 73.3 | 7.0 | 7.2 |
| $n$-$C_3H_7$ | $n$-$C_8H_{17}$ | 33966-22-2 | EtOAc | 71 | 128–216 | 73.8 | 74.2 | 7.2 | 7.25 |
| $n$-$C_4H_9$ | $n$-$C_4H_9$ | | | | 153–241[c] | | | | |
| $n$-$C_4H_9$ | $n$-$C_5H_{11}$ | 33903-88-7 | EtOAc | 75 | 140–229 | 73.1 | 73.7 | 6.8 | 6.8 |
| $n$-$C_4H_9$ | $n$-$C_6H_{13}$ | 33903-89-8 | EtOAc | 75 | 117–226 | 73.45 | 73.7 | 7.0 | 7.05 |
| $n$-$C_4H_9$ | $n$-$C_7H_{15}$ | 33903-90-1 | EtOAc | 67 | 114–218 | 73.8 | 74.0 | 7.2 | 7.3 |
| $n$-$C_4H_9$ | $n$-$C_8H_{17}$ | 33903-91-2 | EtOAc | 72 | 121–214 | 74.1 | 73.9 | 7.4 | 7.3 |
| $n$-$C_5H_{11}$ | $n$-$C_5H_{11}$ | 33903-92-3 | EtOAc | 78 | 145–222 | 73.45 | 73.4 | 7.0 | 7.2 |
| $n$-$C_5H_{11}$ | $n$-$C_6H_{13}$ | 33903-93-4 | EtOAc | 62 | 123–215 | 73.8 | 73.3 | 7.2 | 7.1 |
| $n$-$C_5H_{11}$ | $n$-$C_7H_{15}$ | 33903-94-5 | EtOAc | 69 | 108–210 | 74.1 | 74.1 | 7.4 | 7.2 |
| $n$-$C_5H_{11}$ | $n$-$C_8H_{17}$ | 33903-95-6 | EtOAc | 74 | 116–207 | 74.4 | 74.4 | 7.6 | 7.6 |
| $n$-$C_6H_{13}$ | $n$-$C_6H_{13}$ | | | | 124–213[d] | | | | |
| $n$-$C_6H_{13}$ | $n$-$C_7H_{15}$ | 33903-96-7 | Hexane | 74 | 118–206 | 74.4 | 74.2 | 7.6 | 7.5 |
| $n$-$C_6H_{13}$ | $n$-$C_8H_{17}$ | 33903-97-8 | Hexane | 66 | 107–202[e] | 74.7 | 74.2 | 7.7 | 7.8 |
| $n$-$C_7H_{15}$ | $n$-$C_7H_{15}$ | 1819–00–7 | | | 122–199[d,f] | | | | |
| $n$-$C_7H_{15}$ | $n$-$C_8H_{17}$ | 33903-99-0 | Hexane | 57 | 121–198[g] | 75.0 | 74.8 | 7.9 | 7.6 |
| $n$-$C_8H_{17}$ | $n$-$C_8H_{17}$ | | | | 126–195[d,h] | | | | |

[a] Satisfactory analytical data (±0.4% for C and H) were reported for all new compounds listed in the table with some exceptions: Ed. These follow for per cent carbon calculated and found (R, R′): 71.4 and 70.9 ($C_2H_5$, $n$-$C_3H_7$); 72.7 and 72.1 ($C_2H_5$, $n$-$C_6H_{13}$); 73.1 and 73.7 ($n$-$C_4H_9$, $n$-$C_5H_{11}$); 73.8 and 73.3 ($n$-$C_5H_{11}$, $n$-$C_6H_{13}$); 74.7 and 74.2 ($n$-$C_6H_{13}$, $n$-$C_8H_{17}$). [b] Reference 9. [c] M. J. S. Dewar and R. S. Goldberg, *J. Org. Chem.*, **35**, 2711 (1970); reference in footnote *b*, Table I. [d] Reference 10. [e] Smectic range 106–107°. [f] Monotropic nematic–smectic transition at 110°. [g] Smectic range 114–121°. [h] Smectic range 122–126°.

## Results and Discussion

The data from Table II are presented graphically in Figures 1 and 2. Figure 1 shows the effect on the nematic–isotropic (N–I) transition temperatures of *p*-phenylene di-*p*-*n*-alkoxybenzoates produced by varying one terminal *n*-alkyl group while holding the other constant. Figure 2 treats the melting points and smectic–nematic transition temperatures[19] in the same manner. Because of congestion of data points and intersections of curves, Figure 2 is divided into two parts with the plots for the $C_1$ through $C_4$ esters above and those for the $C_5$ through $C_8$ esters below.

In Figure 1, there is a rather regular drop in N–I transition temperature with increasing length of the varied *n*-alkyl group for all curves. This is consistent with results for other homologous series and reflects the decreasing thermal stability of the nematic mesophase with decreasing molecular rigidity and polarity (increasing *n*-alkane character).[2] For the same reason, the curves lie at progressively lower temperatures as the length of the constant alkyl group increases. This is not a regular progression, however. The curves are grouped in pairs ($C_1$–$C_2$, $C_3$–$C_4$, $C_5$–$C_6$, $C_7$–$C_8$), suggesting that there is, *e.g.*, very little difference in disruptive effect on the mesophase between $CH_3$ and $C_2H_5$, and between $n$-$C_3H_7$ and $n$-$C_4H_9$, but the latter two groups have a significantly greater effect than the former. The drop in N–I transition point on traversing a curve from the $CH_3$ to the $n$-$C_8H_{17}$ homolog varies from 71° for the $C_1$ series to 34° for the $C_8$ series. Both the N–I transition temperatures and the melting points (Figure 2) of the ethyl homologs are generally higher than would be expected from interpolation based on the other data points. This recalls the homologous series of 4,4′-di-*n*-alkoxyazoxybenzenes in which the ethyl compound has the highest melting and N–I transition temperatures.[20,21]

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[19] For a discussion of smectic mesophases, see A. Saupe, *Mol. Cryst. Liq. Cryst.*, **7**, 59 (1969).

[20] W. Maier and G. Englert, *Z. Phys. Chem.* (*Frankfurt*), **19**, 168 (1959).

[21] C. Weygand and R. Gabler, *J. Prakt. Chem.*, **155**, 332 (1940).

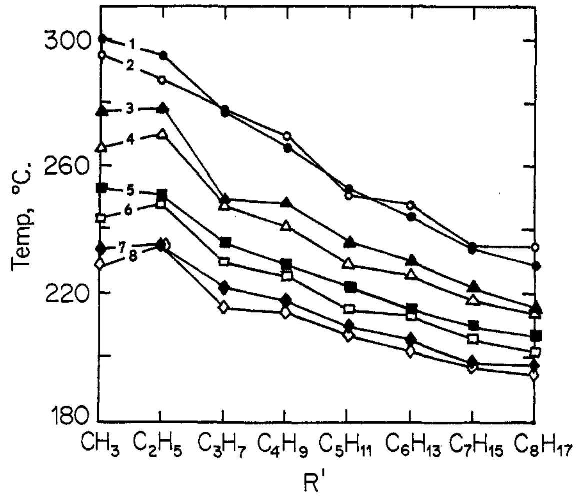

Figure 1.—Nematic-isotropic transition temperatures of *p*-phenylene di-*p*-*n*-alkoxybenzoates (2). For each curve, R is constant (R = $CH_3$ for curve 1, $C_2H_5$ for curve 2, etc.) while R′ is varied from $CH_3$ through *n*-$C_8H_{17}$.

The melting point curves (Figure 2) are much less regular than those for the N–I transitions, being strongly influenced by molecular symmetry and by the ethyl group effect just described. Good examples of this are the $C_4$ and $C_5$ curves. Traversing the former from left to right, the melting point rises on going from the methyl to the ethyl homolog and then remains almost constant through the pentyl compound before dropping off as dissymmetry and increasing alkane character exert their effects. In the $C_5$ curve, there are two obvious maxima at the ethyl and symmetrical pentyl homologs. The $C_1$, $C_2$, and $C_3$ curves decline steeply between the ethyl and butyl to hexyl homologs as dissymmetry and alkane character increase. The melting point of the $CH_3$–*n*-$C_4H_9$ ester is 88° below that of the $CH_3$–$CH_3$ ester (134 *vs.* 222°). The right-hand portions of these curves and the entire curves for the $C_6$, $C_7$, and $C_8$ series are fairly level, reflecting the dominant effect of the long alkyl chains. However, the influences of symmetry and the ethyl group can still be detected. Smectic mesomorphism appears only in the $C_6$, $C_7$, and $C_8$ series.

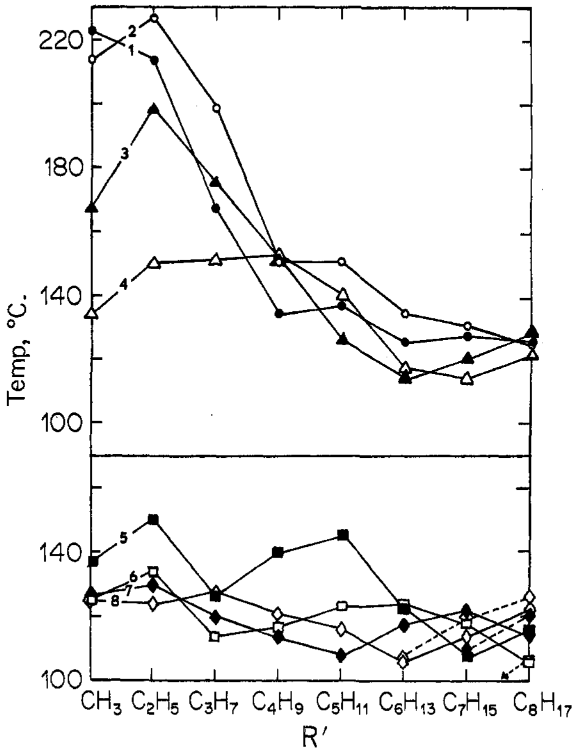

Figure 2.—Melting points and smectic–nematic transition temperatures of *p*-phenylene di-*p*-*n*-alkoxybenzoates (2). For each melting point curve, R is constant (R = $CH_3$ for curve 1, $C_2H_5$ for curve 2, etc.) while R′ is varied from $CH_3$ through *n*-$C_8H_{17}$. Smectic–nematic transition temperatures are indicated by the same symbols, but are connected by dotted, rather than solid, lines.

The data show that the introduction of dissymmetry produces the expected melting point depression without lowering the N–I transition temperature drastically (198° minimum). The lowest temperatures of transition to nematic liquid are 107 and 108°, *i.e.*, 14–15° below the lowest value for the symmetrical ester series. The new materials are still too high melting to be of practical interest, but they show promise. Their high N–I transition temperatures suggest that this chemically stable system would tolerate much more molecular dissymmetry without losing its nematic mesomorphism. Highly asymmetric esters and their mixtures should exhibit markedly lower melting points. Work along this line is in progress.