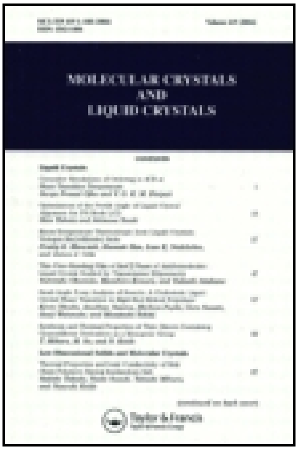

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Effect of Molecular Structure on Mesomorphism: 5. Comparison of Methyl and Trifluoromethyl as Lateral Substituents in the Solid and Nematic Phases.[1]

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Effect of Molecular Structure on Mesomorphism

5. Comparison of Methyl and Trifluoromethyl as Lateral Substituents in the Solid and Nematic Phases.[1]

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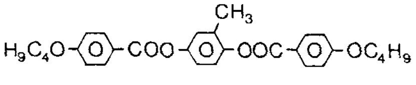
Two laterally-substituted nematogenic liquid crystals, methyl-*p*-phenylene-di-*p*-butoxybenzoate and trifluoromethyl-*p*-phenylene-di-*p*-butoxybenzoate, have been studied by differential scanning calorimetry, powder x-ray diffraction, and polarized light microscopy (hot stage microscopy and hot-wire stage microscopy). Comparison of thermodynamic data for the nematic-isotropic transitions of these two compounds suggests a strongly repulsive electronic interaction between molecules in the nematic phase of the trifluoromethyl compound. Detailed molecular structural augments are presented to rationalize the thermodynamic data. The room temperature solid phases of the two compounds were found to have different crystal structures. However, the high temperature solid phases were found, by a novel application of hot-wire stage microscopy, to be isomorphous.

The use of calorimetric thermal methods has been shown to be a valuable aid in understanding various liquid crystalline phases.[2] Recently Dewar and Griffin[3] used calorimetric DTA to examine the effects of lateral substituents in the nematic phase of a series of substituted *p*-phenylene di-*p*-anisates. Thermodynamic (ΔH and ΔS) values obtained[3] for the nematic–isotropic (N → I) transition allow an interpretation of substituent effects which is more definitive than that proposed[4] on the basis of transition temperatures alone. The essential feature of this new explanation[3] of protruding lateral substituents is that they act to lower the N → I temperature (compared to the parent hydrogen-substituted compound) mainly by increasing the entropy change (ΔS) accompanying the N → I transition. Since at the first order N → I transition, $\Delta G = 0$; then $\Delta H = T\Delta S$. Thus, an increase in ΔS, assuming a constant ΔH, will lower the value of T.

In an effort to expand the understanding of substituent effects we decided to examine two closely related compounds, 1 and 2, shown below.



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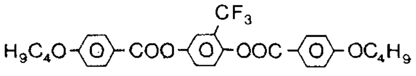


2

The only structural difference between these two compounds is in the lateral substituent. Trifluoromethyl is not only slightly larger but also has a considerably different electron configuration than methyl. The differences between the two groups are the structural probes by which the nematic liquid crystalline phases will be examined. Differential scanning calorimetry and polarized light microscopy were employed for this purpose. Powder x-ray diffraction was used to determine similarities or differences in room temperature crystal structures, and hot-wire fusion techniques provided information on the solid phase polymorphism of these compounds.

EXPERIMENTAL

Synthesis:

Methyl-p-phenylene-di-p-butoxybenzoate Methylhydroquinone, (Aldrich) 1.24 grams (0.01 moles), was dissolved in a small volume of pyridine (20 mls) at room temperature. To this stirred solution was added p-butoxybenzoyl chloride, 4.25 grams (0.02 moles). After stirring overnight at room temperature, the resulting solution (upon acidification with dilute HCl) afforded a white solid. It was collected by suction filtration and washed with water. After air drying the filter cake was recrystallized twice from ethanol-chloroform to yield 3.1 grams (65%) of 1 as white feathers.

Trifluoromethyl-p-phenylene-di-p-butoxybenzoate Trifluoromethylhydroquinone[5] was esterified in like manner to yield 52% of beautiful fine white needles.

Quantitative elemental analysis (combustion) for these two compounds gave acceptable results. Thin layer chromatography gave results consistent with a single component (high purity) sample. These compounds showed the following infrared spectral data: Compound 1 (KBr pellet): 3036(w), 2954 with shoulder(m), 2868(m), 1726(s), 1609(s), 1513(m), 1255(s), 1154(s), 1072(s) cm^{-1}. Compound 2 (KBr pellet): 3071(w), doublet centered at 2941(m), 2865(w), 1742(s), 1612(s), 1513(m), 1255(s), 1163(s), 1122(s), and 1067(s) cm^{-1}.

Calorimetry

Quantitative calorimetry was obtained with a Perkin-Elmer 1B differential scanning calorimeter. This instrument was calibrated for temperature measurement by fusion of ultra purity naphthalene, indium, tin, lead, and benzoic acid. We used indium to calibrate for enthalpy determination at all sensitivity settings used in this study. Baseline construction for enthalpic determination was performed according to Young *et al.*[6] Measurement of peak areas was performed by planimetry. Data in Table I represent average values from multiple determinations. From calibration data and the degree of internal consistency of multiple runs we are confident of a 4% maximum error in relative values and a 10% maximum error in absolute values for our enthalpic determinations for the N → I transition. A smaller error range is in effect for the C → N transition.

Optical microscopy:

A Reichert Kofler micro hot stage used in conjunction with a Leitz polarized light microscope served to allow determination of transition temperatures and identification of liquid crystalline textures. (Transition temperatures obtained by microscopy agreed within two degrees with values from D.S.C.) The photograph was made using a Polaroid attachment at 200 magnification.

X-Ray Diffraction:

A General Electric XRD-5 x-ray diffractometer employing the standard θ-2θ method was utilized.

Partial monochromatization of the incident radiation was accomplished with a nickel filter. The incident radiation was focused onto the sample via a conventional slit system. X-rays scattered from the finely powdered samples were colummated through two receiving slits and detected with a scintillation detector. The reported intensities have been corrected for background but not by polarization and Lorentz factors. Uncertainty in d spacings are *ca.* ±0.02 Å, while uncertainties in the calculated intensities are no more than ±3%.

Mixed fusion studies:

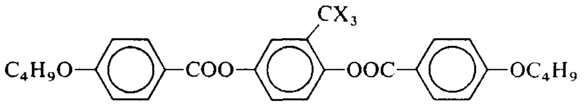
Mixed fusion preparations were made using the Kofler contact method[7] and studied using conventional hot stage microscopy and then by hot-wire stage microscopy. The hot-wire stage was a modified version[8] of a design of Hartshorne.[9] A specially designed voltage regulator[8] was employed for this work.

Results and discussions

Table I gives thermodynamic data (temperatures, enthalpies, and entropies of transition) for compounds 1 (methyl) and 2 (trifluoromethyl) as obtained by differential scanning calorimetry. Solvent crystallized and melt crystallized (one previous run) samples are entered separately. A period of one month

TABLE I

Thermodynamic data for compounds 1 and 2 obtained by D.S.C. (in heating mode).



X	$T^a_{C\to N}$	$\Delta H^b_{C\to N}$	$\Delta S^c_{C\to N}$	$T^a_{N\to I}$	$\Delta H^b_{N\to I}$	$\Delta S^c_{N\to I}$
H[d]	115.3[e]	7.50	19.30	206.0	0.77	1.61
H[f]	114.8[g]	7.48	19.27	206.2	0.74	1.54
F[d]	102.1[h]	8.97	23.89	151.8	0.57	1.35
F[f]	98.4[i]	8.48	22.91	152.2	0.60	1.40

[a] in °C.

[b] in kcal/mole.

[c] in entropy units.

[d] solvent crystallized sample.

[e] a crystal–crystal ($C_1 \rightarrow C_2$) transition occurs at 50.7° with a ΔH of 1.65 kcal/mole and a ΔS of 5.10 entropy units.

[f] melt crystallized sample (previously run), one month lapsed after inital run.

[g] the temperature region for a $C_1 \rightarrow C_2$ transition was not scanned on melt crystallized sample.

[h] shoulder on low temperature side of endotherm, not resolvable.

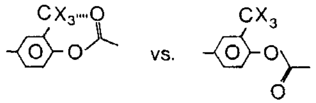
[i] a crystal–crystal transition occurs at 95.6°, but it is not resolvable; therefore, the ΔH and ΔS values for the C → N transition are for the combined transitions ($C_1 \rightarrow C_2 \rightarrow N$)

elapsed between the initial calorimetry and the second thermal regimen. The major change in the thermal behavior of these compounds, on the second calorimetric scan, is that the trifluoromethyl compound 2 shows definite solid phase polymorphism absent in the solvent recrystallized material. With that exception, the thermodynamic values for each compound are quite similar; appearing independent of thermal history. The crystal → nematic transition enthalpy for 1 is lower than that of 2, but becomes slightly higher if the crystal–crystal ($C_1 \rightarrow C_2$) transition values are considered with those of the C → N transition. A small shoulder on the low temperature side of the C → N endothern for 2 may reflect a crystal–crystal transition at a temperature very close to the C → N temperature.

Values for the nematic–isotropic (N → I) transition are quite informative. The N → I temperature for 2 is considerably lower than that of 1. Each quantity, ΔH and ΔS, is, for the N → I transition, decreased for 2 compared to 1. However, the entropy decrease is less than the enthalpy decrease. This inequality in $\Delta(\Delta H)$ and $\Delta(\Delta S)$ from 1 to 2 leads to lowering of the N → I transition temperature. On a molecular level two interpretations seem plausible:

1) The larger trifluoromethyl group forces the long axes of the molecules further apart thereby weakening intermolecular bonding (and as a corollary lessening the molecular order of the mesophase). This explanation, based on size only, is difficult to reconcile with previous studies[3] of similar systems. If, however, the lone pair electrons on the fluorine atoms are also considered, an alternative explanation based on electron-electron repulsion appears reasonable; a nematic phase in which the highly polar trifluoromethyl groups force neighboring molecules further apart due to repulsive interactions. The intermolecular bonding loss (due to electron-electron repulsion) is greater than loss of positional order.

2) An intramolecular process in which the CF_3 substituent causes a decrease in rotational freedom of the (carbonyl) carbon-(σ-bonded) oxygen bond. This restriction in the nematic phase, in which a "flat" molecule is required, may be lifted in the isotropic phase where bond rotation, as shown above, would be less constrained. The trifluoromethyl substituent should offer more resistance to such a rotation than the methyl substituent due to its size and also to the carbonyl (0) lone pair-(F) lone pair electronic repulsion. In the isotropic phase such a rotation for 1 may be more free (little electronic



repulsion), but still quite restricted for 2 due to electrostatic repulsion as described above. Thus the smaller ΔS for 2 is explicable by considering the electronic repulsion as overwhelming the relaxation of rotational constraints at the N → I transition for compound 2.

The x-ray powder patterns of 1 and 2 (Table II) clearly indicate that at room temperature the crystalline forms of these two compounds are not isomorphous. The powder patterns indicate rather, that the two compounds have distinctly different crystal structures. No attempt has been made to do a detailed crystal structure analysis of either compound.

TABLE II

X-ray powder patterns

Trifluoromethyl,2

	Relative intensity[a]	$2\theta°$, degrees[b] ($\pm 0.05°$)	d, Å (± 0.02 Å)
1	100	18.00	4.92
2	44	22.33	3.97
3	40	19.78	4.48
4	25	10.01	8.84
5	17	27.77	3.21
6	15	8.77	10.04
7	15	26.30	3.37

Several other small, broad peaks also occur.

Methyl,1

	Relative intensity[a]	$2\theta°$, degrees[b] ($\pm 0.05°$)	d, Å (± 0.02 Å)
1	100	21.08	4.17
2	80	12.51	7.07
3	40	25.40	3.50
4	19	9.41	9.40
5	15	19.28	4.57
6	14	17.80	4.98
7	12	18.19	4.82

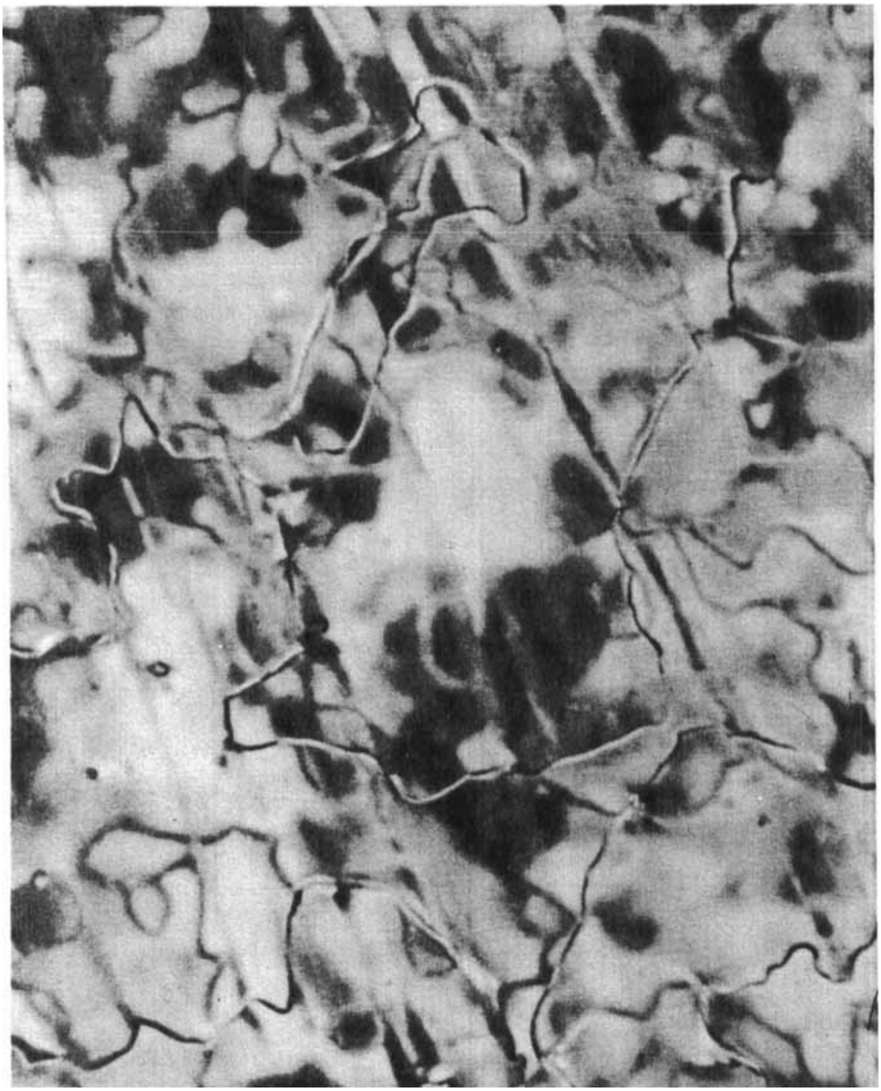
Several other small, broad peaks also occur.

[a] Relative intensities have not been corrected by Lorentz-polarization factor.

[b] Nickel filtered copper x-rays have been utilized.

Optical microscopy

Both compounds exhibit identical nematic textures of the Schlieren type. However, it is possible to obtain a threaded texture for both of them. No smectic phase is seen even on extensive supercooling of the nematic phase. A photograph of the nematic phase of compound 1 in the threaded texture is shown below.



Photograph of compound 1 in its nematic phase.

Fusion studies

A mixed fusion preparation (by the Kofler contact method) confirmed, upon examination by hot stage microscopy, that the room temperature solid phases of the compounds are not identical. The nematic phases of the two are totally miscible. It was not possible to obtain information from hot stage microscopy concerning possible isomorphy of the high temperature solid phases of these compounds due to extremely rapid crystallization of the entire micro-sample once solidification from the supercooled nematic phase had begun. Fortunately, we were able to overcome this difficulty by using a specially designed[8] hot-wire stage.

Examination of the binary mixture with this stage (oriented with the wire perpendicular to the zone of mixing) offered unequivocal evidence of an isomorphous relationship between the high temperature solid phases of these two compounds. A linear relationship between C → N (and N → C) transition temperatures with concentration was clearly seen as a diagonal line across the sample representing this transition under the polarizing microscope equipped with the hot-wire stage. A schematic, condensed partial phase diagram for this binary system is presented below.

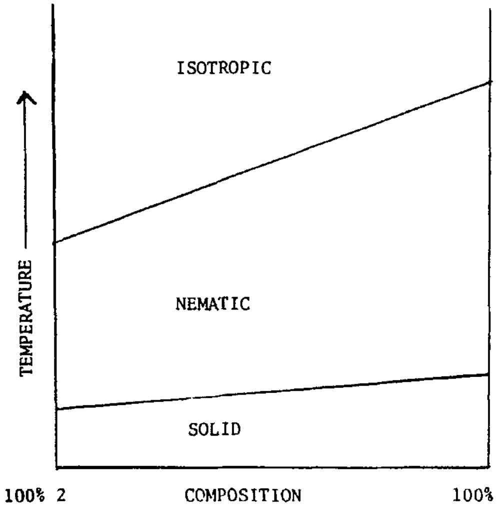


FIGURE 1 A schematic, condensed binary phase diagram of compounds 1 and 2.

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