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Liquid crystals of 4-octyloxy-*N*-(benzylidene)aniline derivatives bearing trifluoromethyl or trifluoromethoxy end groups

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Seven new derivatives of 4-octyloxy-*N*-(4-substituted benzylidene) aniline have been synthesized. 4-Trifluoromethyl and 4-trifluoromethoxy derivatives exhibit stable smectic B and A phases, respectively, while both the 4-methyl and 4-methoxy derivatives have monotropic nematic phases. Fundamental liquid crystalline properties such as entropies of the phase transitions, microscopic textures, smectic layer spacings, orientational order parameters, and molecular dipole moments were determined. It has been revealed that moderately polar nature of these mesogens act to stabilizing monolayer smectic states. The smectic A phase of 4-trifluoromethoxy derivative exhibit very high orientational order. None of the disubstituted compounds, 3,5-bis(trifluoromethyl), 3,5-dimethyl, and 3,5-dimethoxy derivatives were mesogenic. The effect of terminal trifluoromethylation on the liquid crystalline properties is discussed.

1. Introduction

Numerous pieces of work have been carried out over more than a decade on the unusual liquid crystalline properties of strongly polar mesogens, for example, smectic A–smectic A (S_A–S_A) phase transitions, reentrant phase transition, etc., caused by the strong antiferroelectric intermolecular interactions [1]. Detailed experimental studies, however, have been concerned almost exclusively with the terminal cyano or nitro compounds. Studies on possibly novel characteristics exhibited by the polar mesogens other than cyano or nitro compounds are nonetheless of considerable interest. Terminal trifluoromethyl or trifluoromethoxy compounds, for example, would be interesting due to their fairly strongly polar nature. High chemical stability compared to the cyano compounds is also an advantage. In fact, the terminal trifluoromethylated liquid crystalline compounds have attracted recent attention in high-speed active matrix display devices requiring materials of low viscosity, high dielectric anisotropy, and extremely high chemical stability [2–4]. In this work seven compounds of 4-octyloxy-*N*(substituted benzylidene)aniline (XBOOA) family have been synthesized, and the fundamental liquid crystalline properties studied. Three of the compounds are 4-trifluoromethyl, 4-trifluoromethoxy, and 3,5-bis(trifluoromethyl) derivatives, and the other four are 4-methyl, 4-methoxy, 3,5-dimethyl, and 3,5-dimethoxy derivatives for comparison. This paper is also an extension of our studies on the effect of terminal polar substituents on the nature of liquid crystals [5, 6].

2. Experimental

The compounds are listed in table 1. The materials were synthesized by the condensation of 4-octyloxyaniline with the corresponding benzaldehydes. After several recrystallizations from ethanol, and molecular distillation, chemical analyses gave good agreement with the formulae.

The mesomorphic phase sequences were studied with a DuPont 9900 differential scanning calorimeter and Olympus POS polarizing microscope equipped with a homemade heating stage. For quantitative calorimetric measurements, the enthalpy of the phase transition was calibrated by the melting of the zone-refined specimens of benzoic acid and biphenyl. The smectic structures were studied with a Mac Science MXP X-ray diffractometer and with a homemade Fourier transform NMR spectrometer working at 55 MHz for protons. The X-ray scattering angle

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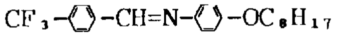
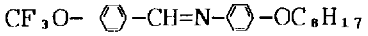
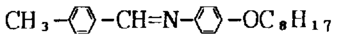
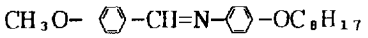
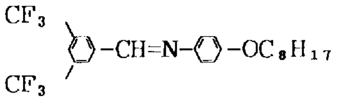
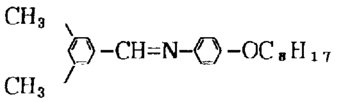
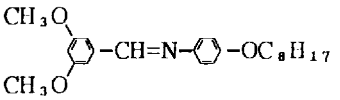
Table 1. Temperatures and entropies of phase transitions. Observed stable phases are designated by *. The figures represent the temperatures of phase transitions in Kelvin, and the figures in parentheses stand for the discontinuities of entropy at the phase transitions in units of $J\,K^{-1}\,mol^{-1}$. $\Sigma\Delta S_{tr}$ represents the accumulated entropy of phase transitions for each compound.

	Compounds	Crystal		S_B		S_A		I	$\Sigma\Delta S_{tr}$	Metastable phases
I		*	369·6 (73·8)	*			373·2 (29·3)	*	(103·1)	
II		*			357·5 (87·3)	*	371·9 (17·3)	*	(104·6)	S_B
III		*					351·5	*	(99·0)†	N
IV		*					377·21 (112·1)	*	(112·1)	N
V		*					321·4	*	(110·8)†	
VI		*					324·7 (116·2)	*	(116·2)	
VII		*					316·3 (111·6)	*	(111·6)	

† Transition entropies were accumulated on cooling.

was calibrated by the (00*l*) peaks of the monoclinic *c*-polytype powder of stearic acid. The dipole moments of the terminally substituted molecules were determined with heterodyne beat method in dilute benzene solutions at 25°C.

3. Results and discussion

3.1. *DSC study*

The phase transition sequences studied by the differential scanning calorimetry are summarized in table 1. The 4-trifluoromethyl derivative (compound **I**) exhibited a strongly first order phase transition from the isotropic (I) phase to a stable smectic B (S_B) phase. The transition was enantiotropic, and the entropy of the transition, ΔS_{BI}, was 3·52 R. The DSC thermogram for the trifluoromethoxy derivative (compound **II**) is shown in figure 1 as an example. This compound exhibited a stable smectic A (S_A) and a monotropic S_B phases. To know which category of the S_B liquid crystal, hexatic B (S_B (hex)) or crystal B (S_B (cryst)), this phase belongs to, entropy change ΔS_{BA} was determined for the cooling run. The value of 1·10 R was then obtained which is about twice the mean field theoretical value (0·559 R) predicted by Meyer and McMillan [7]. Huang *et al.* [8], reported by their AC calorimetric measurement a first order asymmetric heat capacity anomaly at the S_B (cryst) to S_A phase transition in 4-octyl-*N*-(4-butoxybenzylidene)aniline (4O·8), while a sharp, symmetric, and nearly continuous thermal anomaly was observed at the S_B (hex) to S_A phase transition in hexyl-((4-pentyloxy)biphenyl) carboxylate (65OBC). The large asymmetric thermal anomaly in figure 1 suggests a crystal B character of the S_B phase of compound **II**. Both the 4-methyl and 4-methoxy derivatives (compounds **III** and **IV**) exhibited monotropic nematic (N) phases on cooling. The transition entropies ΔS_{NI} were 0·31 R and 0·19 R for **III** and **IV**, respectively, and these are smaller than the mean field theoretical value of 0·42 R [9, 10]. No mesophases were found for compounds **V**, **VI** and **VII**. Solid-state polymorphism was observed in **III** and **V**.

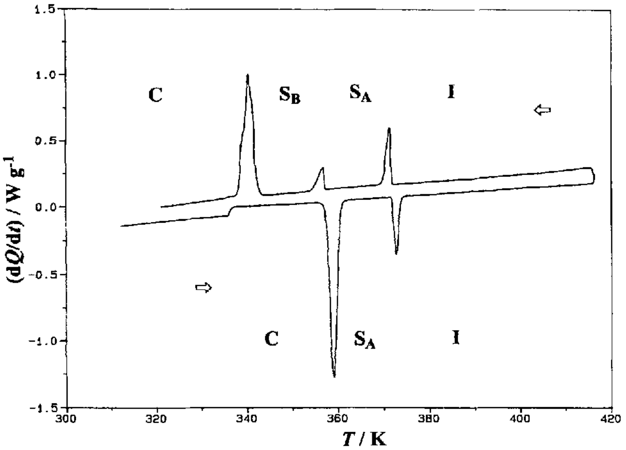


Figure 1. DSC thermogram of compound **II** (4-trifluoromethoxy derivative) at heating and cooling rates of 2 K min^{-1}. Exothermic heat flow dQ/dt is taken positve.

3.2. *Microscopic textures*

The phase transition sequences were also studied by light polarized microscopic observations. Most interesting textural changes were observed for compound **II** and are shown in figure 2. On cooling from the isotropic phase, a typical fan-shaped texture was observed in the S_A phase (see figure 2 (*a*)). Distinct transition bars appeared at the S_A to S_B transition point, T_{BA} (see figure 2 (*b*)). The bars disappeared immediately below T_{BA}, and the original fan-shaped texture was recovered in the S_B phase (see figure 2 (*c*)). On reheating to the S_A phase, very faint transition bars appeared at T_{BA}, and were then replaced by numerous small focal conic defects (see figure 2 (*d*)). When the sample was cooled again to the S_B phase, these defects disappeared on passing T_{BA}, and a fairly smooth texture similar to figure 2 (*c*) was recovered. These textural changes were reproducible during repeated thermal cycles.

Generally it is not easy to distinguish S_B (hex) phase from S_B (cryst) phase. Goodby and Pindak [11] and Gray and Goodby [12, 13] reported that the transition bars are often observed at the S_A–S_B (cryst) transition, while the small defects on the focal-conic fans are often observed in the S_A phase reheated from S_B (hex). Compound **II** exhibited both features. The observation of the transition bars suggests that our phase is S_B (cryst), but the case is not as typical as in 4-(4-alkoxybenzylideneamino)-biphenyls [12] in that they were observed only in a very narrow temperature range (less than *c*. 1 K around T_{BA}), and that the recovered focal conic fan-shaped texture in the S_B phase was fairly stable and showed no noticeable changes after repeated thermal cycles. The origin of the transition bars has not been well understood though a number of explanations have been made [11–14]. At present, it seem clear at least that this phenomenon requires the S_A–S_B transition to be of first order. In the present case, the large latent heat as shown in figure 1 and table 1 is consistent with the texture observation. Although detailed X-ray study is most desirable to fully characterize the present S_B structure, the S_B phase of compound **II** is most probably to be classified into S_B (cryst) judging from the strongly first order nature of the thermal anomaly and the appearance of the distinct transition bars.

The texture of the S_B phase of compound **I** was of mosaic type. The monotropic N phases of compounds **III** and **IV** were characterized by their typical schlieren textures.

3.3. *X-ray and NMR studies of the smectic structure*

In all the smectic phases of compounds **I** and **II**, the first and the second order quasi-Bragg peaks corresponding to the smectic layer spacings d were observed. Table 2 summarizes the results: for the S_B phase in compound **I**, $d = 26{\cdot}3$ Å, and for the S_B and the S_A phases in compound **II**, $d = 26{\cdot}2$ Å and $25{\cdot}2$ Å, respectively. The molecular length along the long axis of these compounds is 25–26 Å based on a stereochemical molecular model. Therefore, the observed d-spacings show that these mesophases are of the untilted monolayer type. It is interesting to note that the first and the second order peaks were observed in the S_A phase of compound **II**, while the second order peak was lacking in the S_{A_d} phase of the 4-cyano derivative (CBOOA) [15]. This means that the S_A phase of compound **II** has a more distinct layer structure than the sinusoidal density wave in CBOOA.

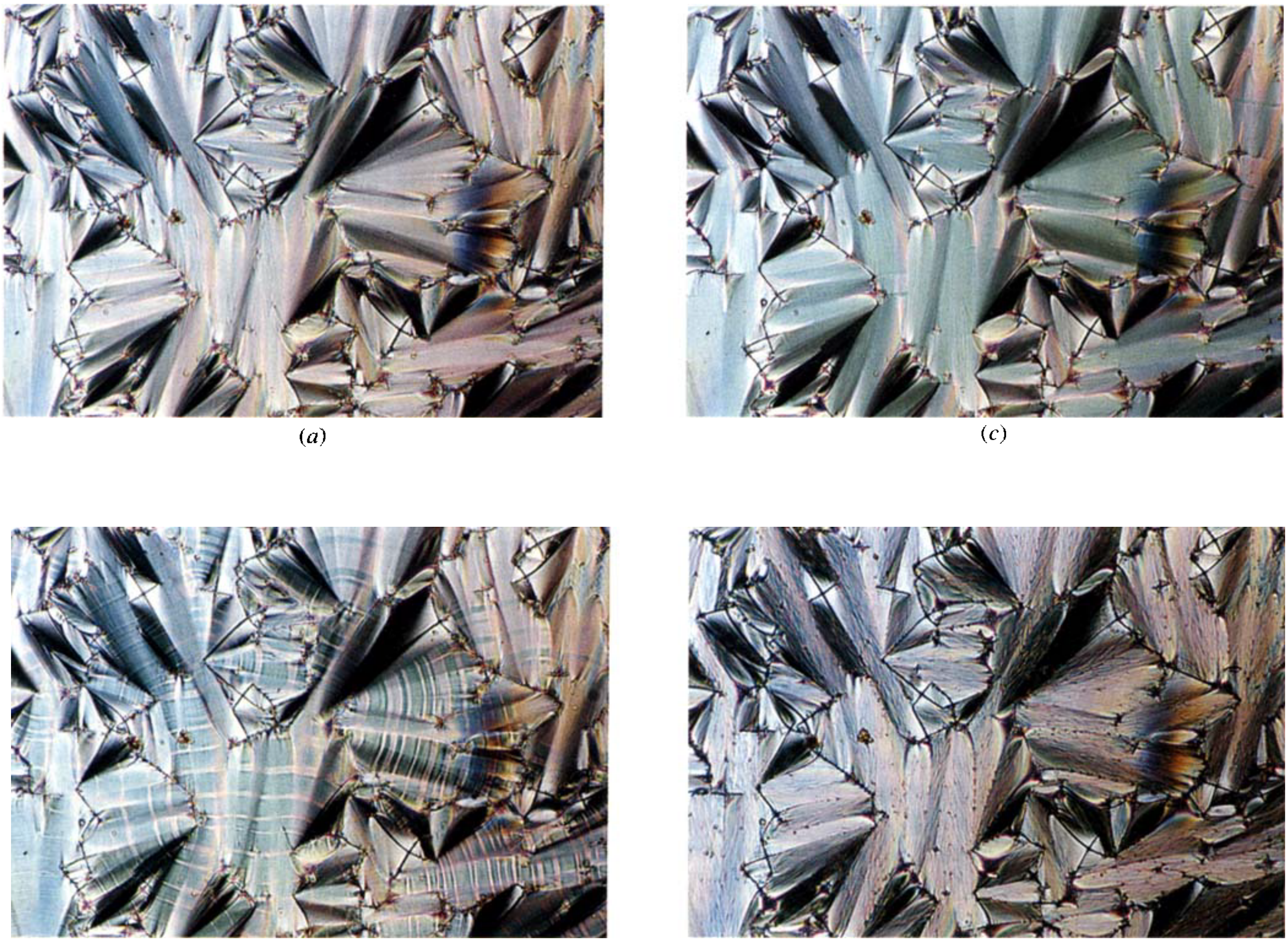
^{1}H NMR studies were carried out to study further the nature of the smectic phases of compounds **I** and **II**. If the smectic phase is of the orthogonal type (in which the director is parallel to the layer normal), the dipolar splitting frequency is given by the equation in SI units [16],

$$\Delta\nu = 3\mu_0/(8\pi^2)\gamma_p^2\hbar r^{-3}p_2(\cos\phi)S|p_2(\cos\theta_o)|. \qquad (1)$$

Here θ_o is the angle between the director and the external magnetic field, r the length of the smallest interproton vector in the phenylene ring, ϕ the angle between this vector and the axis of fast rotational diffusion of the molecule, and $p_2(x)$ the Legendre polynomial of rank two. The second rank orientational order parameter is represented by S. The other notations have their usual meanings. From equation (1), the following relationship is readily obtained,

$$\Delta\nu(\theta_o)/\Delta\nu(0°) = |p_2(\cos\theta_o)|, \qquad (2)$$

which is independent of the magnitude of the orientational order parameter. Figure 3 shows the angular dependence of $\Delta\nu$ in the S_A phase of compound **II**. It is seen that the experimental results follow equation (2), and the dipolar splitting vanishes as θ_o approaches the magic angle (54·7°). It is thus revealed that this smectic phase is of



(*a*) (*c*)

(*b*) (*d*)

Figure 2. Polarized microscopic textures of compound **II** (4-trifluoromethoxy derivative) taken in chronological order, (*a*) at 358·4 K, focal-conic fan-shaped texture in the S_A phase cooled from the isotropic phase, (*b*) at 357·5 K on the first cooling run, distinct transition bars appearing at the S_A to S_B phase transition, (*c*) at 345·4 K, recovered fan texture in the S_B phase, and (*d*) at 360·8 K, numerous small focal-conic defects covering the fan-shaped texture in the S_A phase reheated from the S_B phase.

orthogonal type. The origin of the disagreement at high angle region is not clear. Judging also from the textures, DSC, and X-ray results, the stable smectic phase of compound **II** is S_A. The orientational order parameter S of this phase, estimated by using $r = 0{\cdot}245\,\mathrm{nm}$ and $\phi = 10°$, turned out to be $0{\cdot}83 \pm 0{\cdot}04$. The uncertainty comes from the inconsistency in the angular dependence data mentioned above. Anyway, the orientational order of this S_A phase has proved to be very high, in contrast to the S_{A_d} state observed in the 4-cyano and 4-nitro derivatives, where S varied from 0·67–0·77 (for the cyano derivative) and 0·55–0·68 (for the nitro derivative) depending on temperature [17]. The very high orientational order and the distinct layer structure of the monolayer type are the characteristic features of the S_A phase exhibited by the 4-trifluoromethoxy derivative, in clear contrast with the highly disordered S_{Ad} phase exhibited by the cyano and nitro derivatives.

The NMR investigation could not be extended to the S_B phases; crystallization took place during the measurement in the metastable S_B phase of compound **II**, and the director alignment was not achieved in the S_B phase of compound **I** by cooling from its isotropic melt in the magnetic field.

3.4. *Accumulated entropies of phase transitions*

The accumulated transition entropies are also listed in the table for each compound, and they fall in the range, $\Sigma\Delta S_{tr} = 108 \pm 9\,\mathrm{J\,K^{-1}\,mol^{-1}}$. For compounds **III** and **V**, it was difficult to measure ΔS_{tr} on heating due to the overlap of solid–solid phase transition peaks, and therefore the summation of $\Delta\ S_{tr}$ was done on cooling. The values of $\Sigma\Delta S_{tr}$ are similar for this series of compounds, showing that the room temperature crystalline state has similar entropies. This fact was first pointed out for rod-like molecules by Tsuji *et al.* [18], in the 4-substituted-*N*-(4-hexyloxy)benzylideneanilines, and later confirmed by the present authors in the 4-(halo, nitro, and cyano) substituted analogues of the present series. The values of $\Sigma\Delta S_{tr} = 116 \pm 8\,\mathrm{J\,K^{-1}\,mol^{-1}}$ have been previously reported for these compounds [6]. It is interesting to note that the present result is within its scattering range. Considering that each of the new compounds has one or two additional rotatable segment at one end of the molecule, $\Sigma\Delta S_{tr}$ may be expected to be larger. The fact that the present values are similar or even smaller suggests that the terminal CX_3(O)- groups (X = H or F) may rotate fast enough and contribute little to the steric hindrance in the solid state. This appears to be so even in the 3,5-bis[CX_3(O)] compounds.

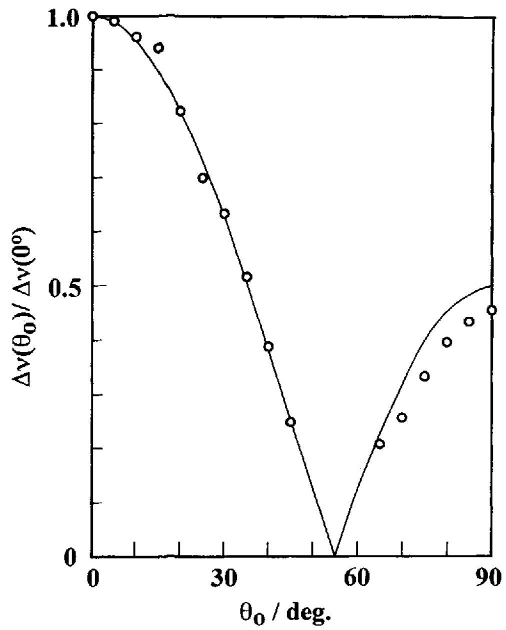


Figure 3. Proton NMR dipolar splitting width as a function of the angle between the director and the external magnetic field in the S_A phase of compound **II** (4-trifluoromethoxy derivative), taken at 361·0 K. The solid line represents equation (2) in the text.

3.5. *Dipole moments of the 4-substituted molecules*

The dipole moments μ were measured for the 4-substituted compounds, **I–IV**, and are listed in table 2, together with the previously studied compounds, where the compounds are listed in an increasing order of μ. It is seen that, for methyl and methoxy derivatives, the values of μ, 1·80 D and 1·91 D, stand between the unsubstituted and the halo compounds, and for trifluormethyl and trifluoromethoxy compounds, the values, 3·54 D and 3·21 D, stand between the halo and the nitro/cyano compounds. It is interesting to note that trifluoromethyl and trifluoromethoxy compounds offer moderately polar mesogens, and enable us to study the effect of molecular polarity on the liquid crystalline properties in a systematic manner.

3.6. *Effect of terminal trifluoromethylation on the liquid crystalline properties*

The most evident effect of perfluorination of the terminal methyl or methoxy substitutents is that the compounds **I** and **II** exhibit stable smectic phases, whereas

Table 2. Molecular dipole moments μ, smectic layer spacings d, and the observed liquid crystalline phases of the 4-octyloxy-*N*-(4-substituted) benzylideneanilines,  .

X	μ/Debye	Smectic layer spacings d/Å S_B	S_A	Stable phases	Metastable phases	Mesomorphic temperature range/K§
H‡	1·77					0
CH_3†	1·80				N	0
CH_3O†	1·91				N	0
F‡	2·52				S_A N	0
Cl‡	2·56	25·1	24·7	S_B S_A		18·1
I‡	2·65					0
Br‡	2·68	25·8	25·4	S_B S_A		22·7
CF_3O†	3·21	26·2	25·2	S_A	S_B	14·4
CF_3†	3·54	26·3		S_B		3·6
NO_2‡	5·14		31·9	S_{A_d} N		22·0
CN‡	5·21		35·7	S_{A_d} N		35·1

† Present study.
‡ Reference [6].
§ Only the stable mesophases were taken.

the hydrogenated counterparts, **III** and **IV** have only metastable N phases. A number of works have been conducted on the liquid crystalline nature of the terminally trifluoromethylated compounds. Some of the examples are poor nematogens [2, 3, 19] and others show a strong smectic-forming tendency [20–25], with a special preference for S_B. The present study confirmed these tendencies.

The smectic-forming tendency may be related to the fact that trifluoromethylated molecules have moderately large dipole moments. It was previously shown for the homologous series of 4-substituted-*N*-[4-(4-octyloxybenzoyloxy)benzylidene]anilines (OBBX series) that moderately polar terminal substituents like halogens stabilize the S_A phase, but extremely polar substituents such as cyano group relatively stabilize the N phase. Table 2 evidently shows that this conclusion holds for the present series, too. The liquid crystalline nature is enhanced in the polar homologues compared to the unsubstituted compound, which is a non-mesogen. It is recognized that the N phase is relatively stabilized in weakly polar and extremely polar compounds, but lost in the moderately polar compounds. On the other hand, monolayer-type S_A and S_B phases were obtained for the derivatives having dipole moments of between 2·52–3·54 D, showing that moderately polar substitutents stabilize the layer structure. When the terminal substituents are extremely polar, antiparallel association of molecules destroys the distinct layer structure and stabilizes the N phase relative to smectic phases. A contrast between the highly disordered S_{A_d} phase in the cyano derivative and the highly ordered monolayer S_A phase in the trifluoromethoxy derivative shows that antiparallel association destabilizes the smectic structure.

4. Summary

Trifluoromethyl, trifluoromethoxy, methyl, and methoxy derivatives of 4-octyloxy-*N*-(4-substituted benzylidene)aniline offer new series of polar liquid crystals. The former two are characterized by moderately polar nature and a smectic forming tendency, while the latter two are characterized by very weakly polar nature and a nematic forming tendency. The 4-trifluoromethyl compound has a stable S_B phase. The 4-trifluoromethoxy compound has a stable S_A and a monotropic S_B phases. The S_A phase exhibits a very high orientational order and distinct layer structure in contrast to the S_{A_d} phase exhibited by the 4-cyano or 4-nitro homologues. The S_B phase is classified into crystal B phase. All of these smectic phases are of monolayer type. Bis-(trifluromethyl), dimethyl, and dimethoxy derivatives of 4-octyloxy-*N*-(3,5-disubstituted benzylidene)aniline did not exhibit liquid crystalline phases, probably due to the bulkiness of the molecules.

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