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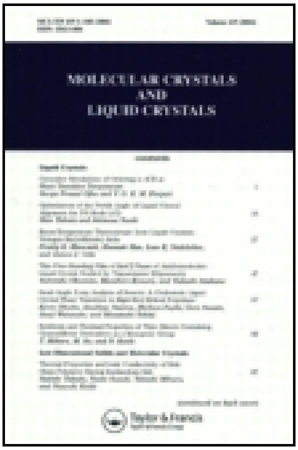

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Mesomorphic Thermal Stability of 3-(4-Alkoxybenzylideneamino)-dibenzofurans and 3-(4-Alkoxybenzylideneamino)-dibenzothiophenes

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Mesomorphic Thermal Stability of 3-(4-Alkoxybenzylideneamino)-dibenzofurans and 3-(4-Alkoxy-benzylideneamino)-dibenzothiophenes

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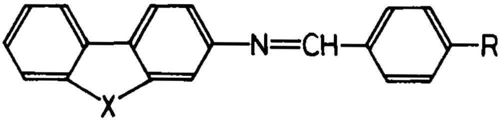
(*Received June 24, 1985*)

The homologous series of two kinds of heteroaromatic liquid crystals(I,X=—O— and —S—) were prepared and their mesomorphic thermal stabilities were investigated. Some factors determining the stability were examined and the results indicate that the bridging atom(X) incorporated in the structure(I) significantly affects the mesomorphic thermal stability.



(I)

R=alkoxyl

The liquid crystalline properties of Schiff's base compounds(I) containing fluorene(I,X=—CH_2—),[1] fluorenone(I,X=—CO—),[1] 9-methyl- and 9H-carbazoles(I,X=—N(CH_3)— and X=—NH—, respectively),[2] 9,10-dihydrophenanthrene(I,X=—CH_2CH_2—),[3] and phenanthrene(I,X=—CH=CH—)[4] have already been reported for their homologous series.

The effect of a hetero atom(X) on the mesomorphic thermal stability has not so far been discussed.

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In the present paper, the thermal stabilities of dibenzofuran and dibenzothiophene analogues(I) were studied from the viewpoints of the molecular geometry and the polarizability.

RESULTS AND DISCUSSION

The transition temperatures and enthalpies of 3-(4-alkylbenzylideneamino)dibenzofurans, 3-(4-alkoxybenzylideneamino)dibenzofurans and 3-(4-alkoxybenzylideneamino)dibenzothiophenes, which are abbreviated as DBFCn, DBFOCn and DBTOCn, respectively, are shown in Tables I, II and III. The n means the number of carbon atoms in the terminal aliphatic chain. Figures 1, 2 and 3 show the mesomorphic trends of each homologous series.

In both cases of DBFCn and DBFOCn, the mesomorphic trends are similar to those of the other reported liquid crystals(I) in the odd-even alternations of nematic to isotropic phase transition temperatures, the appearance of smectic A phase in the region of the longer alkyl chain($n \geqq 7$), the disappearance of nematic phase($n \geqq 14\sim15$), the lower mesomorphic thermal stability for alkyl derivatives than for alkoxy ones by about 30° and so on. However, only DBFC7 was found to have a monotropic smectic G phase with a mosaic texture, which was identified by miscibility test with terephthalylidene-bis(4-butylaniline) [TBBA].[5]

TABLE I

Transition temperatures and enthalpies of DBFCn[a]

n	$T_{C—S_A,N\text{ or }I}$	$\Delta H_{C—S_A,N\text{ or }I}$	$T_{S_A—N\text{ or }I}$	$\Delta H_{S_A—N\text{ or }I}$	$T_{N—I}$	$\Delta H_{N—I}$
1	158.8	35.0				
2	116.8	28.4				
3	104.6	19.9			114.7	0.5
4	92.7	26.6			102.3	0.4
5	97.0	22.4			121.0	0.5
6	88.5	29.6	[77.0][b]		110.7	0.4
7[c]	84.3	27.9	91.3	1.1	120.6	0.8
8	90.2	36.4	97.2	1.6	115.2	0.6
9	83.3	33.7	104.0	1.7	119.0	0.8
10	92.6	44.4	105.9	2.6	114.9	0.9
12	96.0	51.3	109.2	3.3	113.3	1.3
13	87.0	39.0	108.7	2.9	111.8	1.9
16	102.1	69.0	109.1	5.4		

[a] T in °C and ΔH in kJ/mol.

[b] [ ]: monotropic transition.

[c] $S_G - S_A$ monotropic transition appeared at 58.7°C.

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TABLE II

Transition temperatures and enthalpies of DBFOCn[a]

n	$T_{C-S_A,N \text{ or } I}$	$\Delta H_{C-S_A,N \text{ or } I}$	$T_{S_A-N \text{ or } I}$	$\Delta H_{S_A-N \text{ or } I}$	T_{N-I}	ΔH_{N-I}
1	150.5	35.2				
2	129.5	30.2			167.5	0.7
3	133.5	35.6			146.5	0.4
4	124.5	24.7			158.5	0.5
5	115.5	34.4			148.5	0.5
6	112.5	29.7			154.5	0.5
7	113.5	34.2	115.5	0.7	150.5	0.3
8	118.5	38.4	128.5	5.1	152.5	0.4
9	116.2	50.2	132.5	1.9	149.6	0.8
10	113.5	51.4	136.5	2.3	148.6	1.1
11	117.4	61.5	139.0	2.7	146.3	1.0
12	120.4	57.3	140.6	3.5	145.0	1.6
14	116.2	66.5	139.7	3.7	140.5	2.2

[a] T in °C and ΔH in kJ/mol.

DBTOCn also have a normal trend of mesomorphic behaviors such as that of DBFOCn. Smectic A phase is injected at a heptyloxy derivative just as the same as DBFOCn.

In order to compare the mesomorphic thermal stability of DBFOCn with that of DBTOCn, the average values of the nematic to isotropic phase transition temperatures (T_{NI}) from heptyloxy to decyloxy derivatives were calculated as follows:

	DBFOCn	DBTOCn
T_{NI}	150.3°C	167.1°C

The averaged T_{NI} of DBFOCn is lower by 16.8° than that of DBTOCn.

TABLE III

Transition temperatures and enthalpies of DBTOCn[a]

n	$T_{C-S_A \text{ or } N}$	$\Delta H_{C-S_A \text{ or } N}$	T_{S_A-N}	ΔH_{S_A-N}	T_{N-I}	ΔH_{N-I}
5	130.5	43.6			174.9	0.7
6	123.3	42.3			177.6	1.0
7	117.4	28.8	[107.8][b]	0.2	170.2	1.0
8	115.0	28.3	119.4	0.6	170.0	1.2
9	112.3	29.9	128.2	1.0	164.6	1.2
10	109.6	27.4	135.4	1.4	163.5	1.3

[a] T in °C and ΔH in kJ/mol.

[b] [ ]: monotropic transition.

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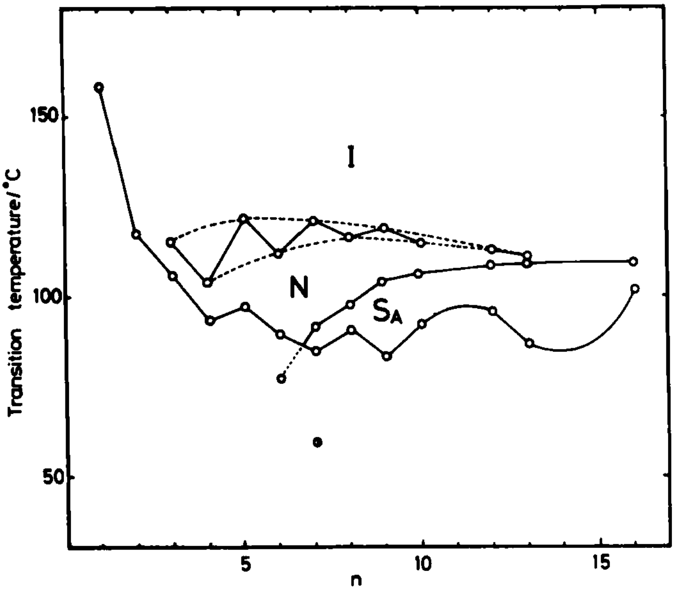

FIGURE 1 Plots of transition temperatures against the number of carbon atoms(n) in the alkyl chain of DBFCn. ◑; monotropic $S_G - S_A$ transition.

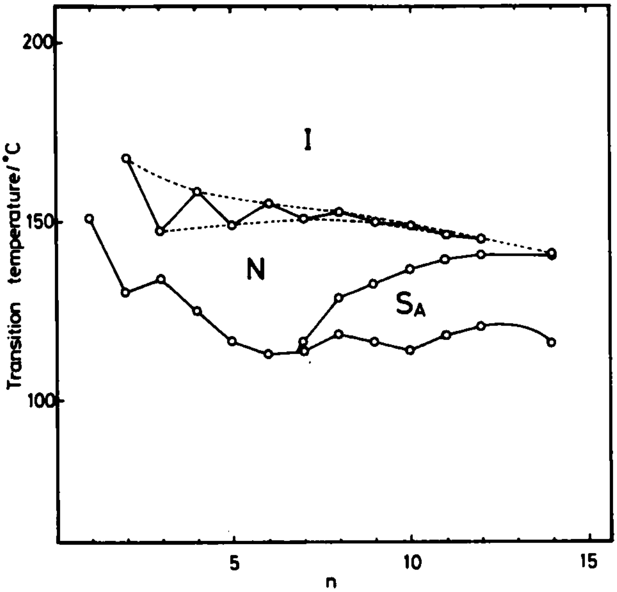

FIGURE 2 Plots of transition temperatures against the number of carbon atoms(n) in the alkyl chain of DBFOCn.

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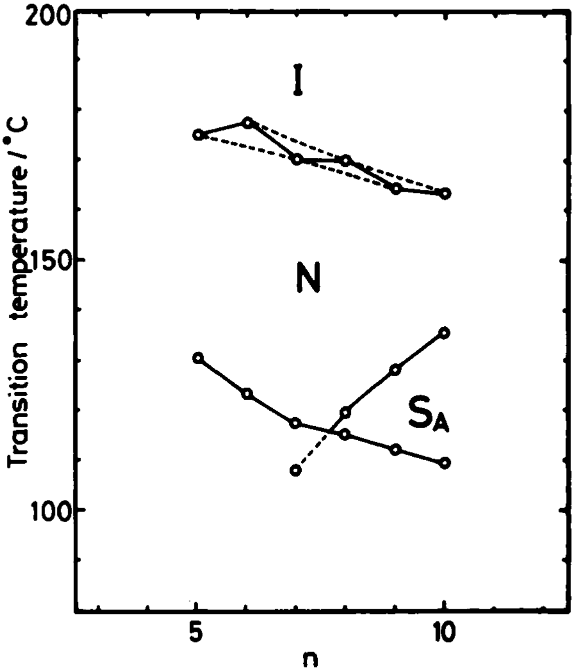

FIGURE 3 Plots of transition temperatures against the number of carbon atoms(n) in the alkyl chain of DBTOCn.

The degree of the molecular interaction would be determined by the intermolecular separation and the polarizability anisotropy. Therefore, an effective molecular volume due to the rotation about the molecular long axis would be crucial for the intermolecular force. Hence, the molecular planarity and the molecular width are important factors for the mesomorphic thermal stability. Thus, it is worthwhile to investigate the conformation of these compounds from the viewpoint of the molecular volume as well as the polarizability anisotropy, which seems to be affected by the degree of the conjugation of π-electrons.

It is generally considered that diarylazomethine is not a co-planar molecule as seen in Figure 3. For example, N-benzylideneaniline[BA] has the twist angles θ_1 about the Ar—N= bond and θ_2 about the Ar—C= bond. In a crystalline state, $\theta_1 = 55°$ and $\theta_2 = -10.3°$ have been reported.[6]

In order to estimate the twist angles θ_1 of DBFOCn and DBTOCn, the UV absorption spectra were measured to give the results in Table IV.

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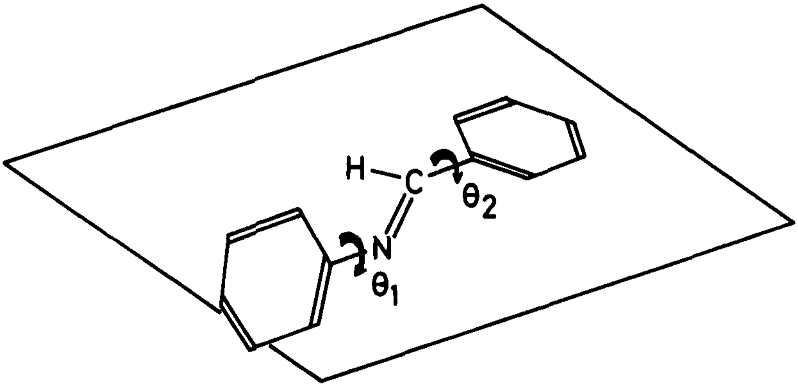

FIGURE 4 Twisted conformation of N-benzylideneaniline.

The band having λ_{max} 340–370nm seems to be assigned to the $\pi-\pi^*$ transition band which is due to the conjugation of the heteroaromatic group to the benzylideneamino moiety.[7] This assignment could be supported by a decreased ϵ_{max} of the longest wavelength band[7,8] of 3-(α-methyl-4-pentylbenzylideneamino)dibenzofuran [DBFC5Me], which seems to have a larger twist angle θ_1 because of the steric hindrance of α-methyl group against the 2- and 4-site protons of dibenzofuran. The absorption coefficients of those bands could

TABLE IV

Results of UV-absorption spectra in $CHCl_3$[a]

Compound	λ_{max}/nm	ϵ_{max}	θ_1/°[b]
BA	310(310)[c]	8400 (7000)	46(50)
SA	339(340)	11800(11200)	35(35)
DBFOC5	343	27400	43
DBFC5Me	ca.340[d]	7400	68
DBFOC5Hy	358	34300	35
DBTOC5	340	28500	43
DBTOC5Hy	358	35200	35
FLOC5[e]	347	27000	42
FLOC5Hy[f]	361	33200	35

[a] All measurements were carried out at room temperature.

[b] Calculated values by the equation: $\cos^2\theta_1 = \epsilon_1/\epsilon_0$.

[c] Values in parentheses are the reported ones (in cyclohexane), except for the θ_1 which were calculated with the equation above.

[d] Appeared to be a shoulder band.

[e] FLOC5:2-(4-pentyloxybenzylideneamino)fluorene.

[f] FLOC5Hy:2-(2-hydroxy-4-pentyloxybenzylideneamino)fluorene.

be used for a rough estimate of θ_1 by the following equation;[9]

$$\cos^2\theta_1 = \epsilon_1/\epsilon_0 \quad (1)$$

where ϵ_1 is the absorption coefficient of the molecule with the twist angle θ_1 and ϵ_0 is the absorption coefficient of its planar analogue.

The application of the equation(1) to the results by P. Skrabal et al.[8] leads to $\theta_1 = 50°$ for BA in cyclohexane. This estimated value for BA agrees well with the results of X-ray analysis[6] and theoretical calculations[8,10]. Salicylideneaniline[SA] has $\epsilon_{max}(\lambda_{max} = 340nm)$ of 11200 in cyclohexane and its θ_1 is calculated to be 35°. The absorption spectra of BA and SA in chloroform have respectively little change for the ϵ_{max} and λ_{max} as compared with those in cyclohexane.

This result would be reasonable considering that the intramolecular hydrogen bonding between a 2-hydroxyl group and nitrogen lone pair electrons in the azomethine linkage could destabilize the twist conformation to make the molecule more planar.[10]

The results of ^{1}H-NMR spectra show that the twist angles θ_1 are comparable to each other in SA, 3-(2-hydroxy-4-pentyloxybenzylideneamino)dibenzofuran[DBFOC5Hy] and 3-(2-hydroxy-4-pentyloxybenzylideneamino)dibenzothiophene[DBTOC5Hy], since δ_c for these molecules are almost the same as shown in Table V. Thus, the twist angles θ_1 for DBFOC5Hy and DBTOC5Hy are considered to be almost the same to each other (about 35°).

The twist angles θ_1 of the others were estimated with the equation(1) and the ϵ_0 were calculated back from the value θ_1 of the 2-hydroxy derivatives.

The estimated twist angles θ_1 are comparable to each other in DBFOC5 and DBTOC5. This result is also supported by the results of ^{1}H-NMR chemical shifts.

The twist angle θ_1 could influence the environment of the two ortho-site protons of dibenzofuran and dibenzothiophene(H_a and H_b) and the α-site proton of benzylidene moiety (H_c).

The chemical shift gaps $\Delta\delta_c$ are 0.14ppm for DBFOC5 and DBFOC5Hy, and 0.12ppm for DBTOC5 and DBTOC5Hy. This indicates that the twist angles θ_1 are almost the same in DBFOC5 and DBTOC5. The $\Delta\delta_c$ for BA and SA(0.30ppm) indicates that BA has a larger twist angle θ_1 than DBFOC5 and DBTOC5, and this result agrees with the results of UV absorption spectra. As for the δ_a and δ_b, the detailed analysis was difficult to be carried out, as these chemical shifts are shadowed by the other aromatic protons' multiplet signals. Compared with the relation between aniline and BA, how-

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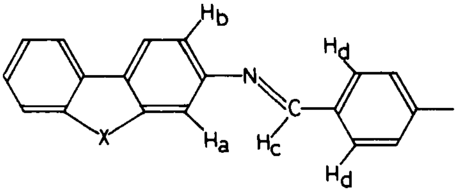
TABLE V

Results of ^{1}H-NMR spectra[a]

	Chemical shift /ppm					
Compound	δ_a		δ_b	δ_c	$\Delta\delta_c$	δ_d
Aniline		6.45		—	—	—
BA	6.9	—	7.3	8.27		[b]
					) 0.30	
SA	6.7	—	7.5	8.57		[b]
3ADBF	6.79		6.65	—	—	—
DBFC5Me	6.95		6.77	—	—	[b]
DBFOC5	7.1	—	7.5	8.42		7.83
					) 0.14	
DBFOC5Hy	7.1	—	7.5	8.56		[b]
3ADBT	6.96		6.67	—	—	—
DBTOC5	7.2	—	7.7	8.45		7.84
					) 0.13	
DBTOC5Hy	7.2	—	7.7	8.58		[b]
2AFL[c]	6.75		6.61	—	—	—
FLOC5	7.1	—	7.5	8.43		7.80
					) 0.12	
FLOC5Hy	7.1	—	7.5	8.55		[b]

[a] In $CHCl_3$ at room temperature. TMS was used as internal standard.
[b] The assignments could not be carried out.
[c] 2AFL:2 – aminofluorene



ever, the gaps between 3-aminodibenzofuran[3ADBF] and DBFOC5, and 3-aminodibenzothiophene[3ADBT] and DBTOC5 in δ_a and δ_b, seem to indicate that θ_1 for DBFOC5 and DBTOC5 are smaller than that of BA, as the chemical shift of the two protons are considered to shift to a higher field when the twist angle increases. In fact, the δ_a and δ_b for DBFC5Me are 6.95 and 6.77ppm, respectively and higher than those of DBFOC5 and lower than those of 3ADBF.

On the other hand, the twist angles θ_2 for DBFOC5 and DBTOC5 seem to be comparable to each other because of the similar values of their δ_d.

Thus, the conformations for DBFOC5 and DBTOC5 are comparable to each other. This relation of their conformations does not seem to change in mesophases in which molecules could rotate freely

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about their long axis. Therefore, the effects of their conformation on the effective molecular volume and the molecular polarizability are considered to be almost the same for DBFOCn and DBTOCn.

The molecular width, however, is also an important factor for the mesomorphic thermal stability. This factor seems to affect the effective molecular volume.

The bond angle ϕ of (II), which is assumed to be the same as that of (I), seems to be crucial for the determination of the molecular width, since the rotation about Ar—N= bond occurs in mesomorphic states as shown in Figure 5. The width decreases as the value of ϕ approaches to 120° and the narrow width leads to a decrease in the molecular effective volume.

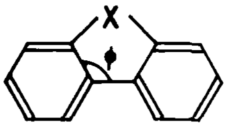
According to the crystal structures by X-ray analyses, the bond angles ϕ of dibenzofuran and dibenzothiophene are 105.6°[11] or 106.3°[12] and 111.4° or 112.4°[13], respectively. Thus, the width decreases in the following order:

dibenzofuran > dibenzothiophene

This indicates the thermal stability of mesophases tends to increase in this order:

dibenzofuran < dibenzothiophene

The order agrees with that of T_{NI} in DBFOCn and DBTOCn.



(II)

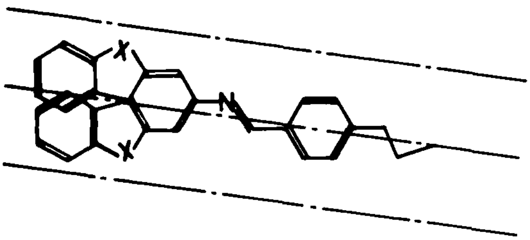


FIGURE 5 Bond angle ϕ and effective molecular volume determined by the ϕ-value.

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K. J. Miller et al. reported an empirical method for calculating average molecular polarizability.[14] According to the calculation method, the average molecular polarizabilities of dibenzofuran and dibenzothiophene could be estimated to be 19.93 and 22.32A^3, respectively. The anisotropy of the molecular polarizability seems to be the same order as the average molecular polarizability because of the same order of the optical anisotropy for dibenzofuran and dibenzothiophene.[15] These orders also agree with that of T_{NI} in DBFOCn and DBTOCn.

Therefore, the order of the mesomorphic thermal stability of DBFOCn and DBTOCn could be explained in terms of the molecular polarizability(anisotropy) and the molecular width. These results indicate that the bridging atom(X) in the structure(I) could significantly affect the mesomorphic thermal stability.

However, 2-(4-alkoxybenzylideneamino)fluorenes[FLOCn], the structural analogues to DBFOCn and DBTOCn, have higher T_{NI} than those of DBFOCn and DBTOCn. The averaged T_{NI} in heptyloxy to decyloxy derivatives is 186.4°.[1]

The average molecular polarizability for fluorene was reported to be 21.15A^3 [14] and the optical anisotropy was measured to be smaller than those of dibenzofuran and dibenzothiophene.[15] This seems to indicate that the mesomorphic thermal stability of FLOCn could not be explained only by the polarizability. The width is not significantly different from those of dibenzofuran and dibenzothiophene. The ϕ-value for fluorene is reported to be 107.6°[16] or 108°[17]. The conformation of FLOC5 estimated by the method described above seems to be almost the same as those of DBFOC5 and DBTOC5, as shown in Tables IV and V. These results might indicate the possibility of the existence of other factors which determine the mesomorphic thermal stability for these kinds of mesogens. The study of this problem is now in progress.

EXPERIMENTAL

Preparation of materials

4-Substituted benzaldehydes: 4-Alkyl-[18] and 4-alkoxybenzaldehydes[19] were purified by column chromatography(silica-gel, benzene-hexane) or by distillation. 2-Hydroxy-4-alkoxybenzaldehydes were prepared by refluxing the mixture of the corresponding alkyl bromide and the equimolar 2,4-dihydroxybenzaldehyde in methanol containing KOH and purified by column chromatography(silica-gel, benzene-hexane).

Heteroaromatic amines: 3-Aminodibenzofuran and 2-aminofluorene were prepared by the catalytic hydrogenation(Pd/C in ethanol) of the nitro derivatives and purified by column chromatography(silica-gel, benzene) and recrystallization from benzene-hexane. 3-Aminodibenzothiophene was prepared according to literatures.[20]

Schiff's base liquid crystals: The Schiff's base compounds were prepared by refluxing the absolute ethanol solution of the equimolar amine and aldehyde and recrystallized from absolute ethanol or hexane more than three times.

All compounds were identifed by elemental analyses, shown in Table VI, IR and ^{1}H-NMR spectra.

TABLE VI

Elemental analyses for DBFCn(A), DBFOCn(B), DBTOCn(C) and the other compounds (D)

(A)

	Calcd. /%			Found /%		
n	C	H	N	C	H	N
1	84.19	5.30	4.91	84.11	5.28	4.92
2	84.25	5.72	4.68	84.22	5.68	4.72
3	84.31	6.11	4.47	84.21	6.10	4.41
4	84.37	6.46	4.28	84.16	6.46	4.27
5	84.42	6.79	4.10	84.25	6.79	4.07
6	84.47	7.09	3.94	84.55	7.13	3.92
7	84.51	7.36	3.79	84.39	7.38	3.68
8	84.56	7.62	3.65	84.24	7.59	3.53
9	84.59	7.86	3.52	84.48	7.98	3.45
10	84.63	8.08	3.40	84.32	8.24	3.46
12	84.69	8.48	3.19	84.39	8.57	3.20
13	84.72	8.66	3.09	84.59	8.62	2.95
16	84.80	9.15	2.83	84.66	9.21	2.77

(B)

	Calcd. /%			Found /%		
n	C	H	N	C	H	N
1	79.76	5.02	4.65	79.90	4.83	4.60
2	79.98	5.43	4.44	80.21	5.26	4.43
3	80.22	5.81	4.25	80.46	5.72	4.34
4	80.44	6.16	4.08	80.48	6.02	4.13
5	80.64	6.49	3.92	80.65	6.40	3.95
6	80.83	6.78	3.77	80.65	6.67	3.96
7	81.01	7.06	3.63	80.85	6.96	3.80
8	81.17	7.32	3.51	81.26	7.24	3.65
9	81.32	7.56	3.39	81.21	7.71	3.31
10	81.46	7.78	3.28	81.39	7.87	3.20
11	81.59	7.99	3.17	81.45	8.12	3.15
12	81.72	8.18	3.07	81.72	8.31	3.04
14	81.95	8.54	2.90	81.87	8.60	2.86

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TABLE VI

Continued

(C)

	Calcd. /%				Found /%			
n	C	H	N	S	C	H	N	S
5	77.18	6.21	3.75	8.58	77.18	6.22	3.61	8.62
6	77.48	6.50	3.61	8.27	77.65	6.47	3.53	8.21
7	77.77	6.78	3.49	7.98	77.60	6.80	3.40	8.00
8	78.03	7.03	3.37	7.71	77.83	7.03	3.29	7.67
9	78.28	7.27	3.26	7.46	78.16	7.23	3.11	7.46
10	78.51	7.50	3.16	7.23	78.36	7.46	3.03	7.24

(D)

	Calcd. /%				Found/%			
Compound	C	H	N	S	C	H	N	S
DBFC5Me	84.47	7.09	3.94	—	84.29	7.05	3.85	—
DBFOC5Hy	77.18	6.21	3.77	—	77.12	6.22	3.74	—
DBTOC5Hy	74.01	5.95	3.60	8.23	73.94	5.83	3.50	8.24
FLOC5Hy	80.83	6.78	3.77	—	80.87	6.79	3.72	—

Measurements

The phase determination was carried out by the optical texture, which was observed by a Nikon polarizing microscope in conjunction with a Mettler FP52 heating stage and FP-5 control unit and often by the miscibility test.

The transition enthalpies were determined by a Daini Seikosha differential scanning calorimeter, model SSC-560S.

^{1}H-NMR and UV-Visible absorption spectra were measured with a JNM-PS-100 NMR spectrometer and a Hitachi 220 double beam UV-Visible spectrometer, respectively.

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