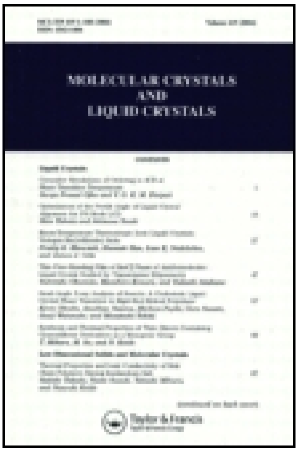

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Crystalline - Smectic C - Cubic - Isotropic - Nematic - Isotropic Polymorphism: Synthesis and Unexpected Behaviour of a New Series of Double-Swallow-Tailed Mesogens

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Crystalline - Smectic C - Cubic - Isotropic - Nematic - Isotropic POLYMORPHISM: SYNTHESIS AND UNEXPECTED BEHAVIOUR OF A NEW SERIES OF DOUBLE-SWALLOW-TAILED MESOGENS

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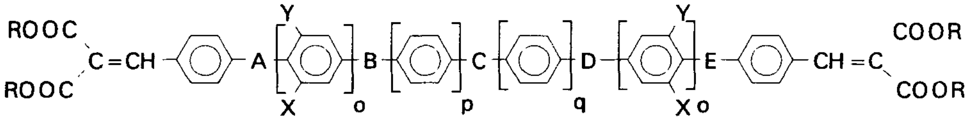
Abstract A new homologous series of six-ring double-swallow-tailed mesogens was prepared and investigated. Liquid-crystalline properties strongly depend on the length of the terminal alkyl chains. Six different phase sequences could be detected, two of them were unknown up to now. The derivatives DS-5...7 show smectic C, cubic and nematic phases, the longer-chain homologues DS-10...14,16 have columnar phases. The substance DS-8 exhibits the most interesting phase sequence cr - S_C - cub - I_{re} - N - I. DS-8 represents the second pure compound with a stable reentrant isotropic phase. Optical , X-ray, and further investigations provide arguments to propose the structures of the different phases.

INTRODUCTION

Polycatenar mesogens[1-3] consist of a rod-like core ending in two half-disk-shape moieties. They can be considered as intermediate between rod-like and disk-like mesogens. Depending on the molecular structure they can exhibit nematic, lamellar, columnar, and cubic mesophases[4]. Double-swallow-tailed compounds are a special case of tetracatenar mesogens[5]. They are characterized by long-chain branches, such as $CH=C(COOC_nH_{2n+1})_2$, at both ends of the rod-like core of the molecules. We found that substances according to the general formula are suitable objects to study relationships between molecular structure und mesophase behaviour.



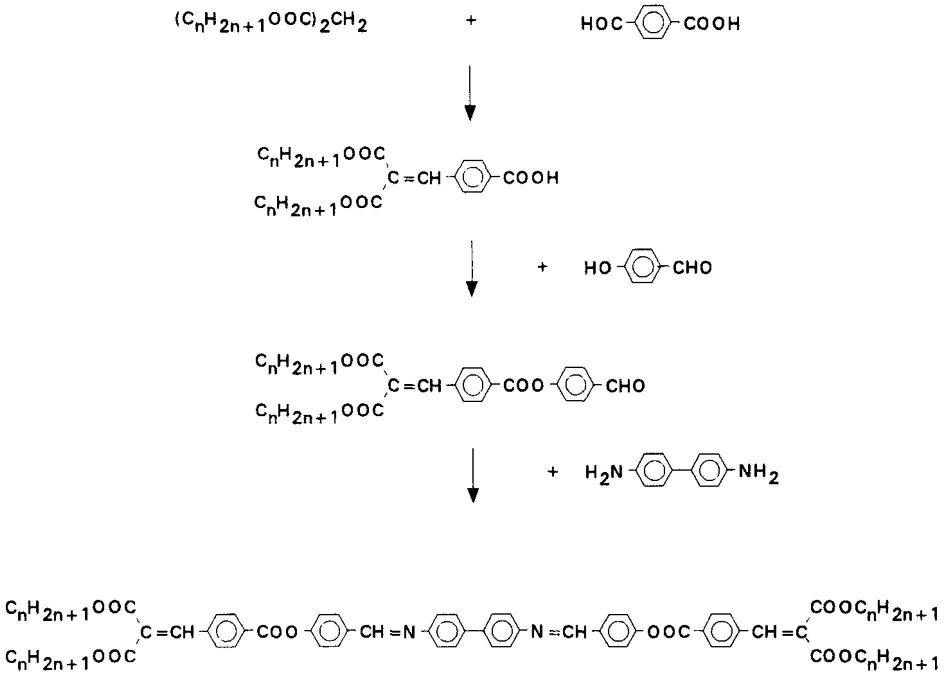
Depending on the molecular design, e.g. the length of alkyl chains R, the number of rings and the type of the connecting groups A - E between them, different liquid crystalline properties can be observed. Whereas three-ring compounds (A = -OOC-, E = -COO-, p =1 ; B, C, D, o, q = --) do not show enantiotropic mesophases, four-ring derivatives (A = -OOC-, E = -COO-,X, Y = H, o = 1; B, C, E, p, q = --) exhibit nematic and smectic C phases[5]. The same behaviour is found at five-ring substances (A = -OOC-, E = -COO-, B = -CH=N-, D = -N=CH-, X, Y = H, o, p = 1; C, q = --) [6]. After extension of the molecules by one additional phenyl ring the six-ring mesogens (A = -OOC-, E = -COO-, B = -CH=N-, D= -N=CH-, X, Y = H, o,p,q =1; C = --) can offer an rectangular columnar phase[6].

But also in the six-ring mesogens relatively slight variations of the molecular structure can cause considerable changes of the liquid crystalline properties. By insertion of angled or flexible segments C in the middle of the molecules the clearing temperatures are strongly decreased, in several cases the formation of anisotropic phases is prevented completely. Small lateral substituents, like CH_3O, C_2H_5O, in the positions X, Y are able to yield substances with cubic phases at convenient temperature additionally to columnar phases[7]. Already the inversion of the direction of the connecting carboxyl groups in the positions A and E changes the polymorphism drastically.

In this paper we want to report to the synthesis and the unexpected mesophase behaviour of a new series of six-ring double-swallow-tailed mesogens DS-5...14,16. The number note together with DS gives the number n of methylene groups in the normal alkyl chains R. In the homologous series all four alkyl groups R in the both terminal positions are lengthened simultaneously. It is shown that similar to the tetracatenar biforked compounds the liquid-crystalline behaviour strongly depends on the number of carbons of the terminal chains. For the middle members of the series unusual phase sequences could be detected.

SYNTHESIS

The pathway to prepare the compounds of interest is shown in the following schema



DS-5...14, 16 (n = 5 - 14, 16)

Knoevenagel condensation of the appropriate dialkyl malonates and terephthalaldehydic acid in the presence of piperidine acetate leaded to the 4-[2,2-bis(alkyloxycarbonyl)ethenyl]benzoic acids. Water formed by the reaction was collected by a water separator. The terminally branched benzoic acids were recrystallized from methanol. Reaction with thionylchloride yielded the acid chlorides, which were esterficated with 4-hydroxybenzaldehyde in toluene with triethylamine to trap the hydrogen chloride. The 4-formylphenyl 4-[2,2-bis(alkyloxycarbonyl)ethenyl]benzoates can be purified by recrystallization from methanol. If the aldehydes were obtained in an oily state, the following reaction can be performed with this raw materials. Final products DS-5...14,16 were prepared by condensation of 4,4′-diaminobiphenyl with the formyl derivatives by refluxing in ethanol under nitrogen. Toluene-p-sulfonic acid served as a catalyst. After cooling the precipitates were separated and recrystallized from dimethylformamide more than once.

Preparative details to the synthesis and properties of the 4-[2,2-bis(alkyloxycarbonyl)ethenyl] benzoic acids and the 4-formylphenyl 4-[2,2-bis(alkyloxycarbonyl)ethenyl]benzoates will be given together with the liquid crystalline properties of the appropriate two-ring swallow-tailed 4-{4-[2,2-bis(alkyloxycarbonyl)ethenyl]benzoyloxy}benzoic acids elsewhere[8,9].

EXPERIMENTAL

The phase transition temperatures of single compounds and mixtures were determined by microscopic investigations as well as by calorimetric measurements (DSC 7, Perkin-Elmer). By calorimetry, in addition, the transition enthalpies were available.
The liquid crystalline phases were identified by characteristic microscopic textures and by X-ray investigations using a Guinier film camera.

RESULTS

Figure 1 shows the phase diagram of this homologous series and demonstrates the unusual and varied polymorphism. Six different phase sequences could be determined. Two of them were unknown up to now: the cubic - nematic transition and the existence of an reentrant isotropic phase below a nematic phase.

It should be pointed to the curve of clearing points (Figure 1). At the beginning the nematic - isotropic transitions are decreased with increasing length of the terminal chains as known yet. But at the compound DS-8 the N - I-curve shows an abrupt break and the next homologue DS-9 exhibits the transition from the cubic into the isotropic phase at temperatures 74 degrees lower than DS-8 . That is an unusual behaviour of the clearing points and gives hints to very variable structures in the different liquid crystalline phases in this homologous series.

The series can be formally subdivided in two ranges. The longer homologues DS-9...14,16 show columnar phases while the short-chain derivatives DS-5...9 exhibit lamellar phases. Generally this is in agreement with the mesophase behaviour reported at polycatenar mesogens bearing five or six terminal alkyl chains[4]. For the members DS 8 and DS 9 the most interesting phase behaviour could be detected.

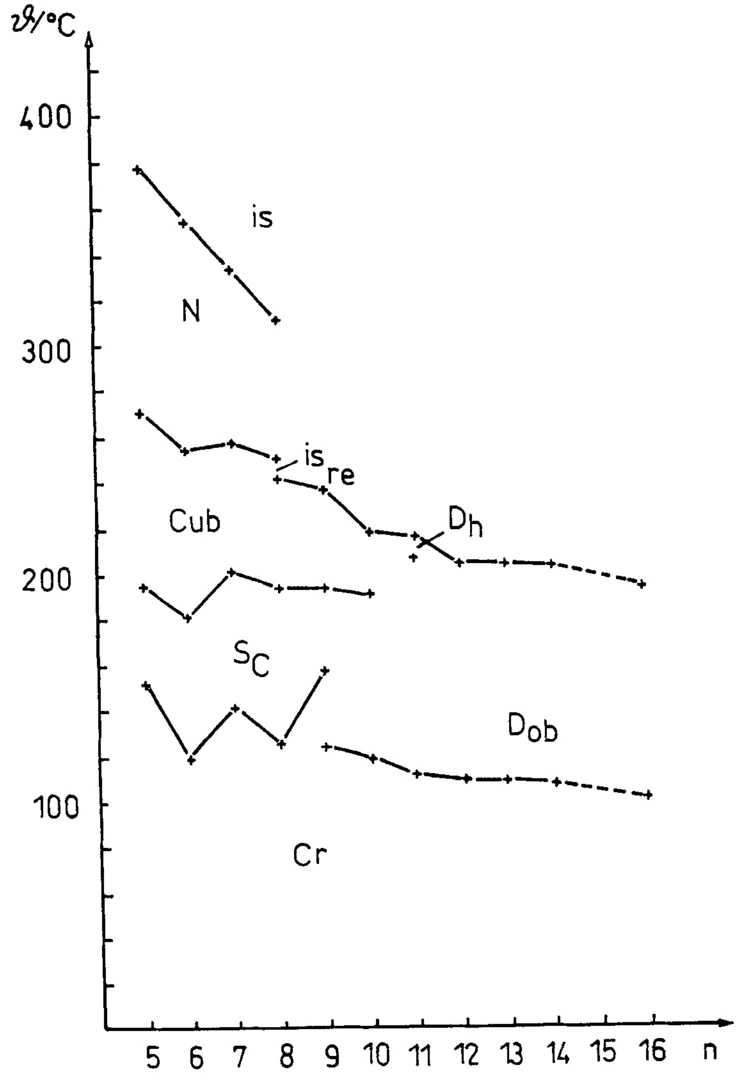


FIGURE 1: Phase diagram of the homologous series DS-5...14, 16

Table I presents the transition temperatures and the transition enthalpies of the substances DS-5...14, 16.

TABLE I Transition temperatures [°C] and transition enthalpies [kJ/mol].

Comp.	n	Mesophases										
DS-5	5	cr	143	S_C	195	cub	271	N	378	is		
			[50.60]		[0.13]		[2.93]		[-]			
DS-6	6	cr	120	S_C	181	cub	255	N	355	is		
			[38.16]		[0.62]		[2.61]		[-]			
DS-7	7	cr	132	S_C	202	cub	258	N	334	is		
			[58.11]		[0.76]		[1.06]		[-]			
DS-8	8	cr	126	S_C	195	cub	243	is_{re}	250	N	312	is
			[58.83]		[0.89]		[2.15		[0.47]		[0.39]	
DS-9	9	cr	125	Dob	158	S_C	195	cub	238	is		
			[55.10]		[0.03]		[0.75]		[1.90]			
DS-10	10	cr	120	D_{ob}	192	cub	220	is				
			[68.06]		[2.13]		[1.90]					
DS-11	11	cr	113	D_{ob}	208	D_h	216	is				
			[71.08]		[2.20]		[1.99]					
DS-12	12	cr	111	D_{ob}	206	is						
			[69.53]		[3.95]							
DS-13	13	cr	110	D_{ob}	206	is						
			[74.60]		[4.25]							
DS-14	14	cr	109	D_{ob}	205	is						
			[63.55]		[4.07]							
DS-16	16	cr	103	D_{ob}	196	is						
			[71.44]		[4.11]							

DS-5...7

It is seen from Table I that the homologues with shorter chain length (n = 5 - 7) exhibit smectic C, cubic and nematic mesophases. The clearing temperatures of these compounds are very high and a noticable decomposition can be observed. Therefore the transition heats could not be measured of DS-5-7. The transition from the smectic C phases into the optical isotropic cubic mesophases are somewhat delayed and occurs over a temperature interval depending on the heating rate. At low heating rates the cubic phase grows slowly into the S_C phase through a temperature range of about 10 °C. If the temperature is kept constant in the moment of first occurence of cubic domains, after some minutes the whole sample is transformed into the cubic phase. Therefore, the temperatures of the beginning of the transitions cub - S_C are given in Table I. On cooling the cubic mesophase remains as a metastable phase up to the crystallization. Only, when this metastable cubic phase is annealed for a longer time the smectic C phase reappears. The S_C phase generally shows a typical schlieren texture.

The cubic mesophase found for the homologues DS-5...10 is characterized by the optical isotropy but also by a very high viscosity. For the supercooled cubic mesophase of DS-5 X-ray measurements were performed.
The transition of a cubic into a nematic phase was unknown up to now. On heating the nematic phase does not appear in form of spherical droplets as known for the transition isotropic--nematic. As seen from Figure 2 the growth of the nematic phase within the cubic phase is anisotropic. In this way a ramified pattern occurs which coalesces to greater droplets. Otherwise, on cooling of the nematic phase the cubic phase begins to separate in form of irregular polygonal area.

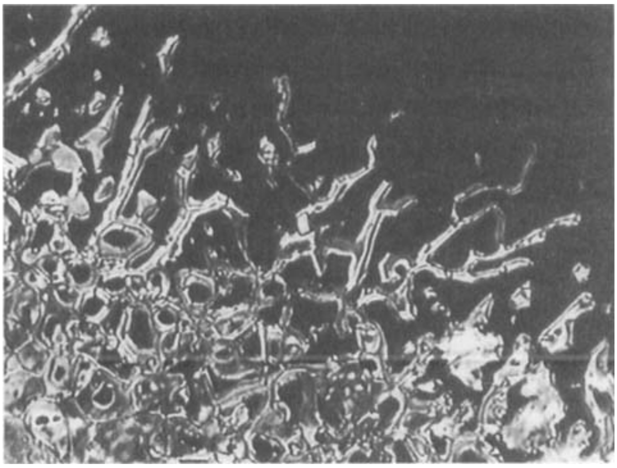


FIGURE 2 Phase transition cubic - nematic on heating of DS-7 at 259 ^{o}C
See Color Plate VII.

DS-8

The most interesting substances of the series are the middle members DS-8 and DS-9. Whereas the short-chain homologues DS-5...7 show a phase sequence S_C - cub - N for the octyl derivative DS-8 between the cubic and the nematic phase an isotropic liquid occurs in the temperature range 243 - 250 °C which can be considered as a reentrant isotropic phase.

The phase sequence:

$$\mathrm{cr} \text{ -- } S_C \text{ -- } \mathrm{cub} \text{ -- } \mathrm{is}_{re} \text{ -- } N \text{ -- } \mathrm{is}$$

was unknown up to now. The phase transitions cubic - reentrant isotropic and reentrant isotropic - nematic can be clearly detected by calorimetric measurements. The transition enthalpy of 2.15 kJ/mol (cubic - reentrant isotropic) is in the same order of magnitude as found for the transition cubic - nematic of the lower members of the series. There are arguments which point to a reentrant isotropic phase and not to a second cubic phase. Whereas the cubic phase possesses a very high viscosity the neighbouring isotropic phase is low-viscous and behave liquid-like.

An indirect evidence of the reentrance of the isotropic liquid is proved by the phase diagram of the binary system of the homologues DS-8 and DS-9. The isotropic phase of the longer-chain derivative DS-9 is miscible with both the upper as well as the reentrant isotropic phase of DS-8. The transition of the optical isotropic cubic into the reentrant isotropic phase is also indicated by refractometric measurements.

Further details to the investigation and the properties of the derivative DS-8 exhibiting a reentrant isotropic phase are given elsewhere[10].

It is not the first case of a reentrant isotropic phase but up to now this phenomenon was never observed on cooling of a nematic phase. The only pure component in which a stable reentrant isotropic phase has been observed was described by WARMERDAM et al.[11,12] in 1988 and belongs to the substance class of truxenes. In the disk-like shaped 2,3,7,8,12,13-hexa(4-n-octadecanoyloxy)truxene the reentrant isotropic and the upper isotropic phase surround a columnar phase.

Before DESTRADE et al.[13] reported to a reentrant isotropic phase in a binary mixture of hexasubstituted truxene derivatives. PRAEFCKE et al. have given hints to the existence of an instable reentrant isotropic phase in mixtures of disk-like hexasubstituted naphthalenes[14]. Two years ago PERCEC et al.[15] described a reentrant isotropic behaviour of poly{4-[3,4,5-tris(n-dodecanoyloxy)benzoyloxy]-4′-[(2-vinyloxy)ethoxy]biphenyl} characterized by a low degree of polymerization (about 5) with narrow molecular-weight distribution.

But first of all the existence of a reentrant isotropic phase was observed by YU and SAUPE[16] in the lyotropic system of potassium dodecanoate, decanol-1, and water.

DS-9

The next member in the homologous series, DS-9, forms a columnar: D_{ob} , a lamellar: S_C, and a cubic phase (see Table I). As seen from the diagram (Figure 1) on cooling of the smectic C phase another liquid-crystalline phase arises at 155 °C. This phase transition is indicated by a pronounced change of the microscopical picture. As seen from the comparison of Figures 3 and 4 the texture of this low-temperature columnar phase remembers to smectic C phases. The calorimetric peak is very small and in the order of the limit of detection (about 30 $Jmol^{-1}$) . But otherwise the transition is clearly reflected in the X-ray measurements.

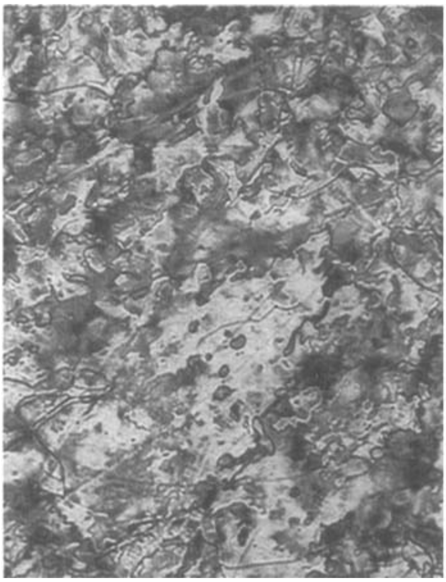


FIGURE 3: Schlierentexture of the S_C phase of compound DS-9 at 159 °C
See Color Plate VIII.

FIGURE 4: Nonspecific texture of the D_{ob} mesophase of DS-9 at 145 °C
See Color Plate IX.

DS-10...14,16

Whereas the substance DS-10 shows one columnar and a cubic phase, the long-chain substituted homologues DS-11...14, 16 do not exhibit lamellar but columnar mesophases, only. Figure 5 shows a typical mosaic texture of the columnar mesophase of compound DS-14 after cooling from the isotropic liquid. The picture of a focal conic texture of the D_h-phase of the derivative DS-11 is given in Figure 6.

FIGURE 5: Mosaic texture of the D_{ob} phase of compound DS-14 at 175 °C
See Color Plate X.

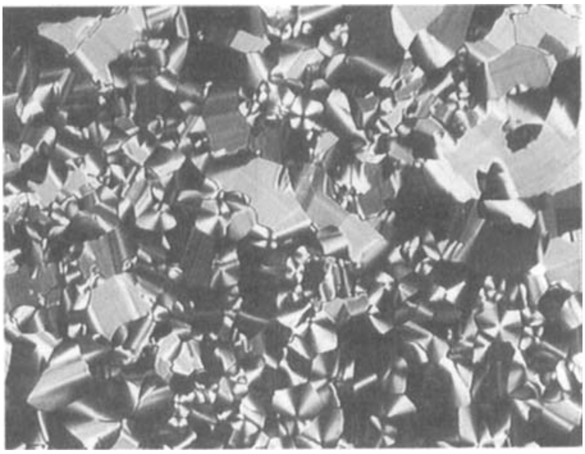


FIGURE 6: Focal conic tecture of the D_h mesophase of the homologue DS-11 at 212 °C
See Color Plate XI.

X-RAY INVESTIGATIONS

To confirm the observed liquid crystalline phases for some homologues X-ray studies have been performed at non-oriented samples. The Guinier patterns of the S_C phases prove the layer structure by the existence of one reflection and its second order. The position of the reflections are nearly independent of the temperature. With increasing chain length the d-values increase scarcely (Table II).

TABLE II Bragg angles and d-values of S_C- phases.

Comp.	ϑ[°C]	θ[°]	d[Å]
DS-5	160	1.34	33.0
		2.66	16.6
DS-7	160	1.29	34.2
		2.55	17.3
DS-8	170	1.24	35.7
		2.48	17.8
DS-9	170	1.23	36.0
		2.49	17.7

The X-ray studies within the cubic phases were difficult because a partial decomposition took place during the exposure time. Therefore the cubic phase of substance DS-5 has been investigated in the supercooled state. The reflections (Table III) could be indexed as described in other cases[17-19]. The calculated lattice parameter (a = 96.1Å) points to an aggregation of molecules.

TABLE III Bragg-angles and indexing of the cubic mesophase of DS-5 at 180 C.

$\theta[^{o}]_{exp.}$	(hkl)	$\theta[^{o}]_{calc.}$
1.12	(211)	-
1.29	(220)	1.30
1.72	(321)	1.72
2.05	(420)	2.05
2.27	(422)	2.25

The X-ray pattern of the columnar structure of different homologues are not unique. With sureness they do not correlate with a hexagonal or rectangular cell. The discussion of a postulated oblique cell shall be given in a forthcoming paper dealing with the structures more in detail..

The next Table IV shows the reflections of the 2D oblique columnar mesophase of compound DS-10. The 2D oblique columnar unit cell can be described with the parameters

a = 83.4Å and b = 45.68Å and with the angle g = 25.6 .

TABLE IV Reflections of the 2D D_{ob} -mesophase of DS-10 at 130 C.

(hk)	$\theta[^{o}]$	d[Å]
(10)	1.22	36.02
(11)	1.25	35.30
(01)	2.24	19.72
(20)	2.44	18.11

At the substance DS-9 a transition from the S_C phase into another one has been observed. Although the texture of this phase is similar to a lamellar one, several inner reflections point to the existence of a columnar structure (Table V). The 2D oblique columnar unit cell can be described with the parameters a = 64.8 Å and b = 36.5 Å and with the angle g = 33.4

TABLE V Reflections of the 2D D_{ob}-mesophase of DS-9 at 130 C.

(hk)	θ[°]	d[Å]
(10)	1.24	35.6
(11)	1.35	32.7
(01)	2.20	20.1
(20)	2.47	17.8

CONCLUSIONS

In the series of six-ring double-swallow-tailed mesogens the liquid-crystalline properties strongly depend on the length of the terminal alkyl chains, as also described for other tetracatenar substances. A varied polymorphism could be observed, as shown by the existence of six different phase sequences. The homologue DS-8 exhibits the most interesting polymorphism cr - S_C - cub - I_{re} - N - I. To investigate the relationsships between molecular structure and liquid-crystalline properties more in detail, further synthetic activities as well as physical measurements to characterize these phases are in progress.

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