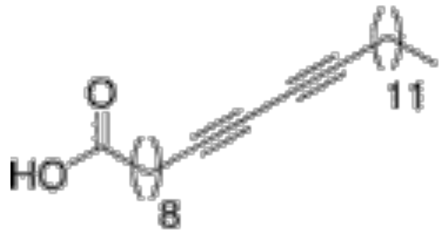
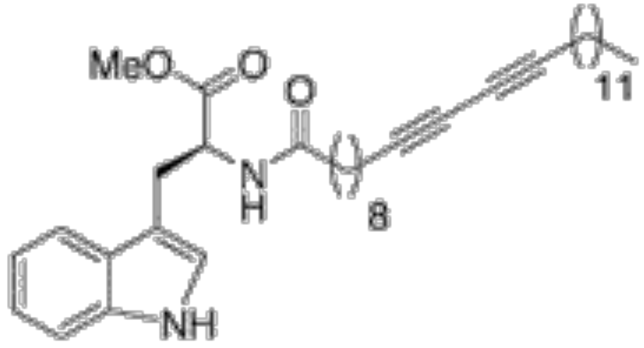
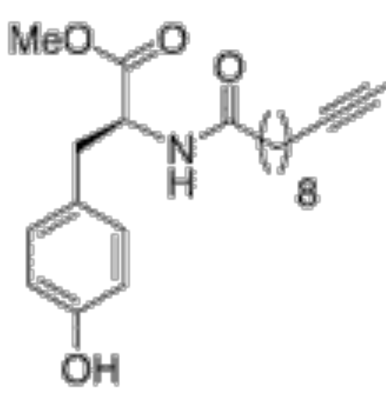
Polydiacetylene Liposome s



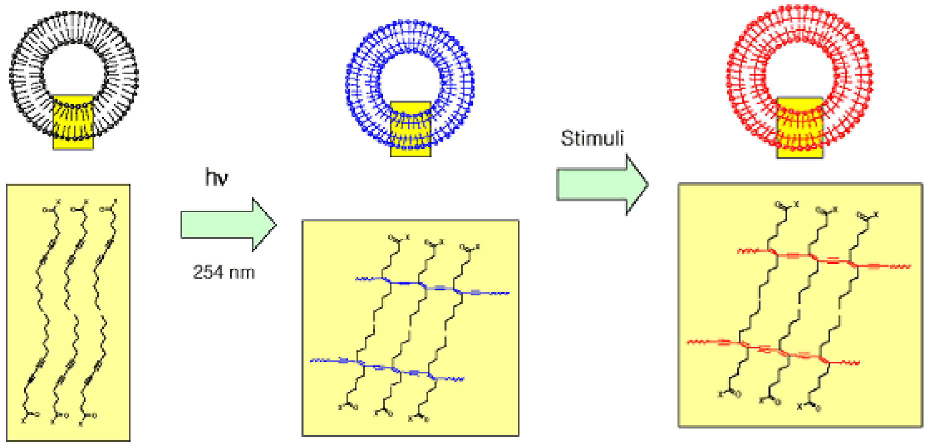
1

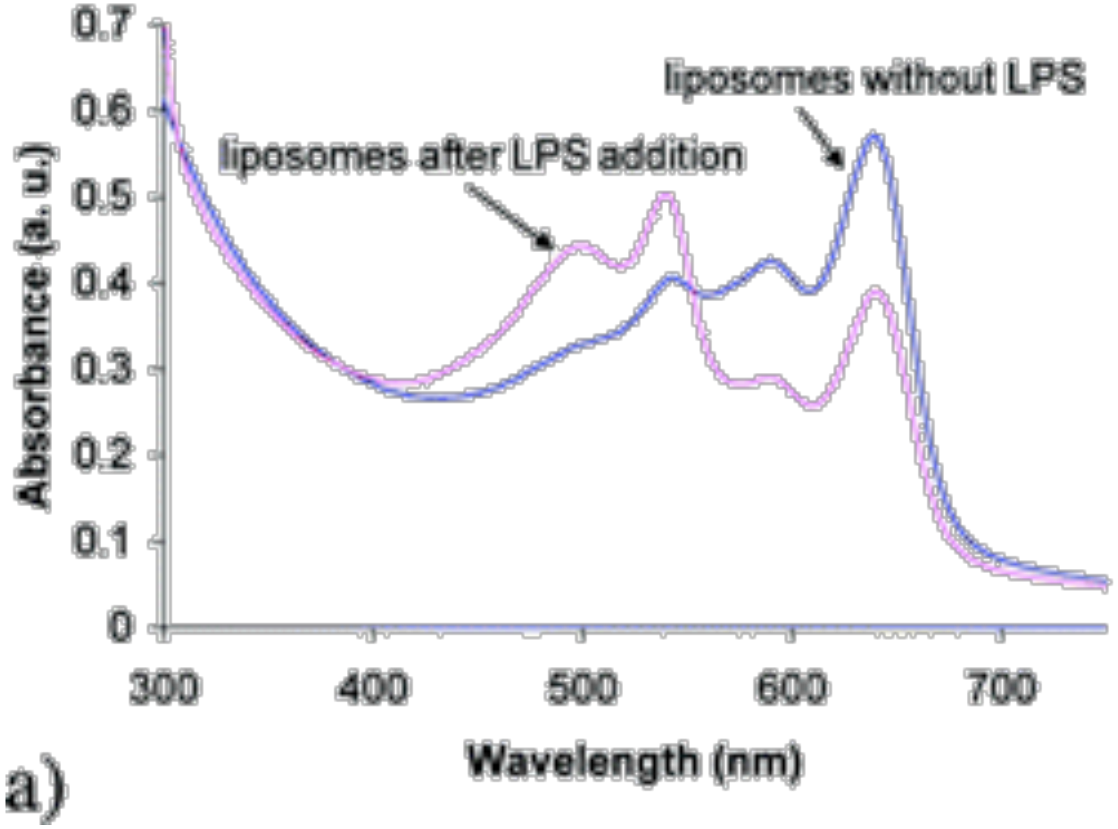


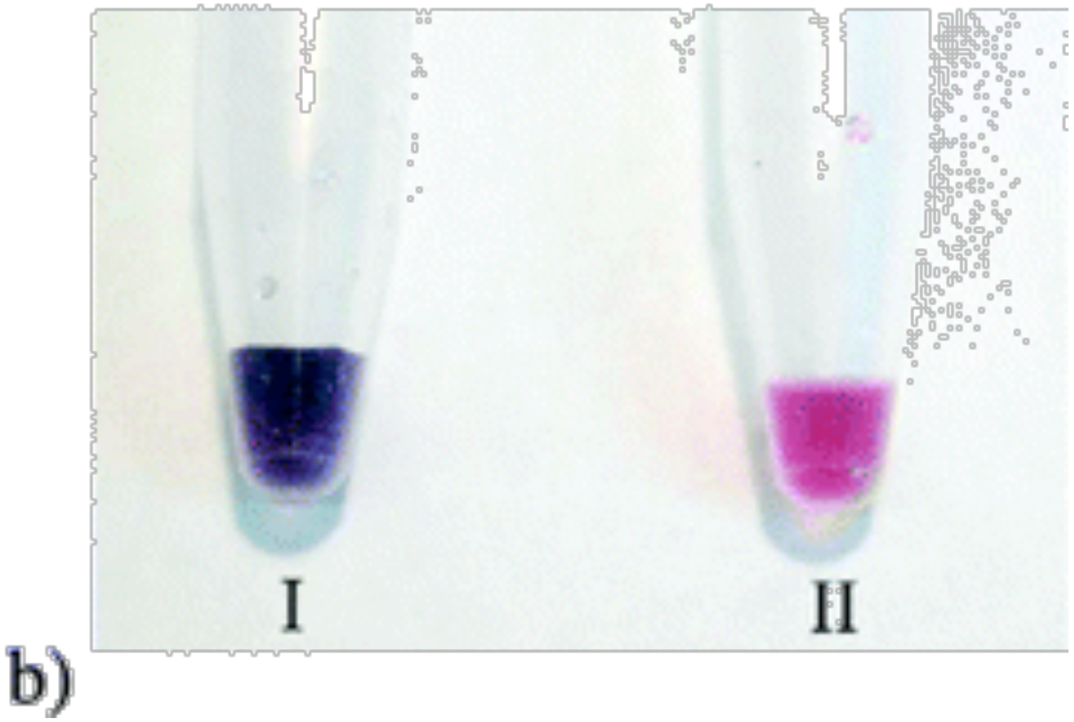
2



3

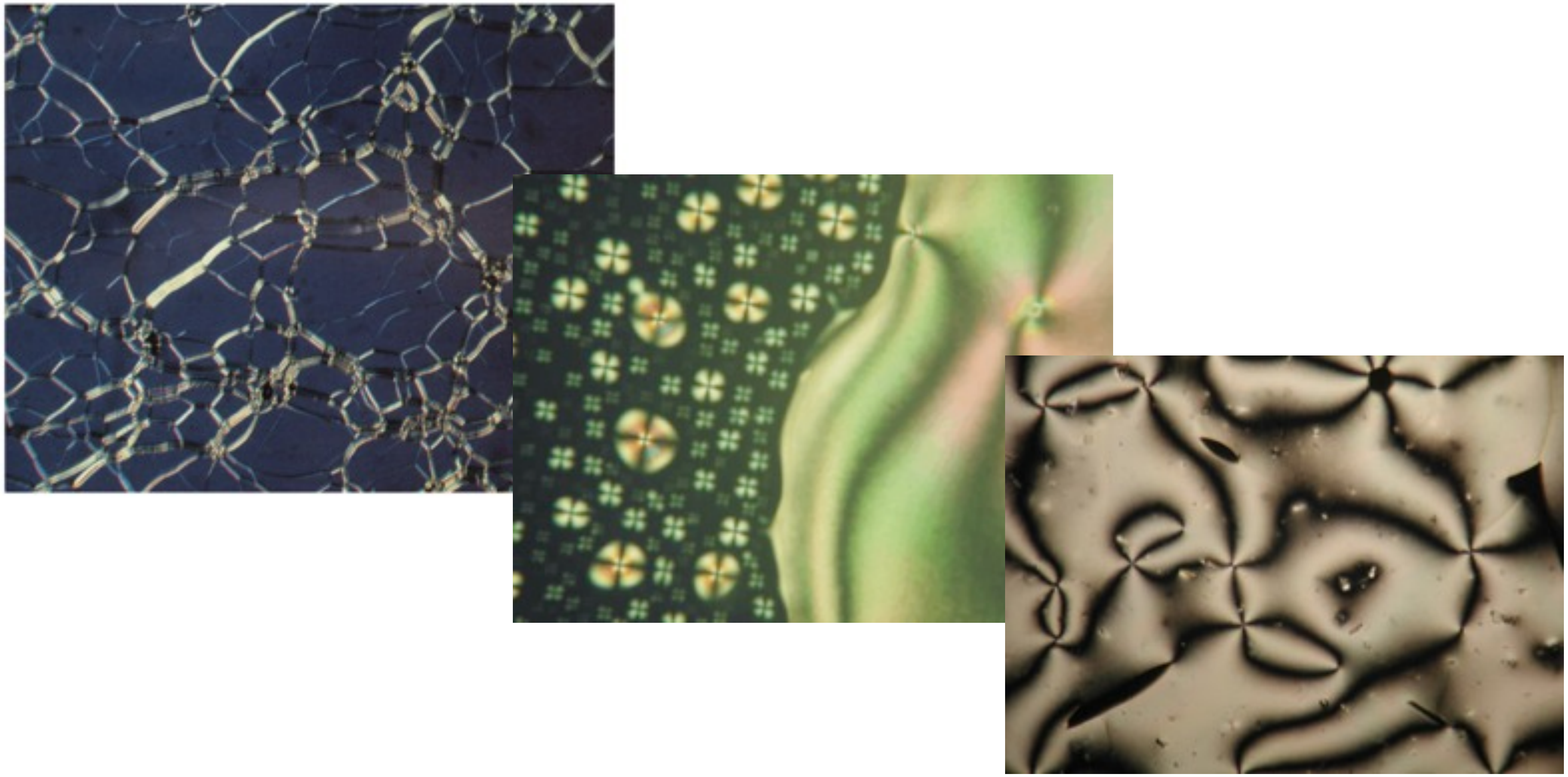


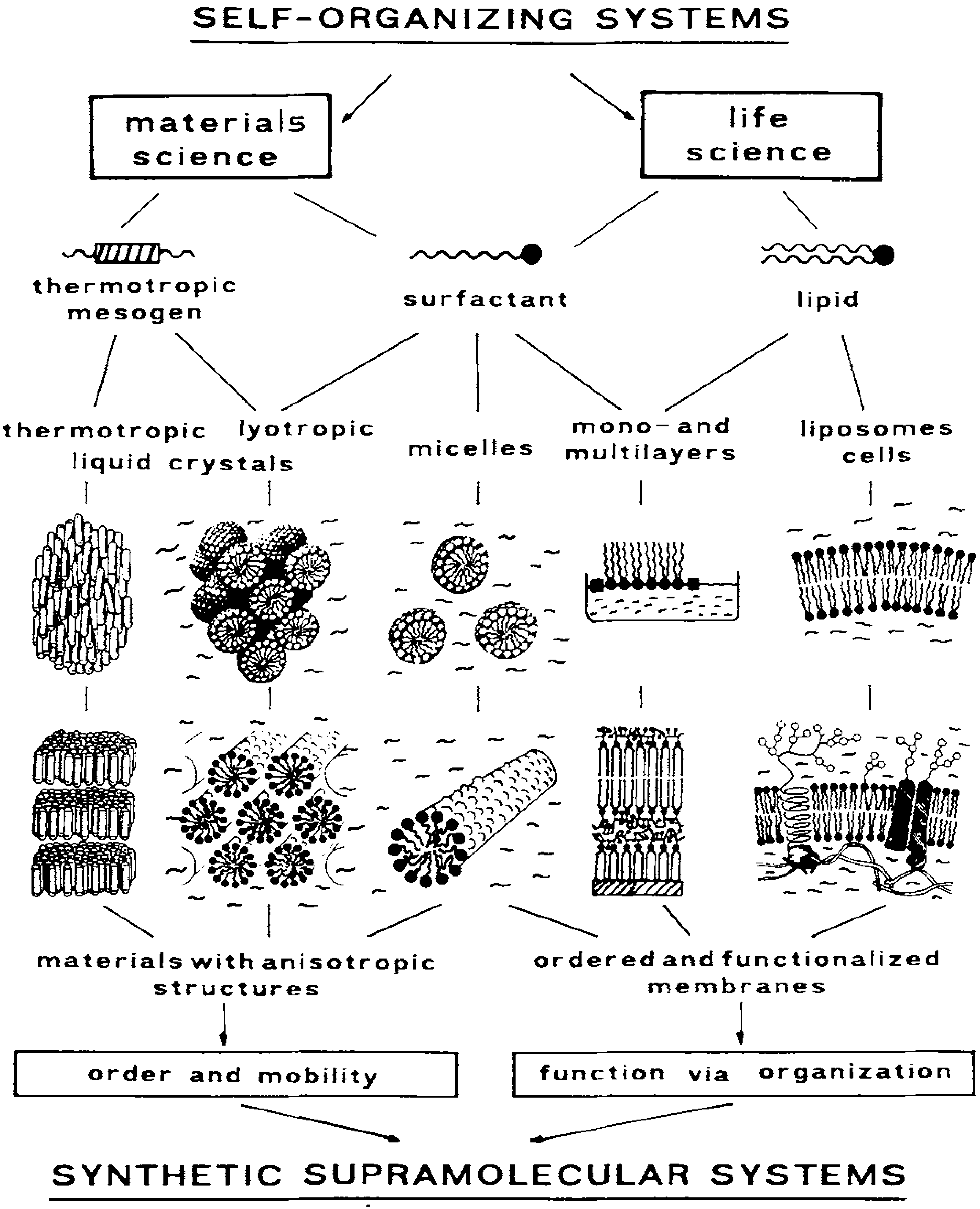




Liquid Crystals

States between crystalline and isotropic liquid





SELF-ORGANIZING SYSTEMS

materials science

life science

thermotropic mesogen

surfactant

lipid

thermotropic liquid crystals

lyotropic liquid crystals

micelles

mono- and multilayers

liposomes cells

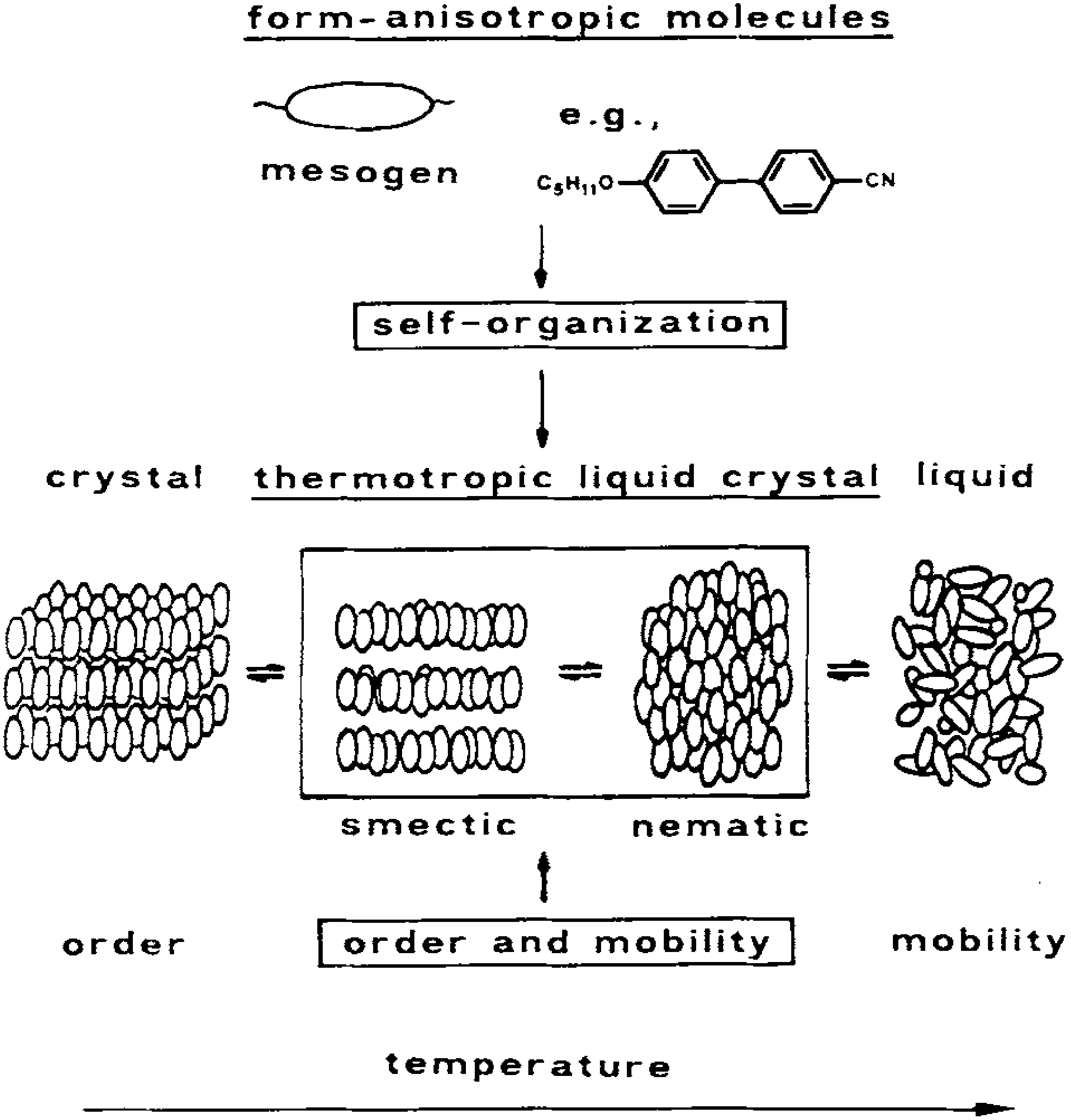
materials with anisotropic structures

ordered and functionalized membranes

order and mobility

function via organization

SYNTHETIC SUPRAMOLECULAR SYSTEMS



form-anisotropic molecules

mesogen

e.g.,

self-organization

crystal

thermotropic liquid crystal

liquid

smectic

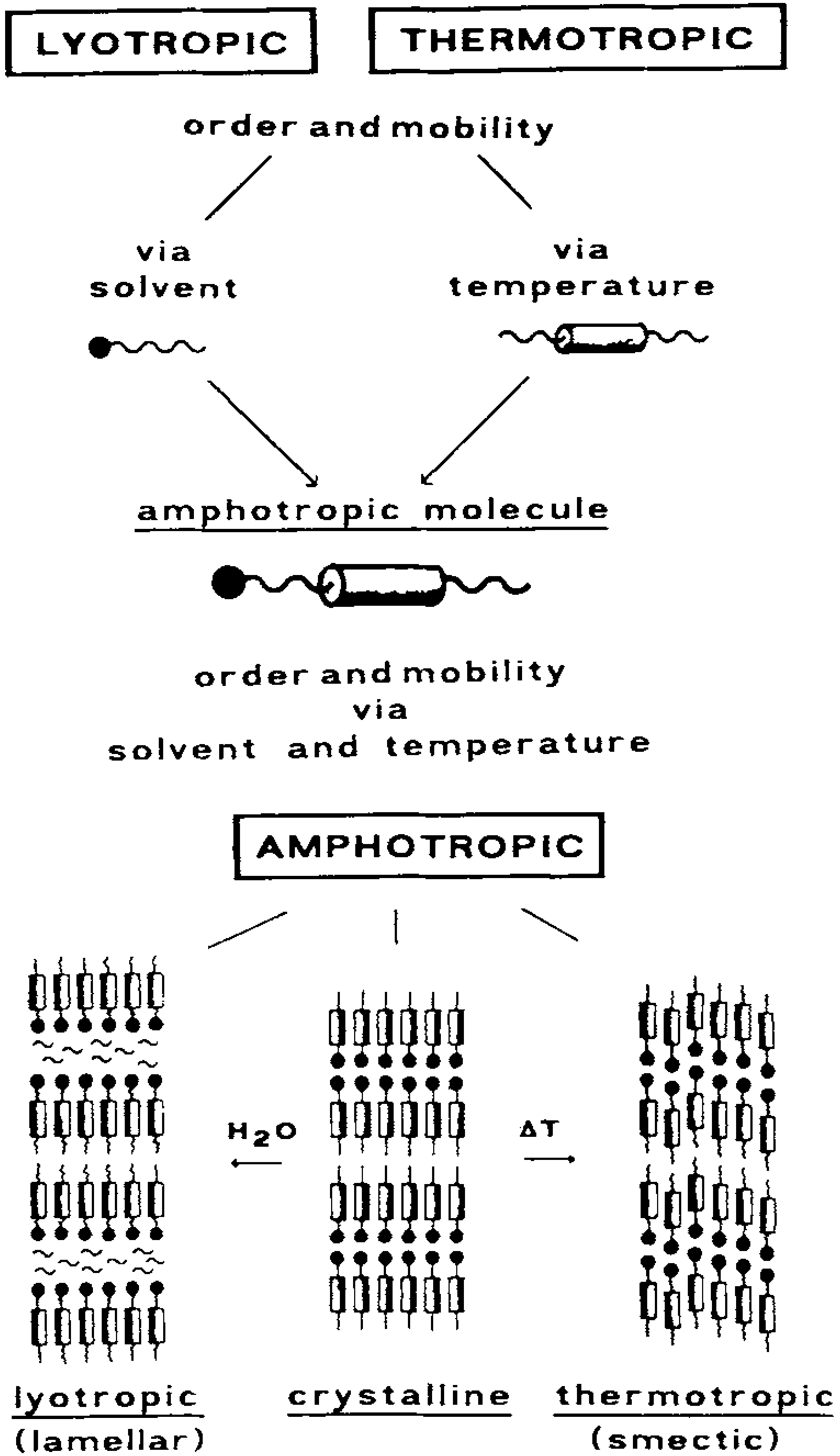
nematic

order

order and mobility

mobility

temperature



LYOTROPIC **THERMOTROPIC**

order and mobility

via
solvent

via
temperature

amphotropic molecule

order and mobility
via
solvent and temperature

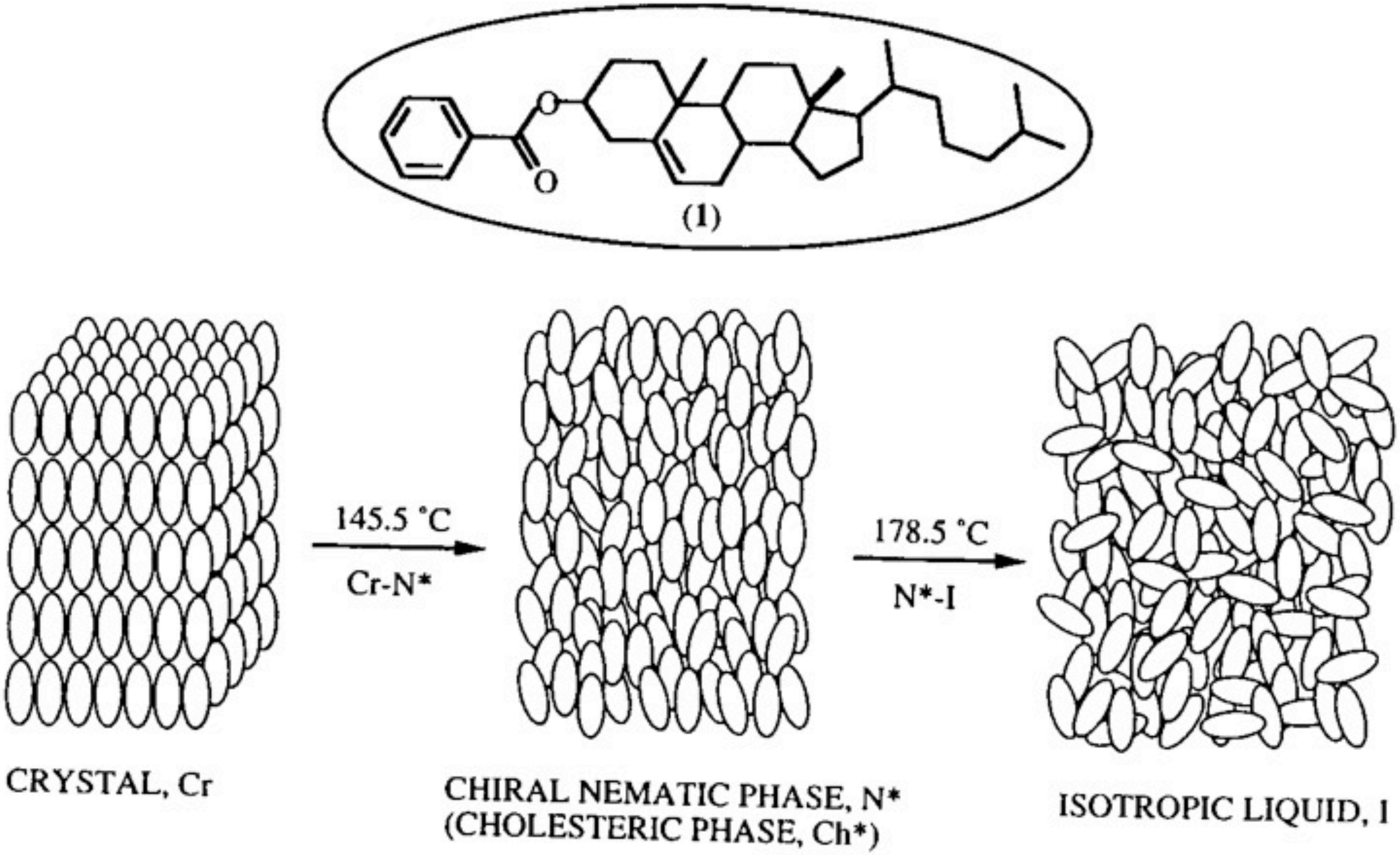
AMPHOTROPIC

lyotropic
(lamellar)

crystalline

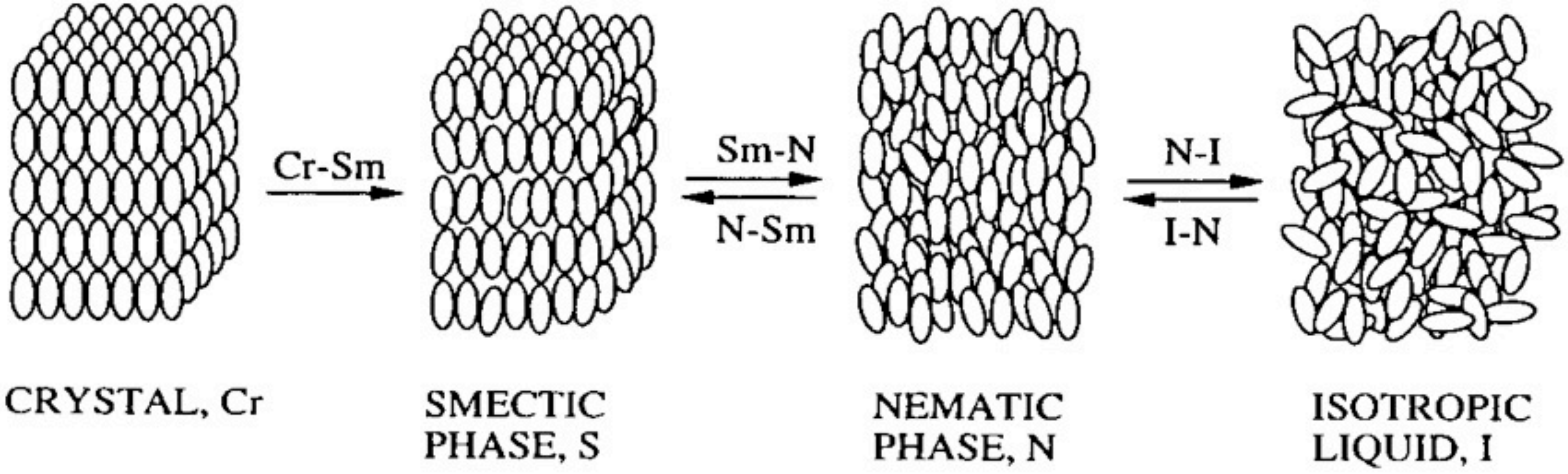
thermotropic
(smectic)

1888: Prof. Reinitzer, botanist

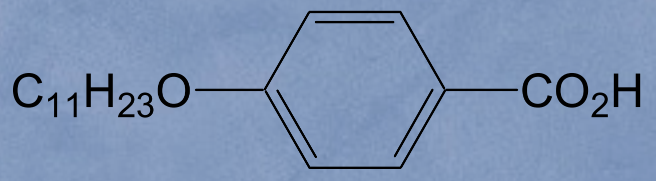


A schematic representation of the melting of crystalline cholesteryl benzoate (1) at 145.5 °C to form a chiral nematic (cholesteric) phase, which in turn forms the isotropic liquid on further heating to 178.5 °C.[30,31]

phase transitions: 1922 G. Friedel



Schematic representation of the structures of a solid, a smectic phase the nematic phase and the isotropic liquid state formed by calamitic organic molecules with a large length-to-breadth ratio.



$$C_{11}H_{23}O\text{-}C_6H_4\text{-}CO_2H$$

$$C \xrightleftharpoons[84.5^{o}]{} S \xrightleftharpoons[128^{o}]{} N \xrightleftharpoons[139.5^{o}]{} I$$

nematic phase

-> long-range orientational order

-> no positional order

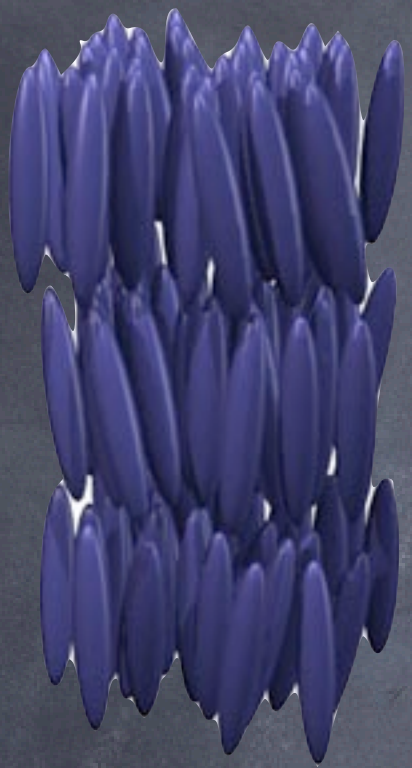
-> center of mass positions are randomly distributed as in a liquid

-> most nematics are uniaxial (approximated as cylinders)

-> can be aligned by an external magnetic / electric field

smectic phase

A



C

-> form well-defined layers

-> Smectic A: molecules oriented along the layer normal

-> Smectic C: molecules tilted away from the layer normal

-> liquid-like within the layers

-> many different smectic phases

chiral nematic (cholesteric) phase

chiral nematic:
-> twisting of the molecules perpendicular to the director

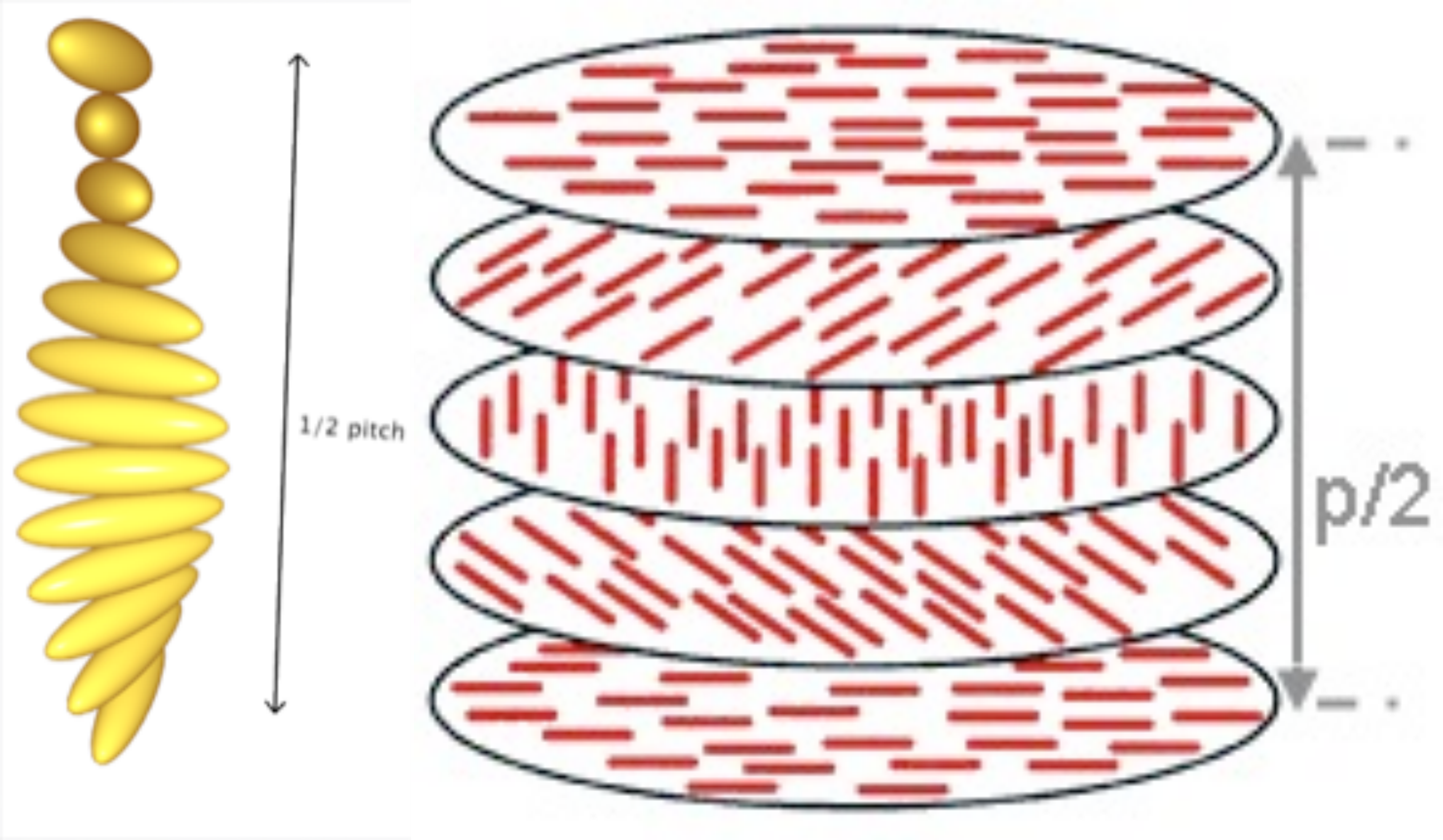
-> finite twist angle due to asymmetric packing

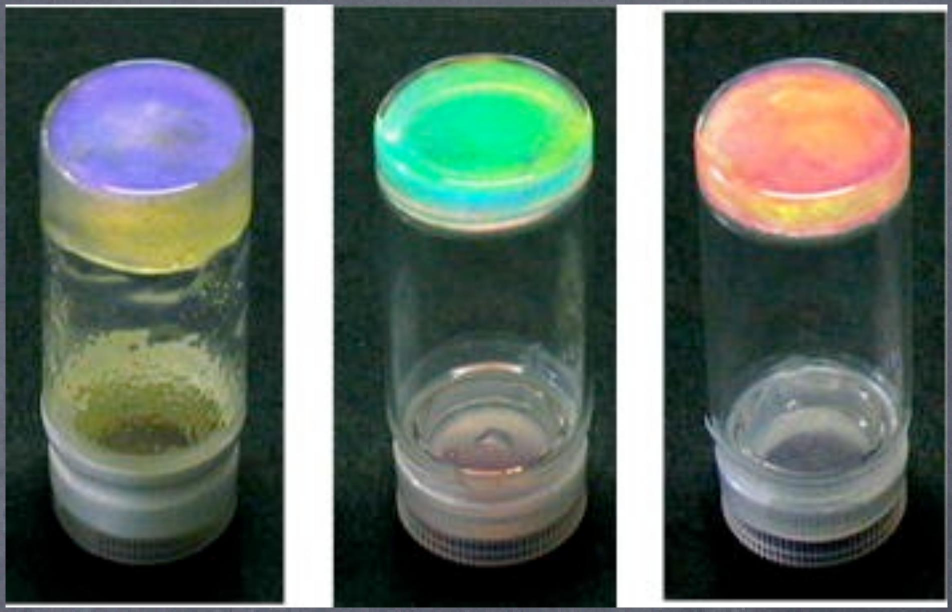
chiral smectic C*:
-> positional ordering in a layered structure

-> molecules tilted by a finite angle with respect to the layer normal

-> chirality induces azimuthal twist from one layer to the next, producing spiral twisting of molecular axis along the layer normal

chiral nematic phase: chrial pitch p





-> distance over which the LC molecules undergo a full 360° twist

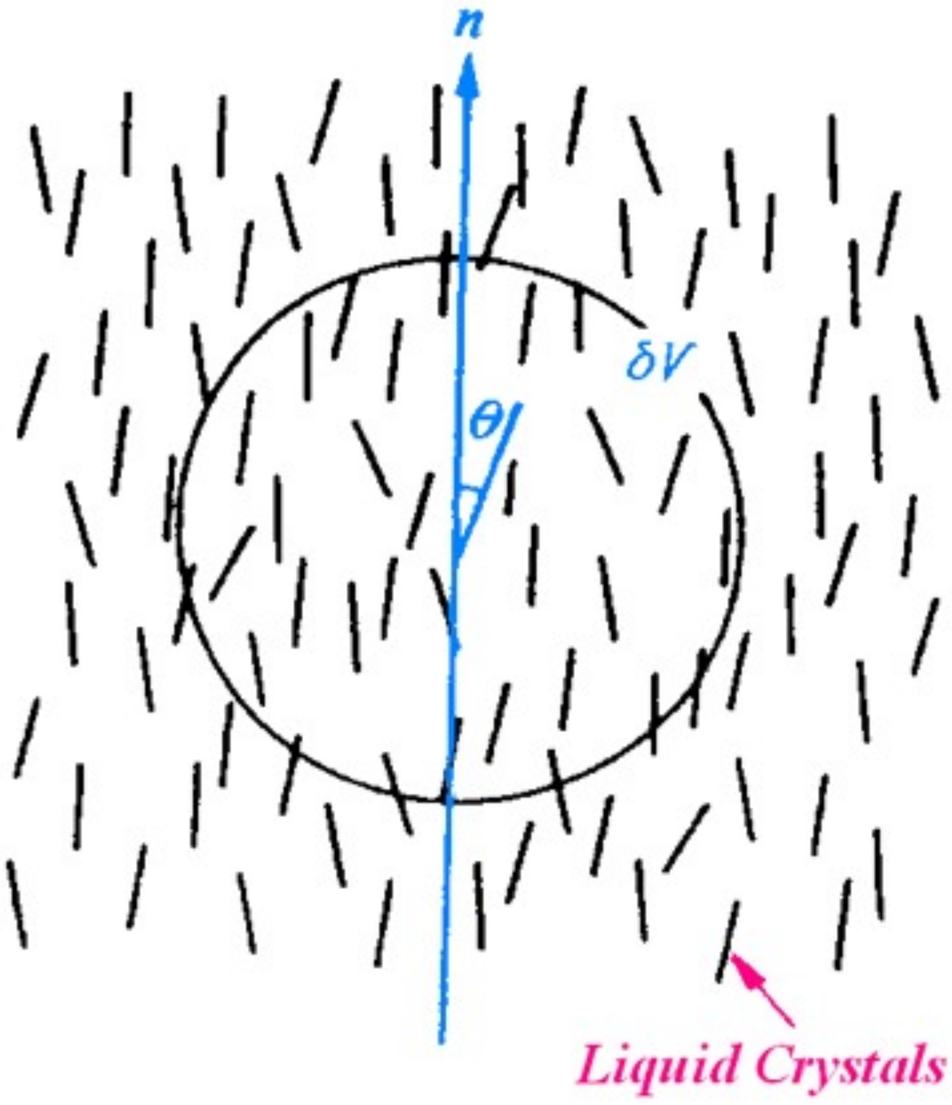
-> pitch, p, typically changes when temperature is altered or when other molecules are added to the LC host

-> if pitch is of the same order as the wavelength of visible light, causes systems to exhibit unique optical properties, such as selective reflection

temperature sensor

- Clear, easy-Lo-read numbers.
- Forenheit/centigrade scale.
- Pressure-sensitive backing.
- Mounts conveniently on outside glass wall of aqurium.

order parameter S



$$S = \langle P_2(\cos\theta) \rangle = \left\langle \frac{3\cos^2\theta - 1}{2} \right\rangle$$

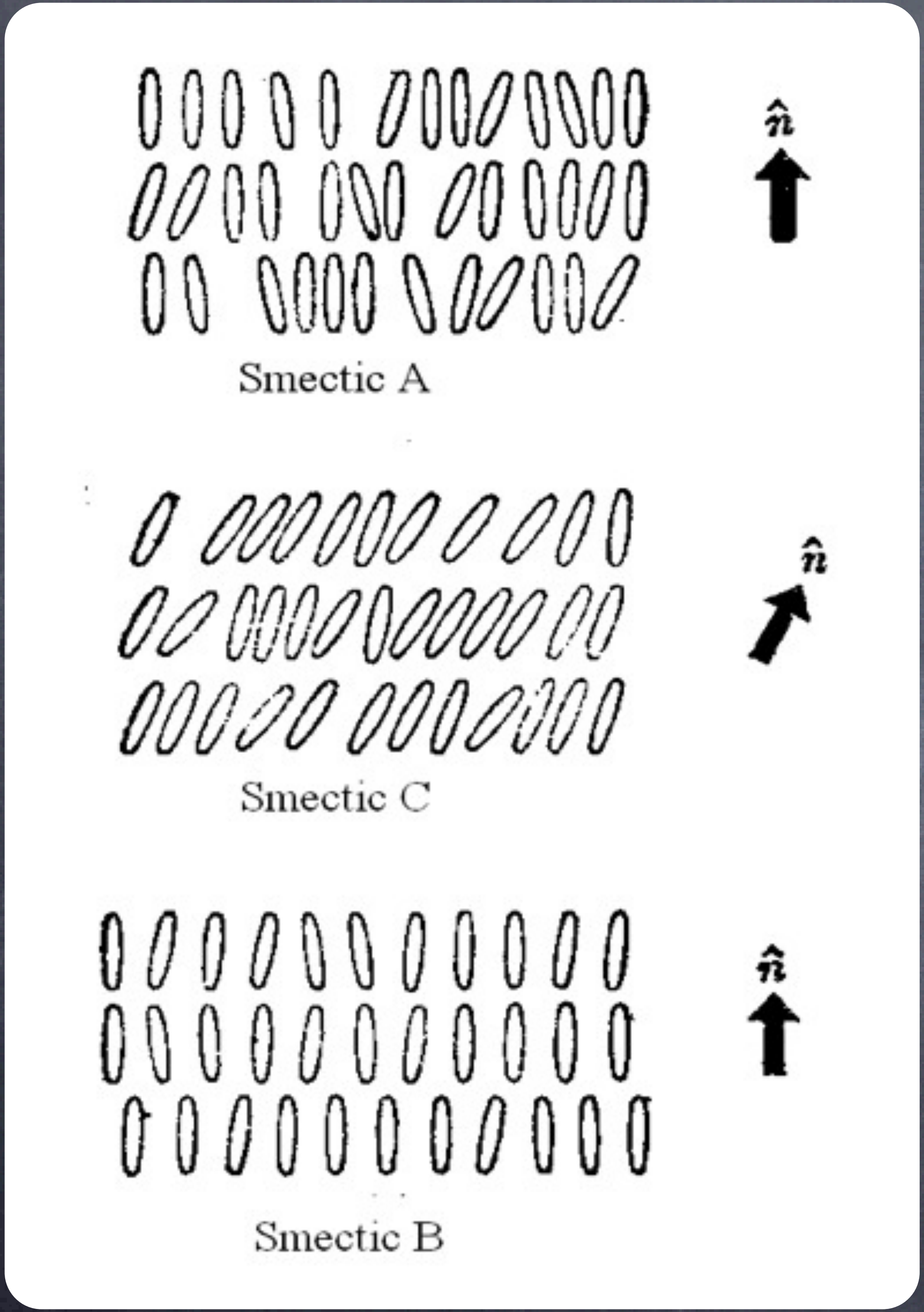
-> generally decreases as the temperature is raised

S=0, isotropic

S=1, Ordered

Nematic, S=0.5-0.6

smectic LCs

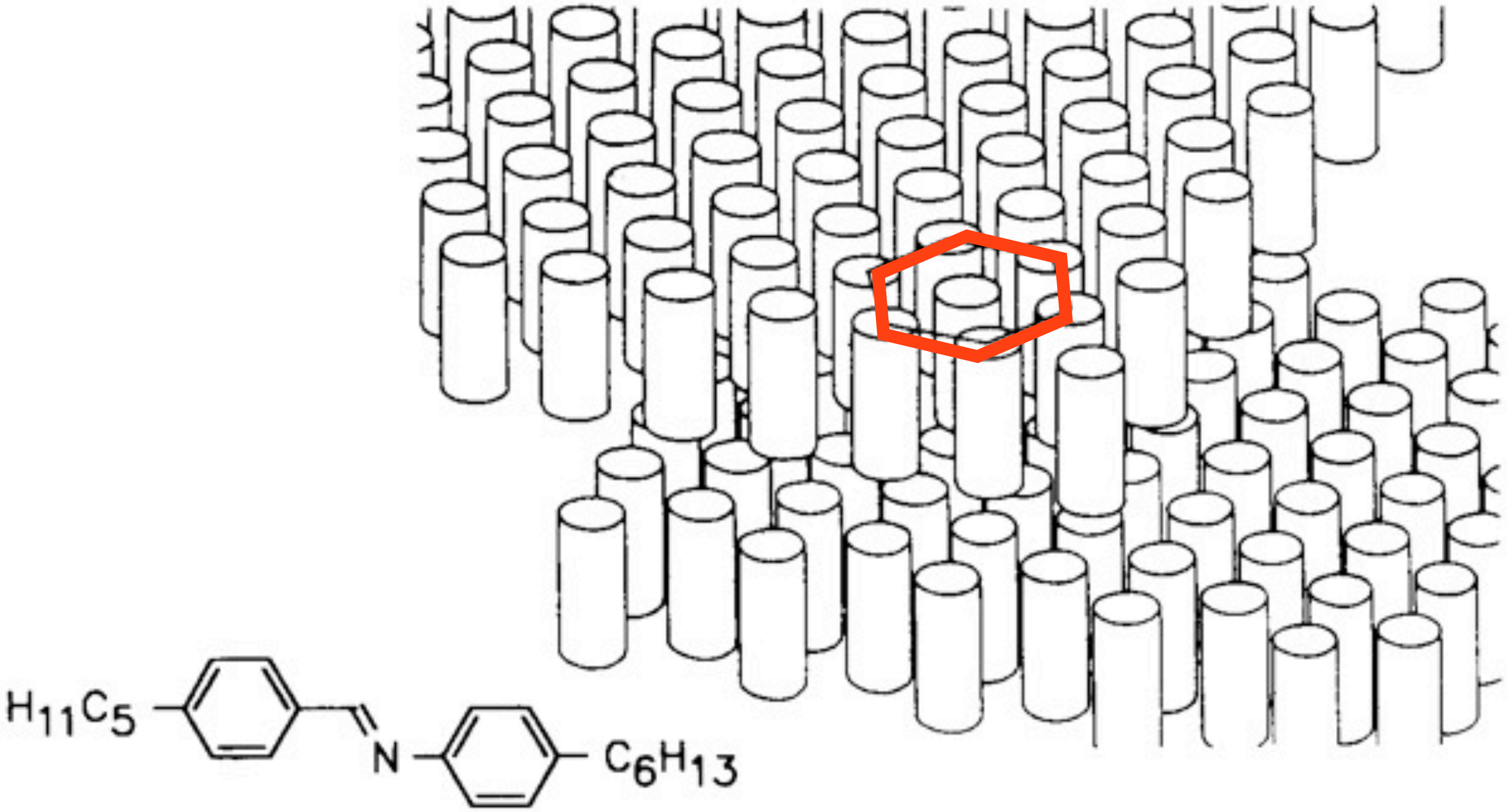


A type: molecular alignment perpendicular to the surface of the layer, but lack of order within the layer.

C type: having a tilted angle between molecular alignment and the surface of the layer.

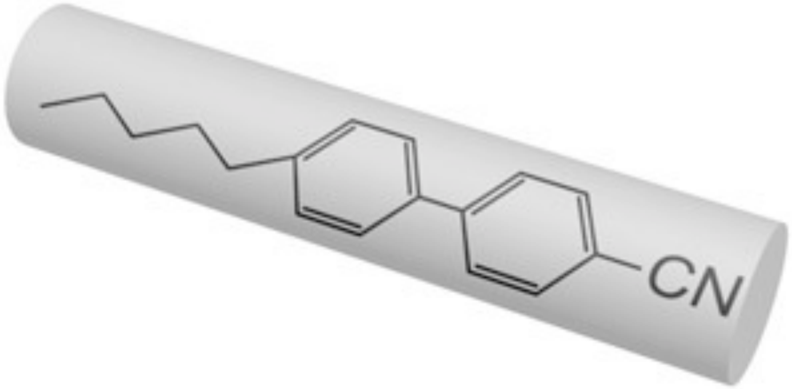
B type: molecular alignment perpendicular to the surface of the layer, having order within the layer.

smectic B LC

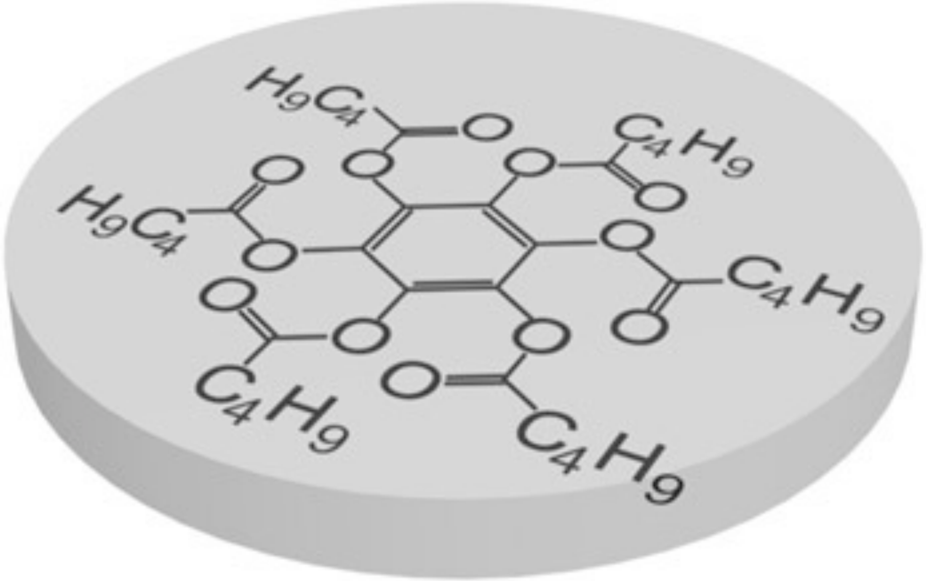


Molecular array in an s_B phase. The molecules are perpendicular to the layer's plane, each at the centre of a hexagonal system, and are free to rotate around their longitudinal axis. 4-Pentylbenzylidene-4′-hexylaniline is such an example

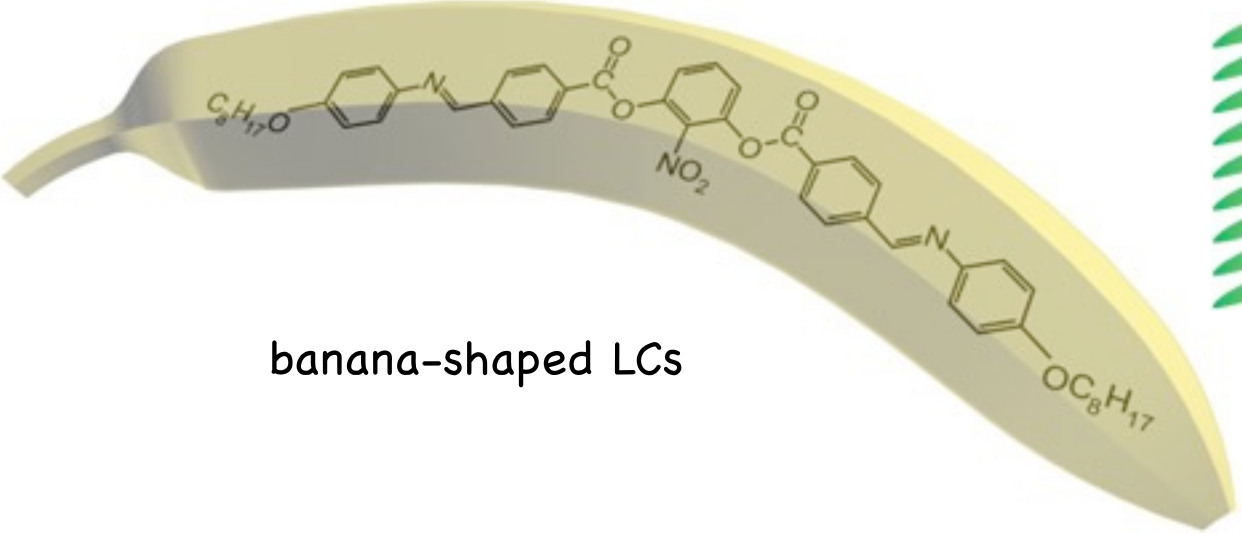
banana shaped LCs



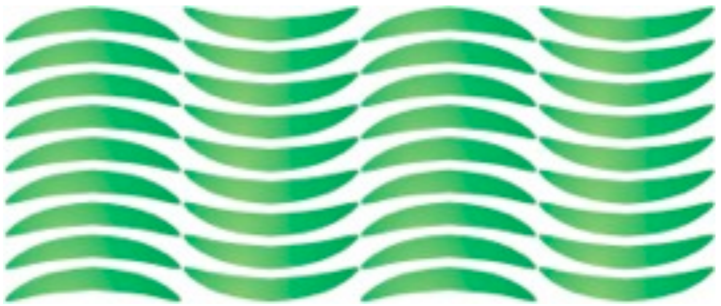
calamitic LCs



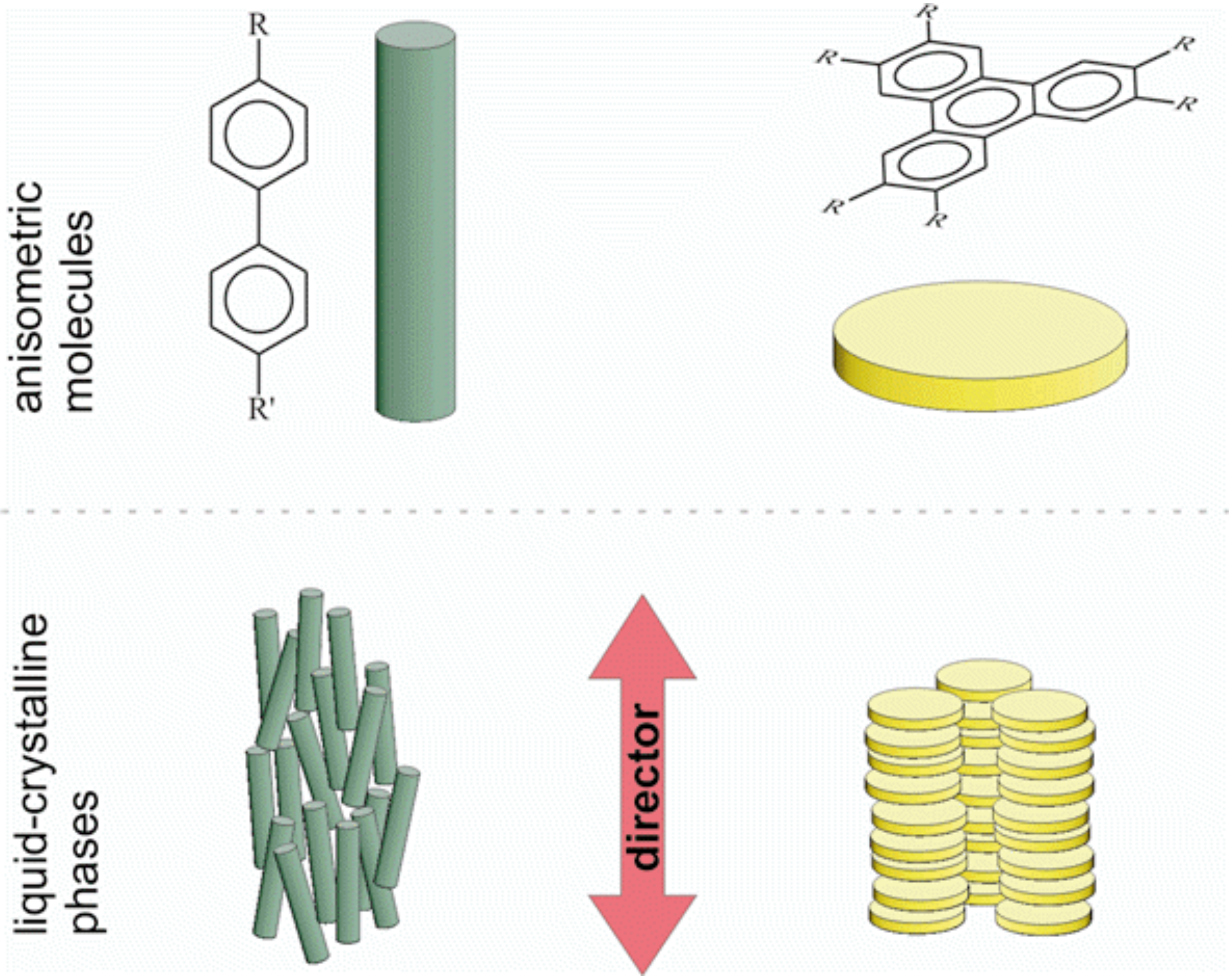
discotic LCs



banana-shaped LCs



discotic LCs



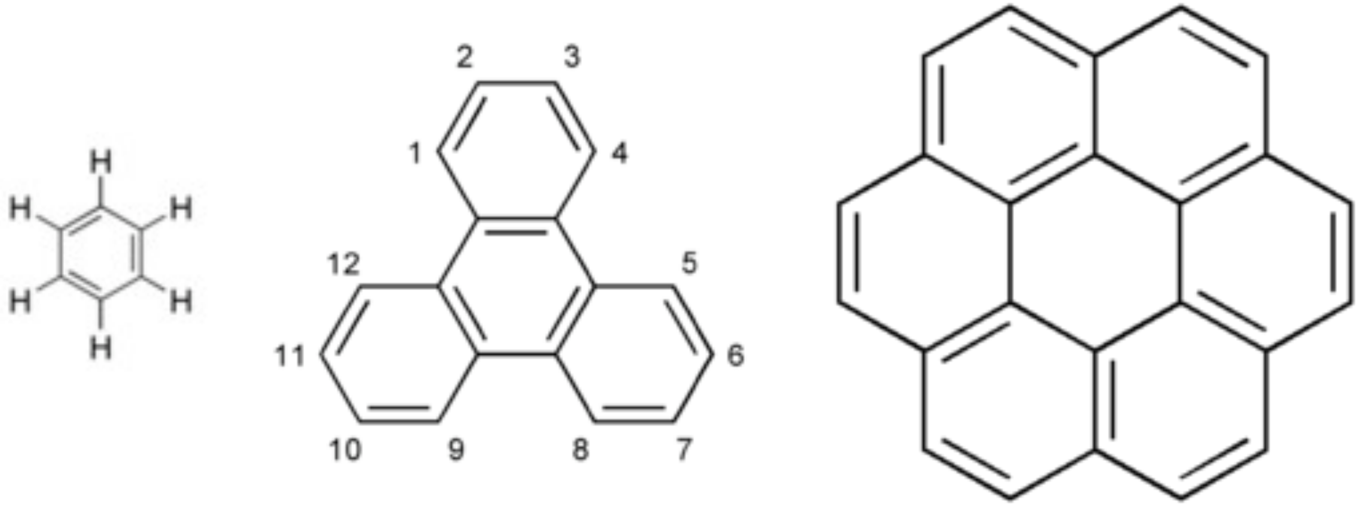
discotic LCs

Nematic phase

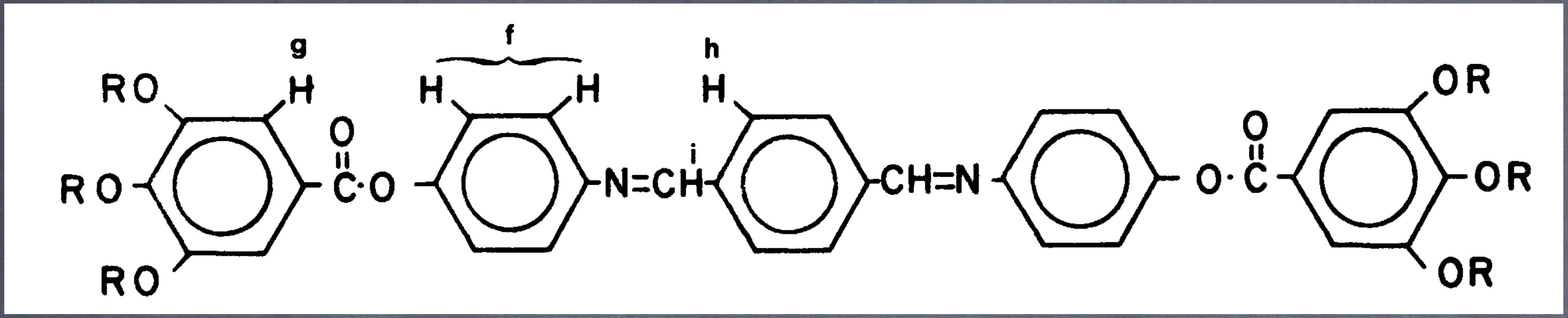
Columnar hexagonal phase

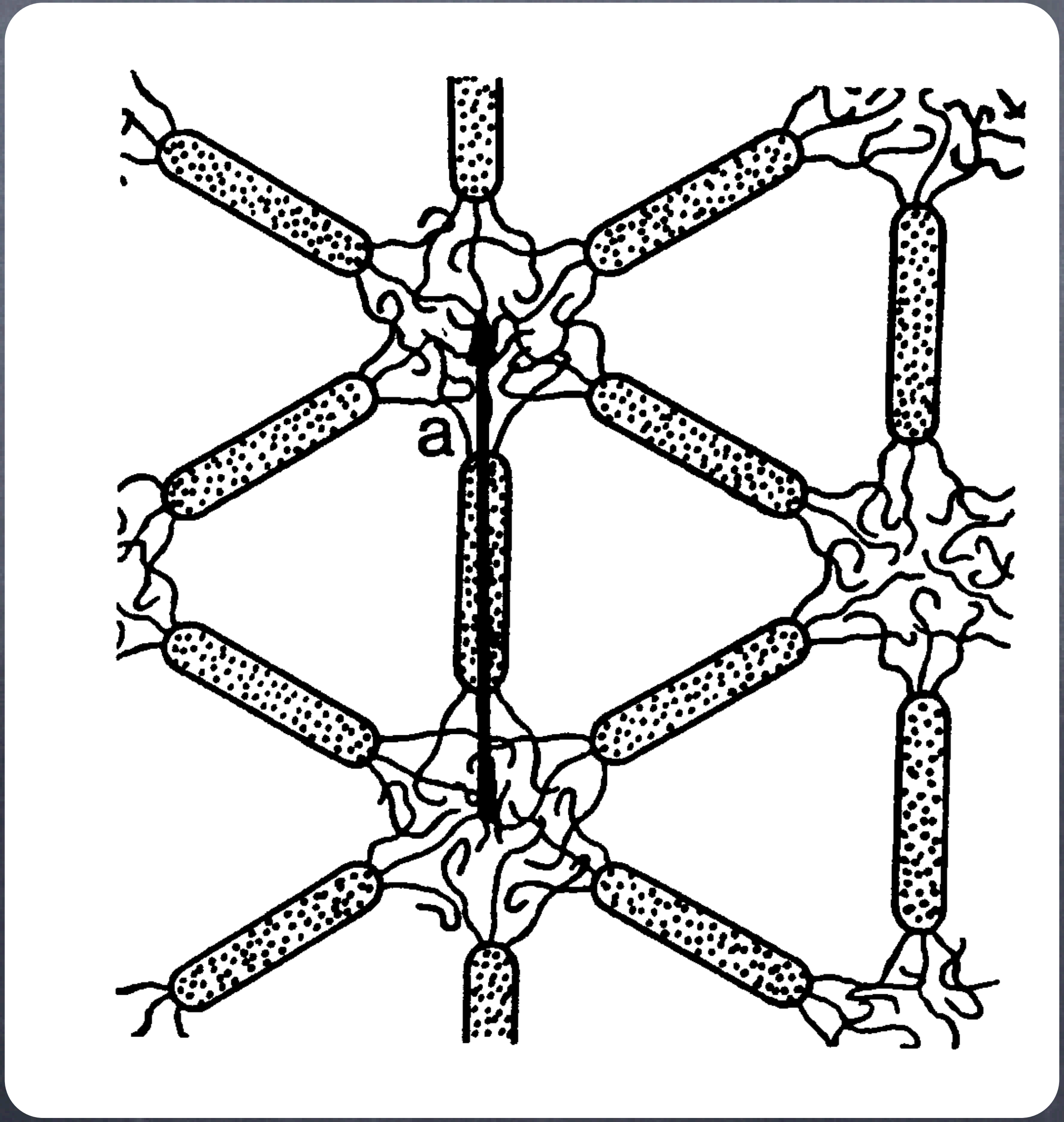
Helical columnar phase

Core centers:
- -> benzene
- -> triphenylene
- -> Coronene
- ->

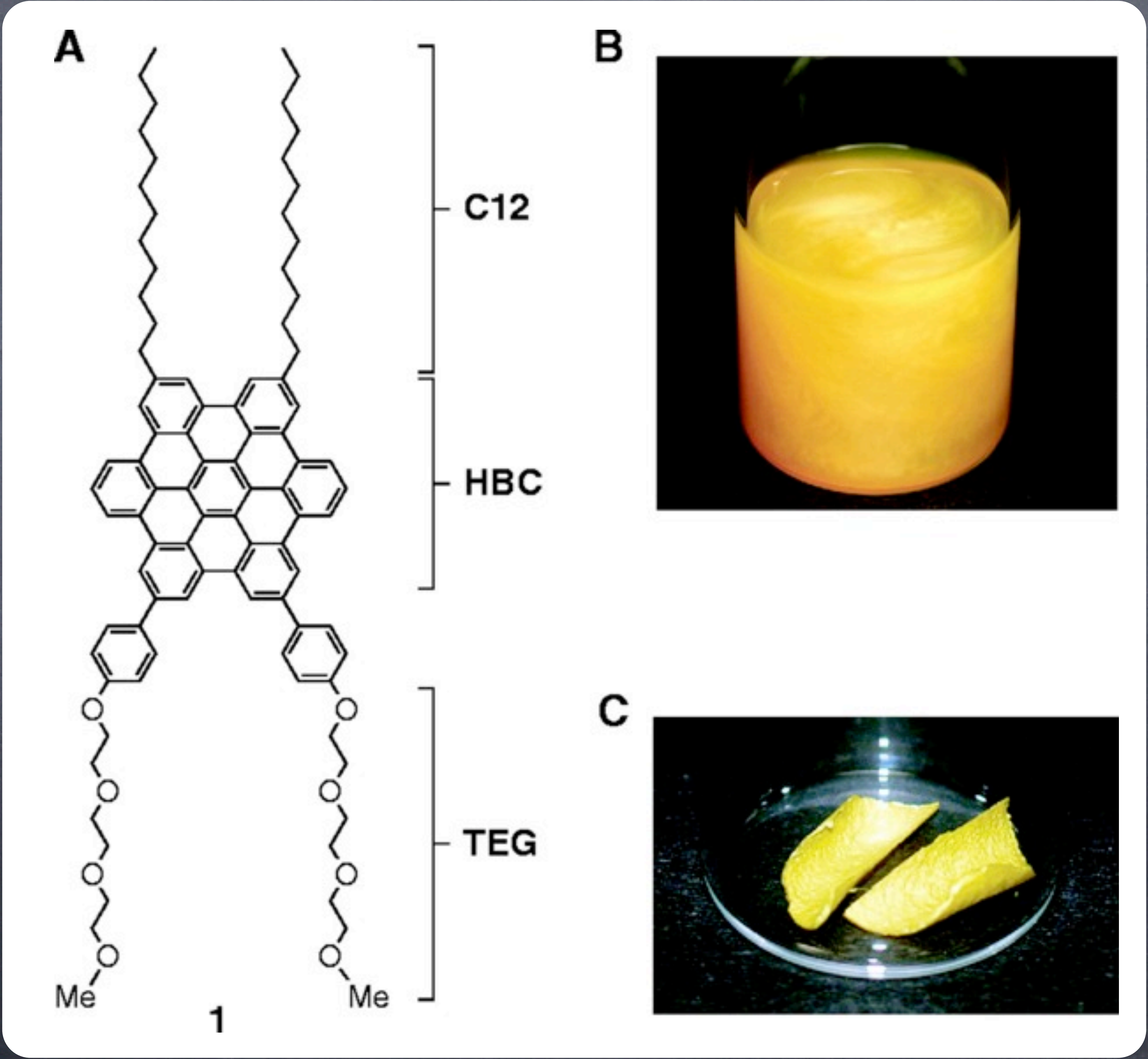


phasmidic mesophase

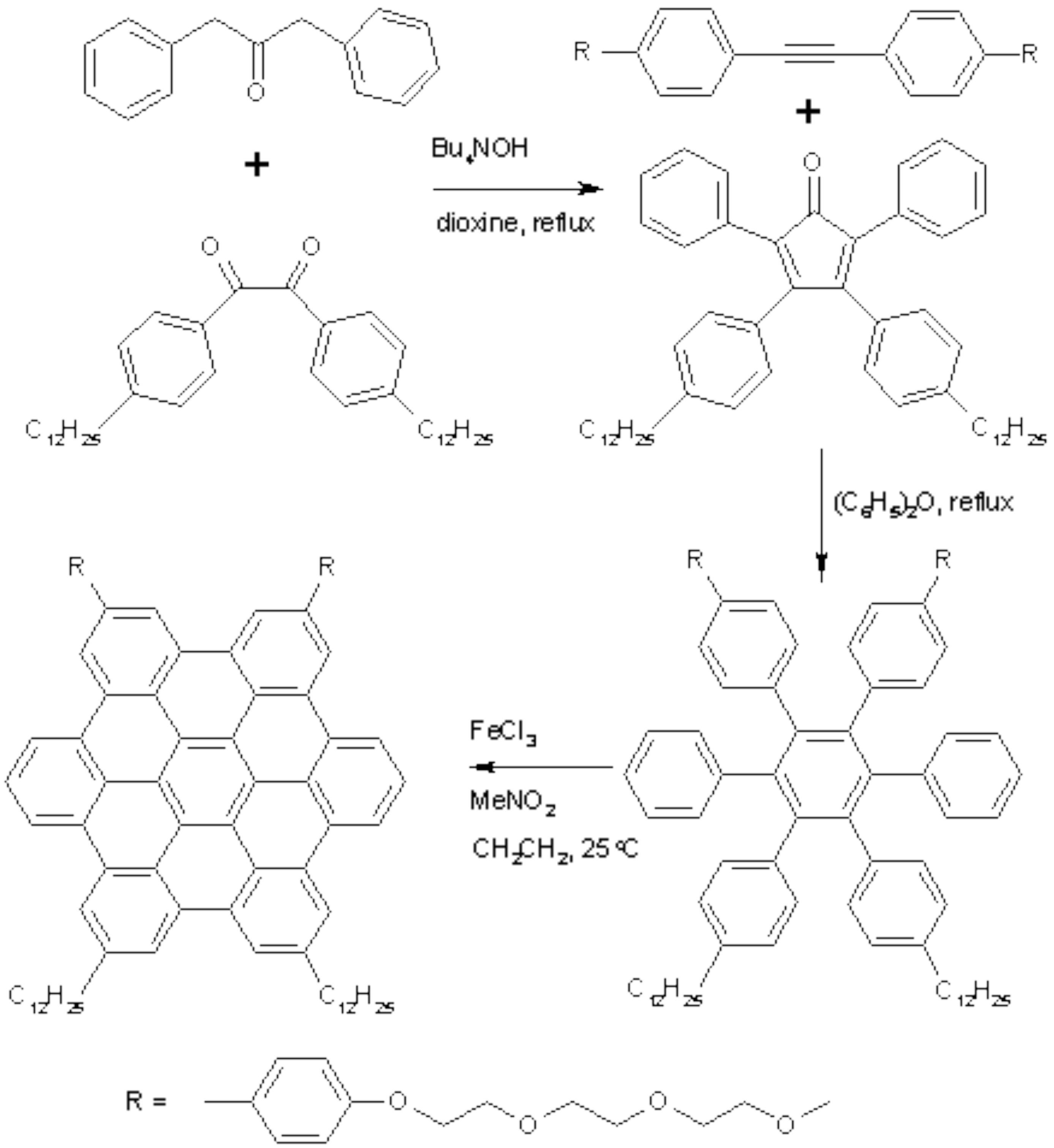




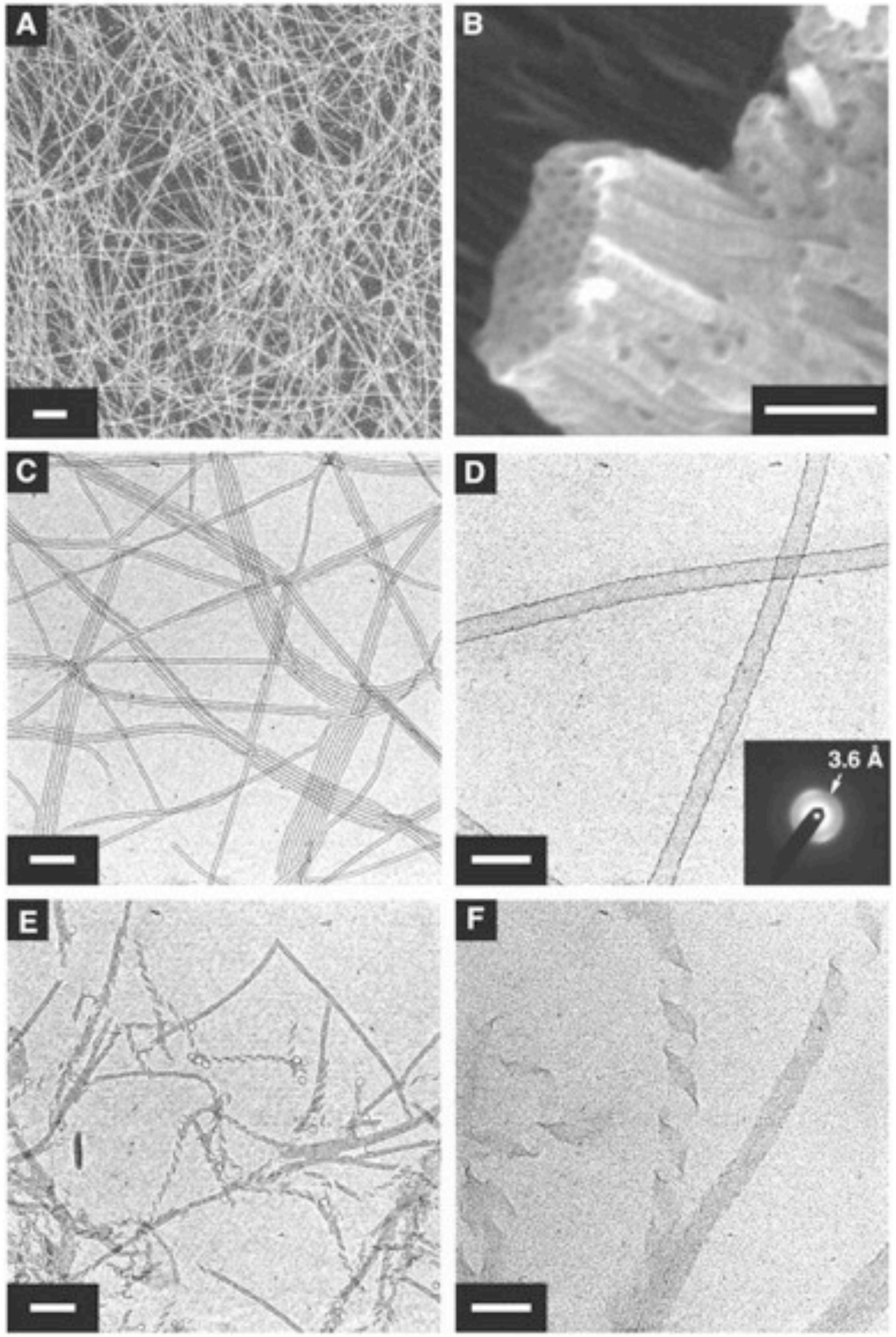
hexabenzocoronene



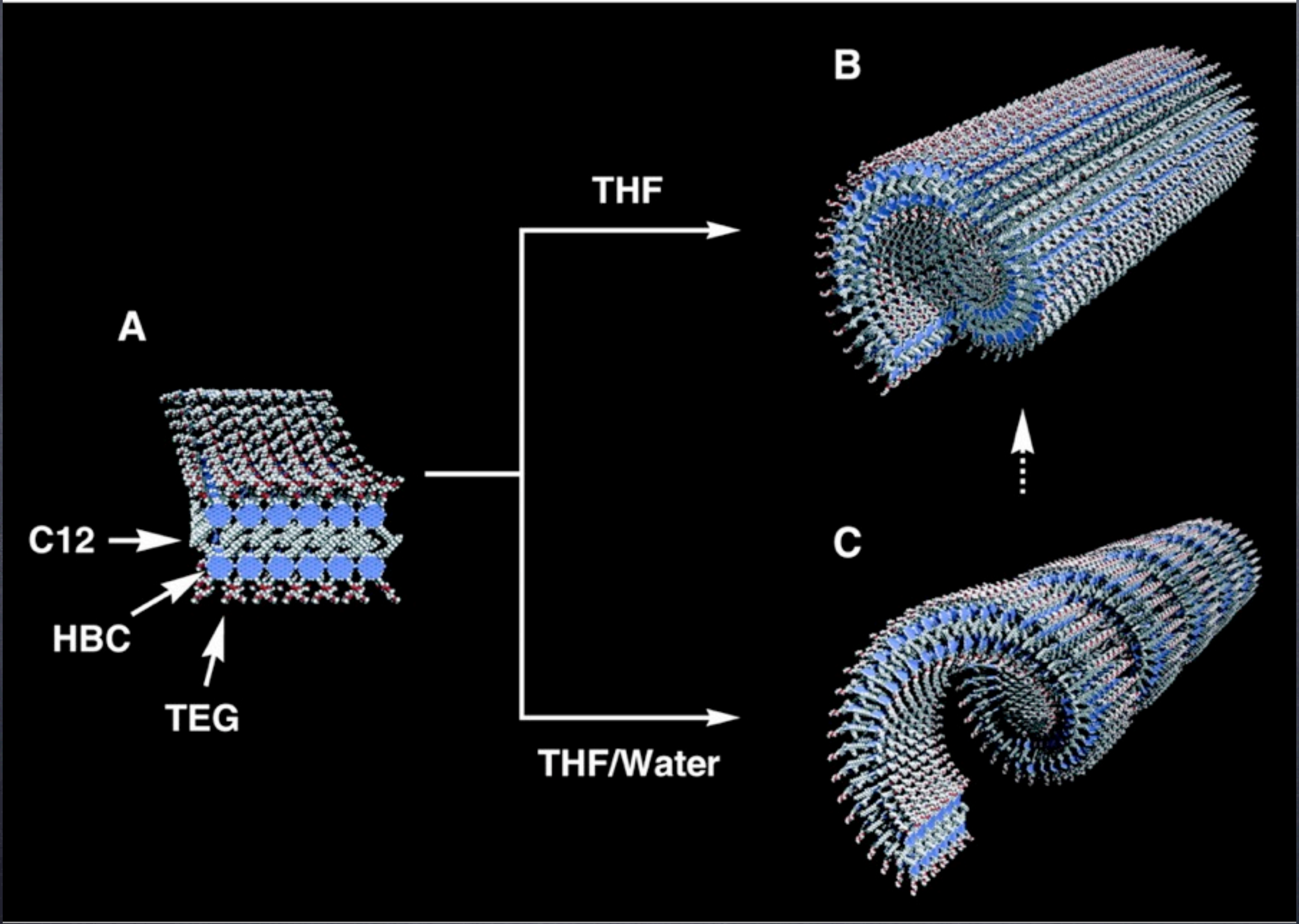
hexabenzocoronene



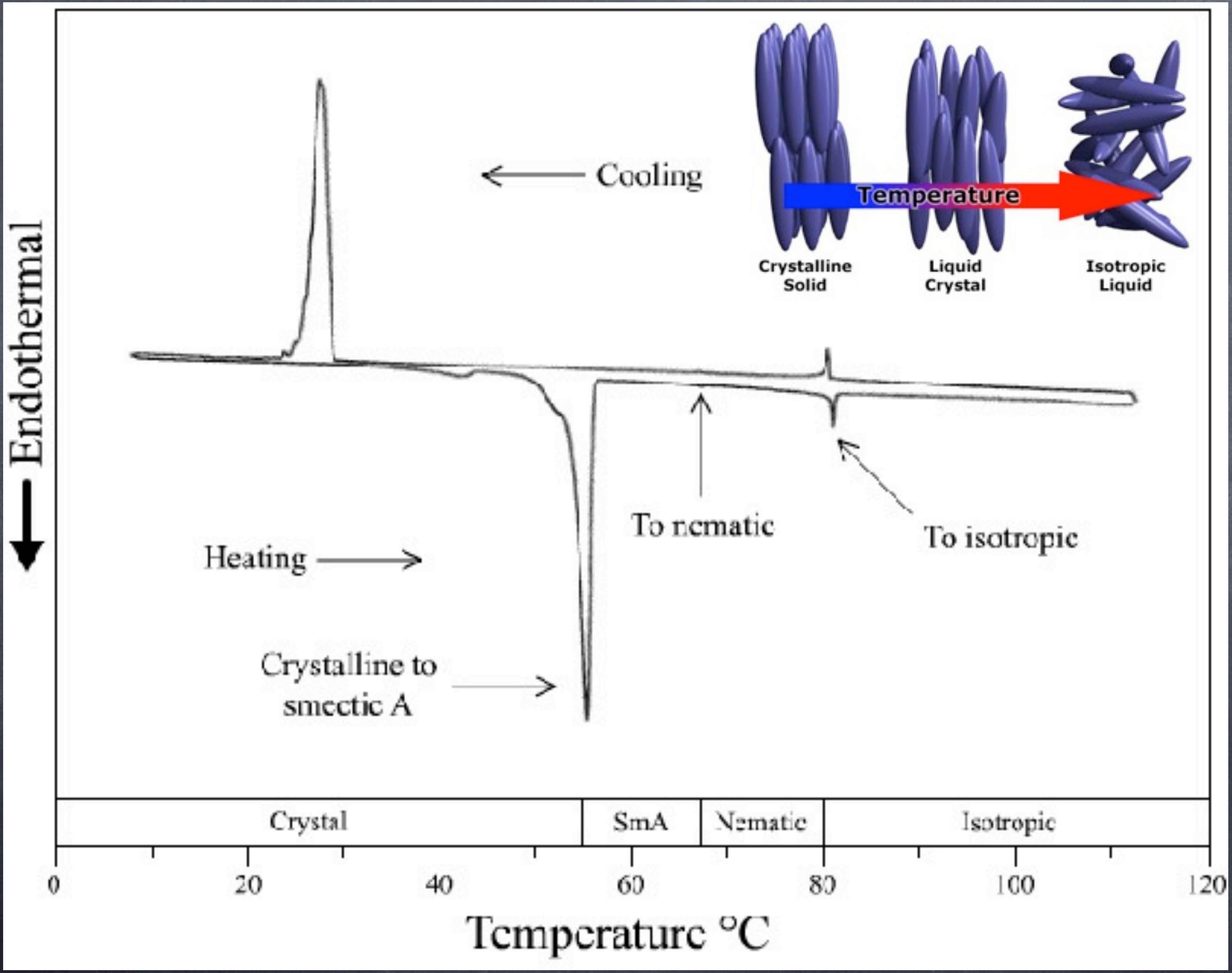
hexabenzocoronene



hexabenzocoronene



Differential Scanning Calorimety



alkylcyanobiphenyl homologues

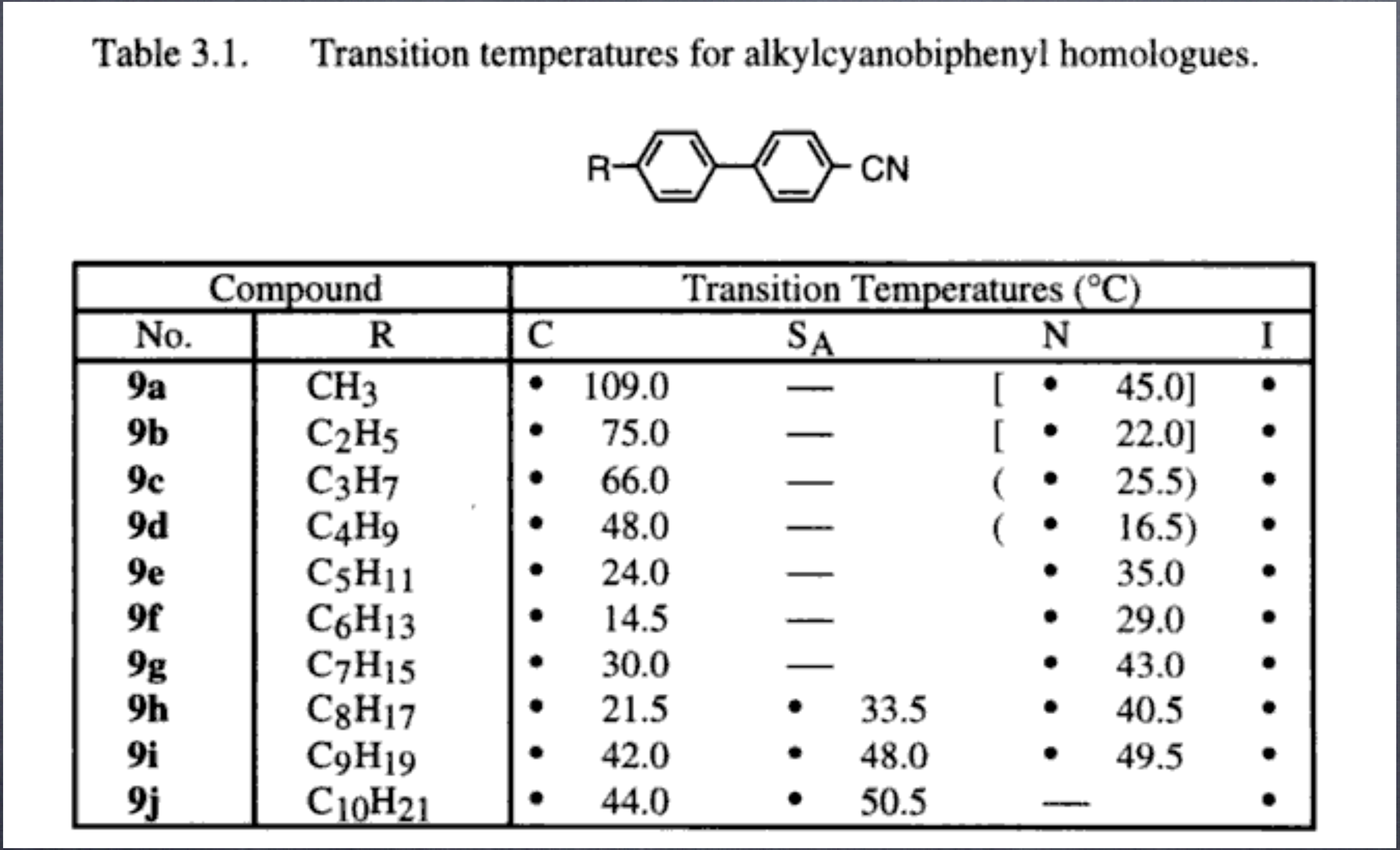


Table 3.1. Transition temperatures for alkylcyanobiphenyl homologues.

Compound		Transition Temperatures (°C)						
No.	R	C		S_A		N		I
9a	CH_3	•	109.0	—		[•	45.0]	•
9b	C_2H_5	•	75.0	—		[•	22.0]	•
9c	C_3H_7	•	66.0	—		(•	25.5)	•
9d	C_4H_9	•	48.0	—		(•	16.5)	•
9e	C_5H_{11}	•	24.0	—		•	35.0	•
9f	C_6H_{13}	•	14.5	—		•	29.0	•
9g	C_7H_{15}	•	30.0	—		•	43.0	•
9h	C_8H_{17}	•	21.5	•	33.5	•	40.5	•
9i	C_9H_{19}	•	42.0	•	48.0	•	49.5	•
9j	$C_{10}H_{21}$	•	44.0	•	50.5	—		•

- first nematics commercially available for display devices
- still used in LC displays for watches, calculators, etc.

alkylcyanobiphenyl variants

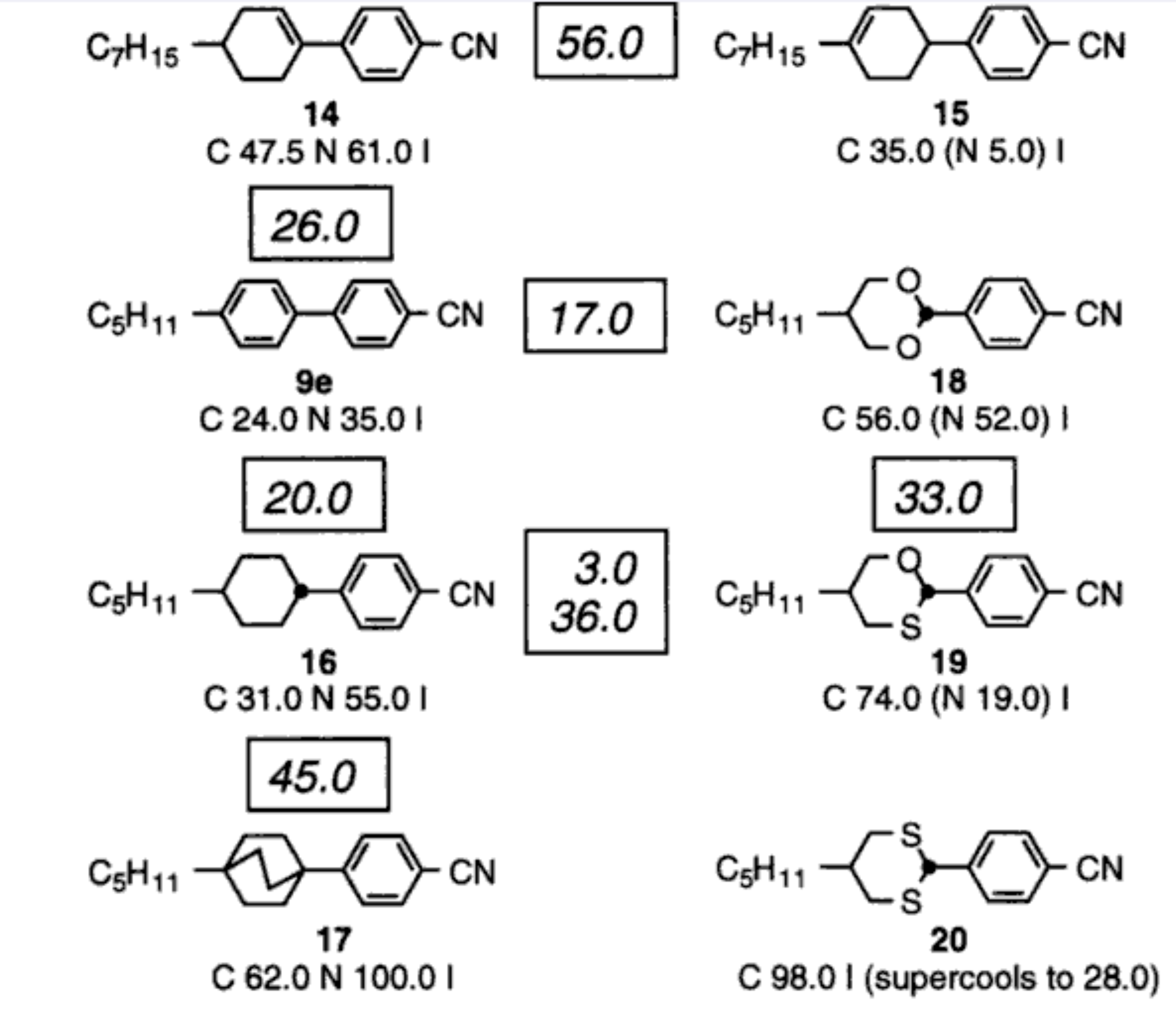
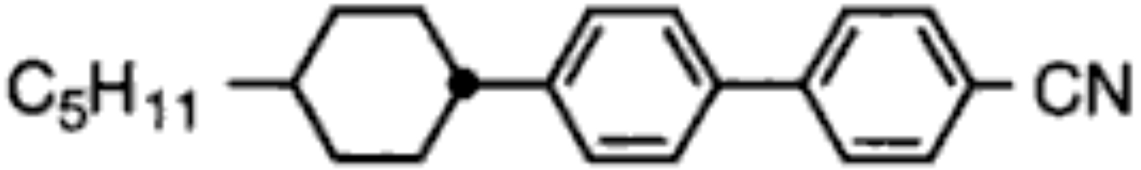
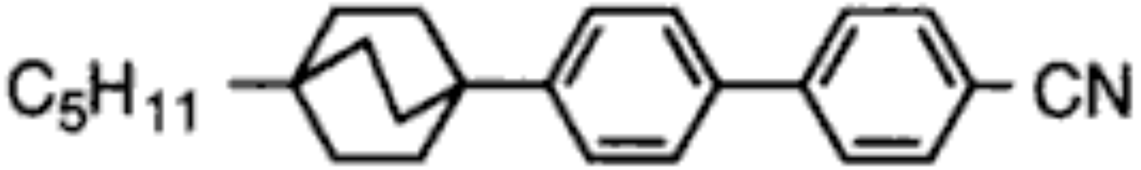


Figure 3.7. Effects of alicyclic core changes on transition temperatures.

alkylcyanobiphenyl variants

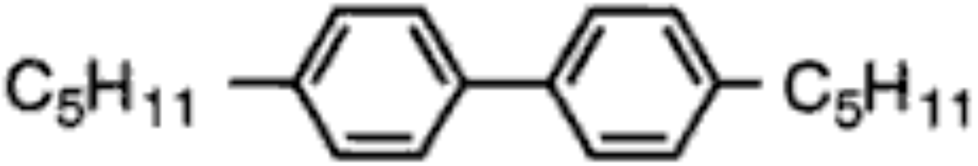


24
C 96 N 222 I



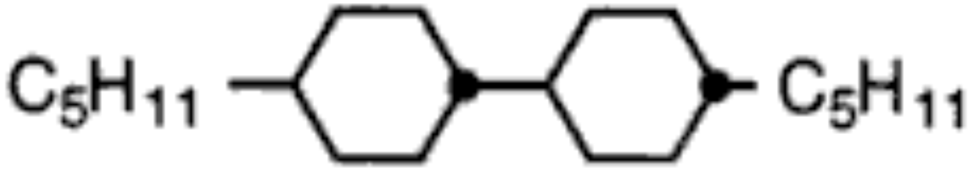
25
C 159 N 269 I

alkylbiphenyl variants



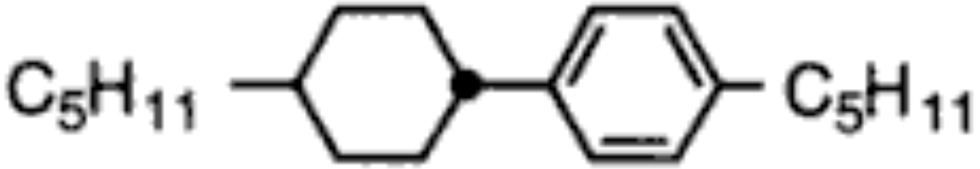
32

C 26.0 S 47.6 S 52.2 I



33

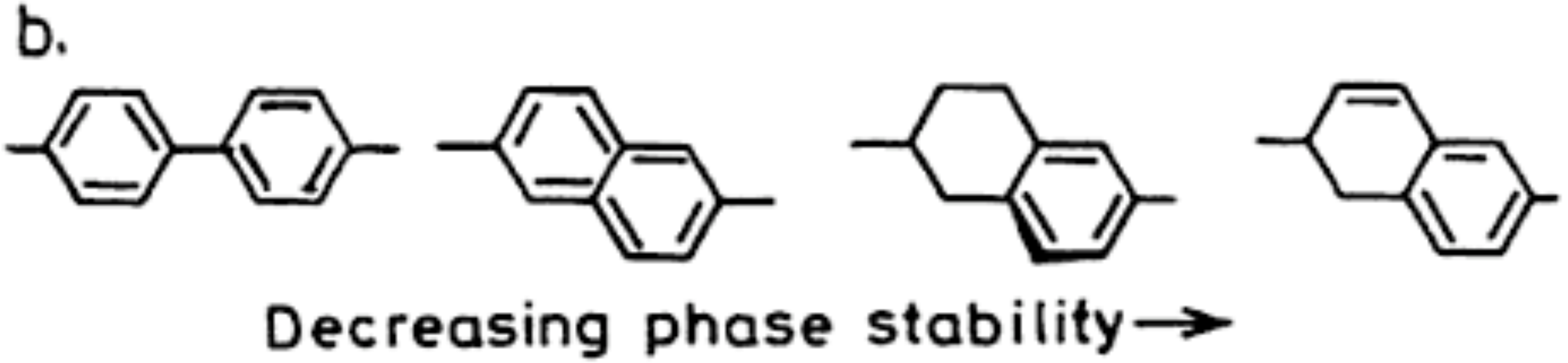
C 40.0 S_B 110.4 I



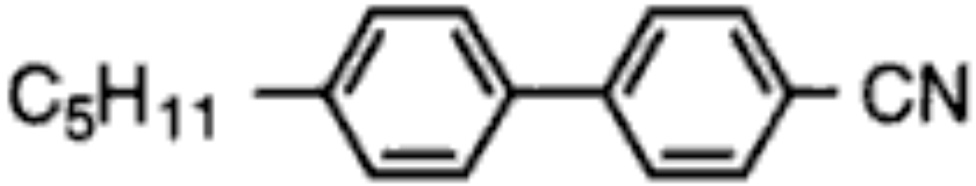
34

C -0.8 (S –8.0 N –5.0) I

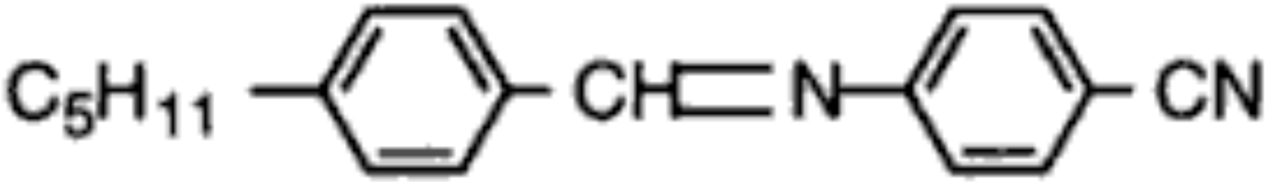
changes of the core results in dramatic changes for the LC
in compound 34: incompatibility of two distinct different core regions!



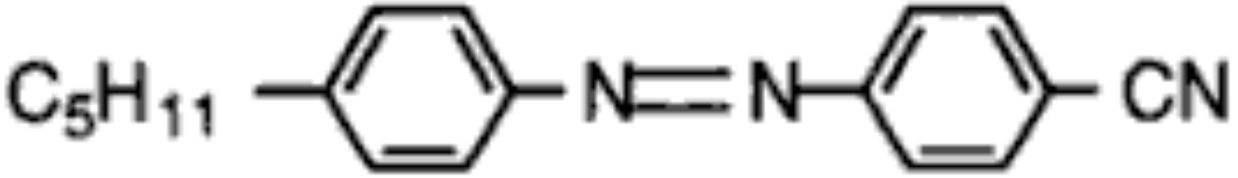
linker variations



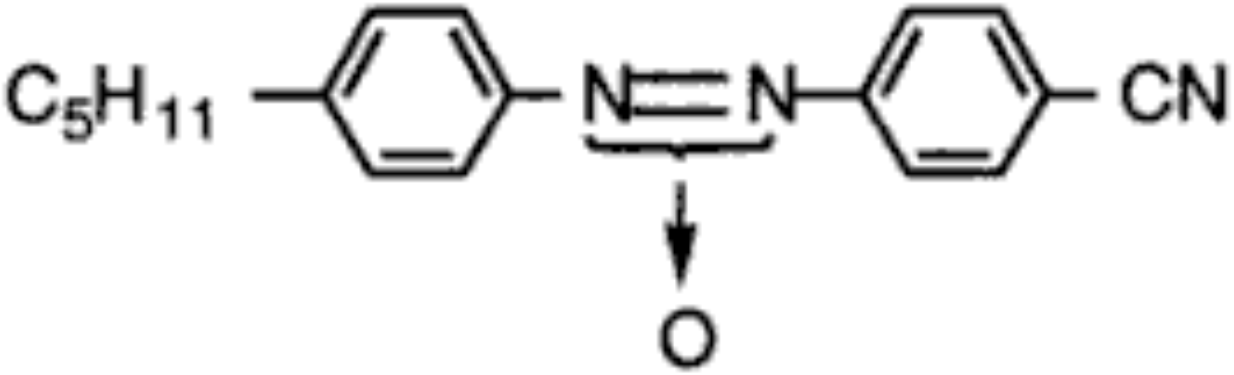
9e
C 24.0 N 35.0 I



57
C 46.4 N 75.0 I



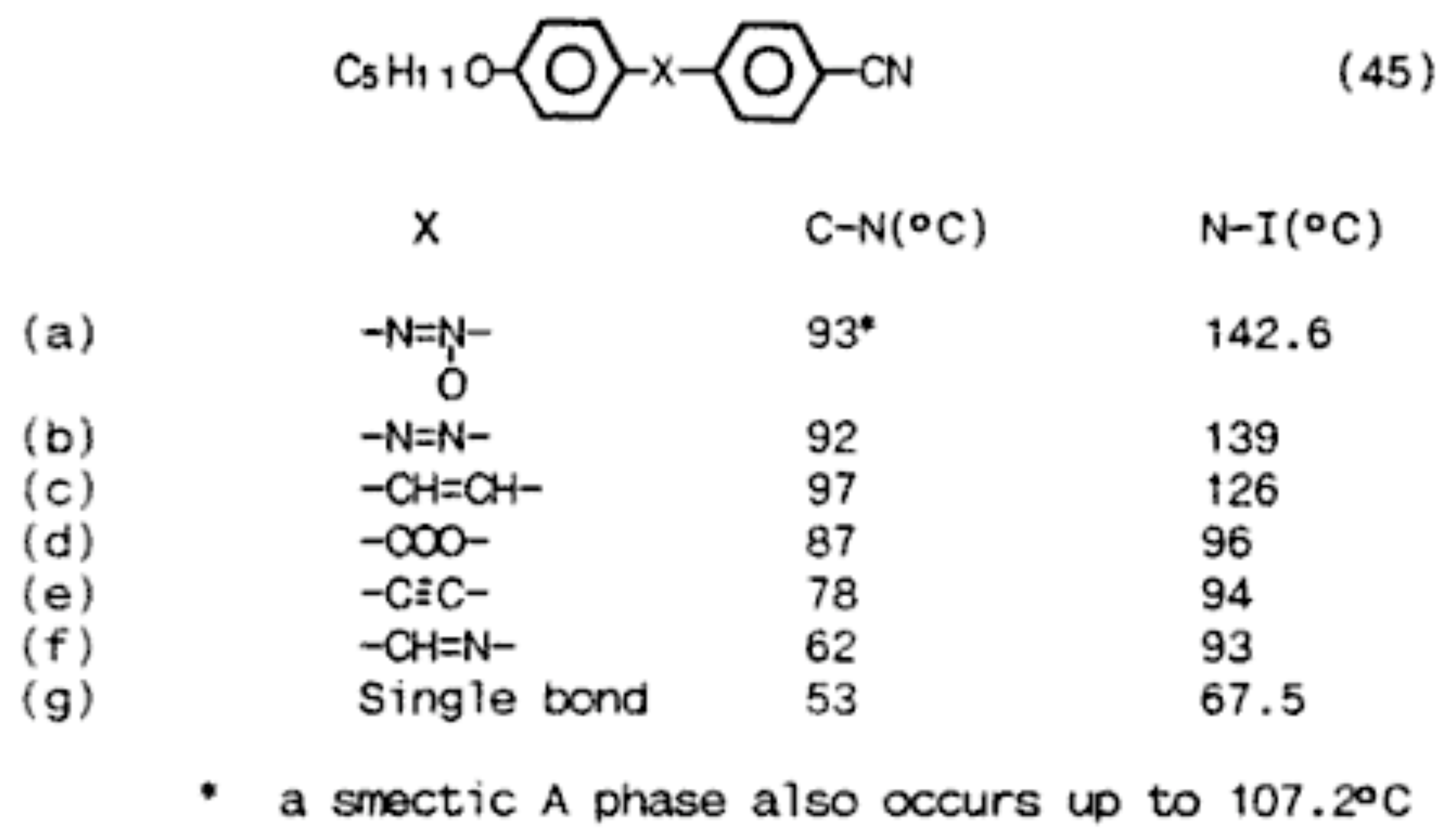
58
C 89.0 (N 86.5) I



59
C 91.0 N 126.0 I

- some linking groups are easily synthesized!
- much higher nematic phase stability
- but melting points are also higher

linker variations

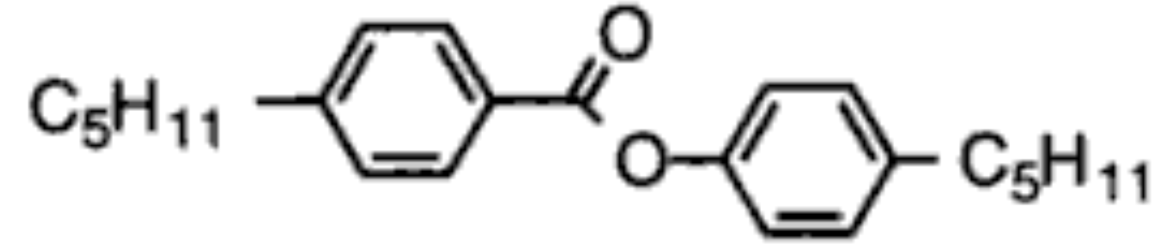

(45)

	X	C-N(°C)	N-I(°C)
(a)	$-N{=}\underset{O}{N}-$	93*	142.6
(b)	$-N{=}N-$	92	139
(c)	$-CH{=}CH-$	97	126
(d)	$-COO-$	87	96
(e)	$-C{\equiv}C-$	78	94
(f)	$-CH{=}N-$	62	93
(g)	Single bond	53	67.5

* a smectic A phase also occurs up to 107.2°C

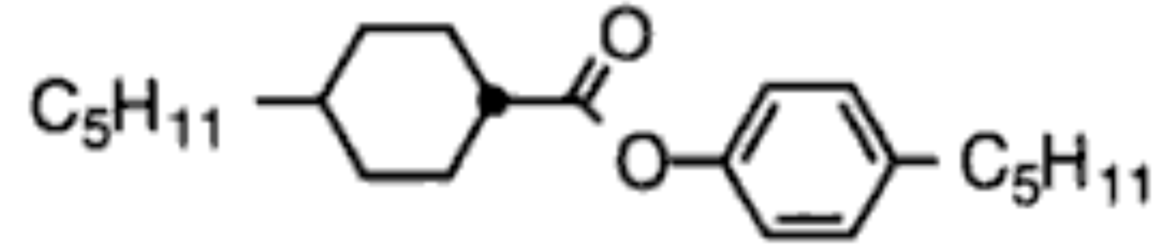
- some linking groups are easily synthesized!
- much higher nematic phase stability
- but melting points are also higher

finding the "right mix"



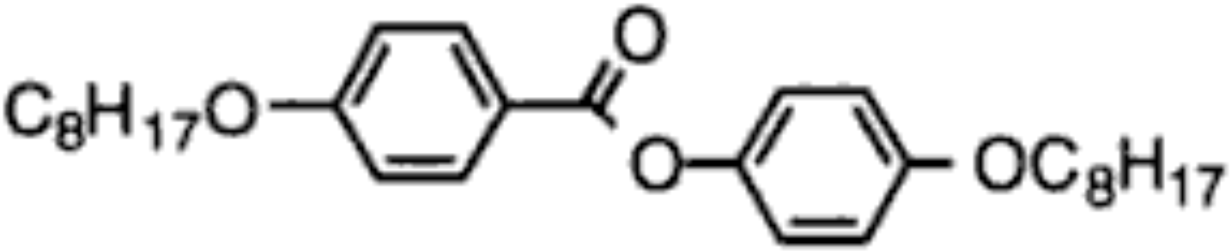
73

C 34.8 (N 26.0) I



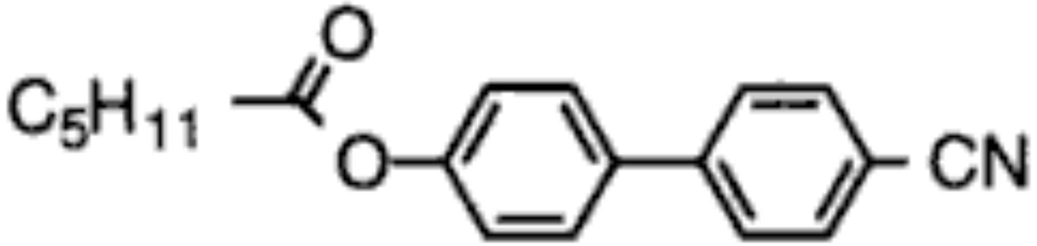
74

C 36.0 (S_A 29.0) N 48.0 I



75

C 63.0 S_C 74.0 N 91.0 I

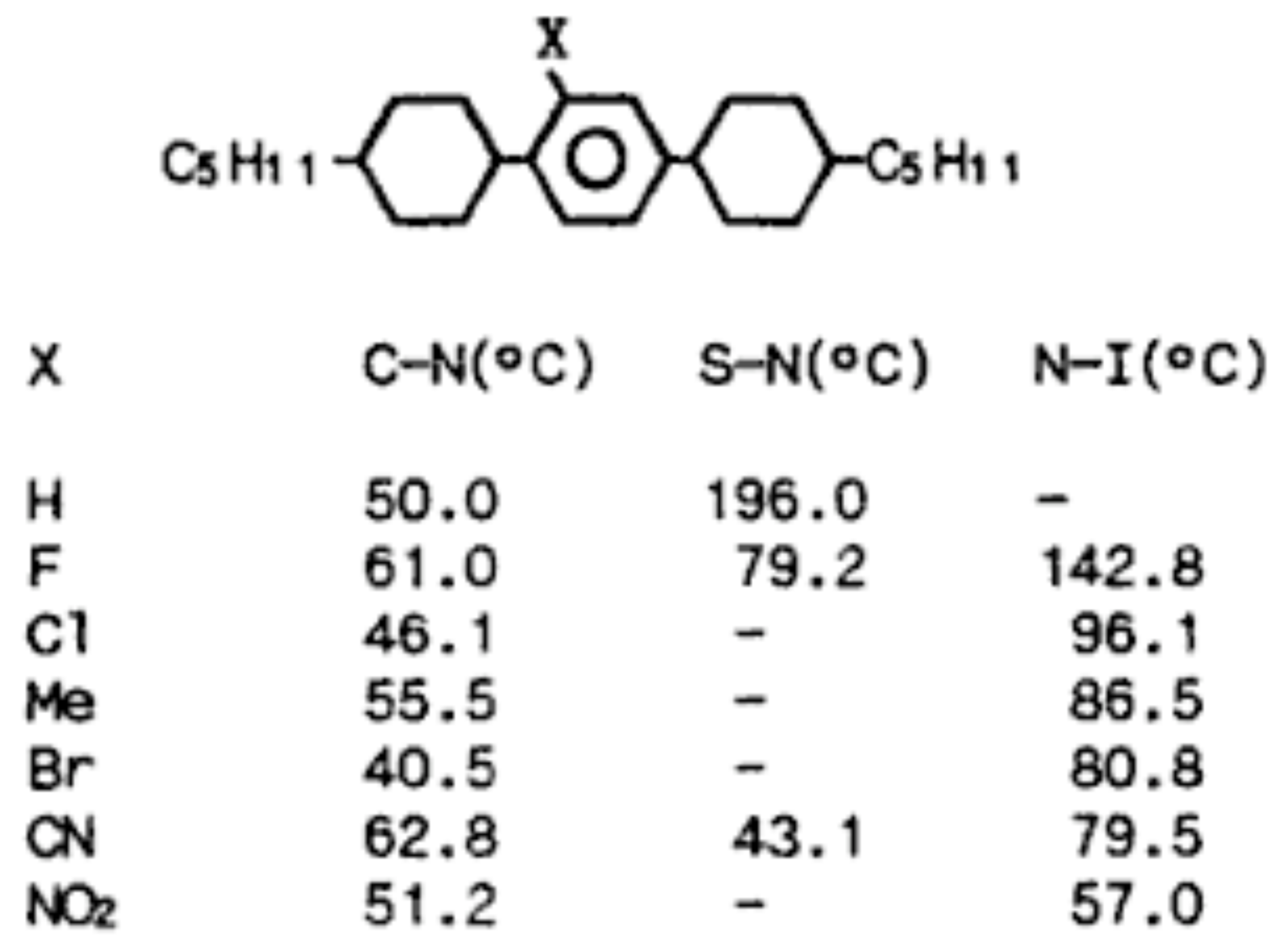


76

C 53.0 N 70.5 I

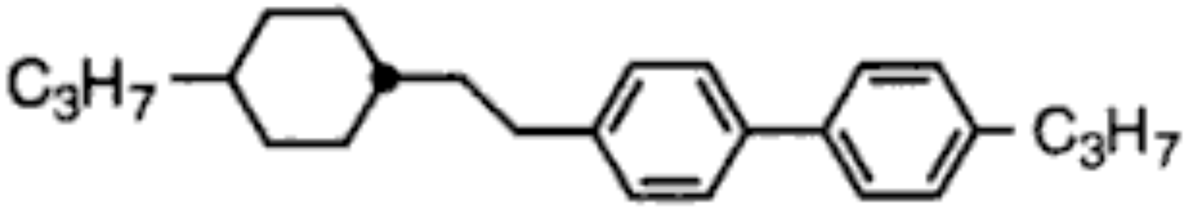
* longer terminal chains stabilize a lamellar arrangement
* resulting smectic phase is titled because of the arrangement of the lateral dipolar units

lateral substituents

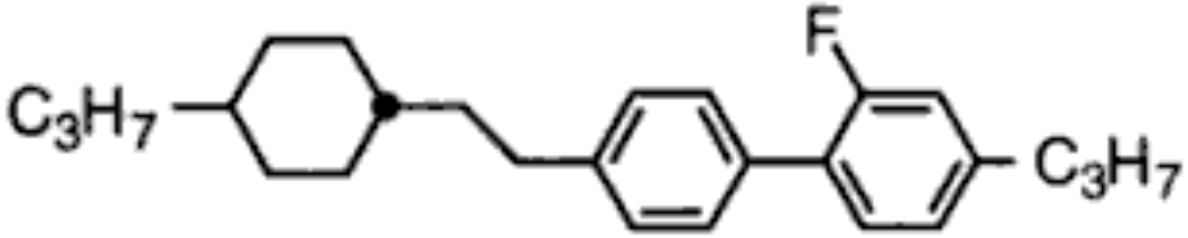


X	C–N(°C)	S–N(°C)	N–I(°C)
H	50.0	196.0	-
F	61.0	79.2	142.8
Cl	46.1	–	96.1
Me	55.5	–	86.5
Br	40.5	–	80.8
CN	62.8	43.1	79.5
NO_2	51.2	–	57.0

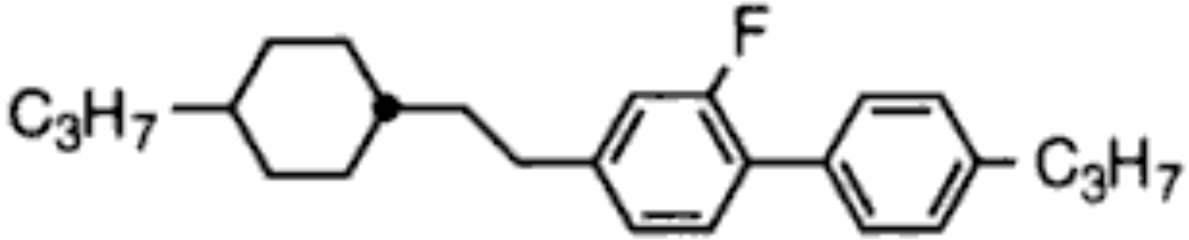
lateral substituents



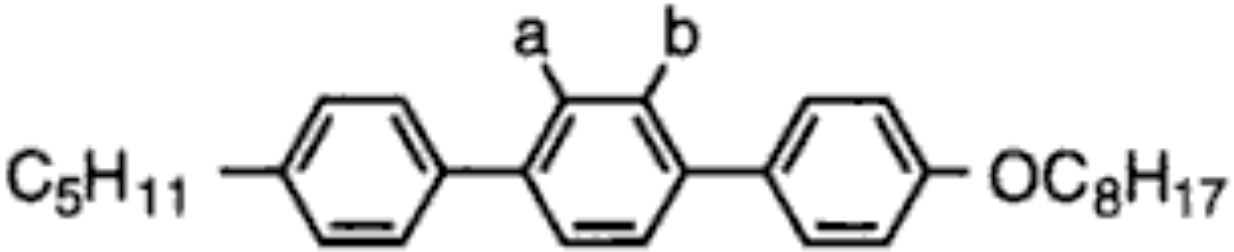
79
C 67.0 S_A 119.0 N 144.0 I



80
C 40.0 N 108.0 I



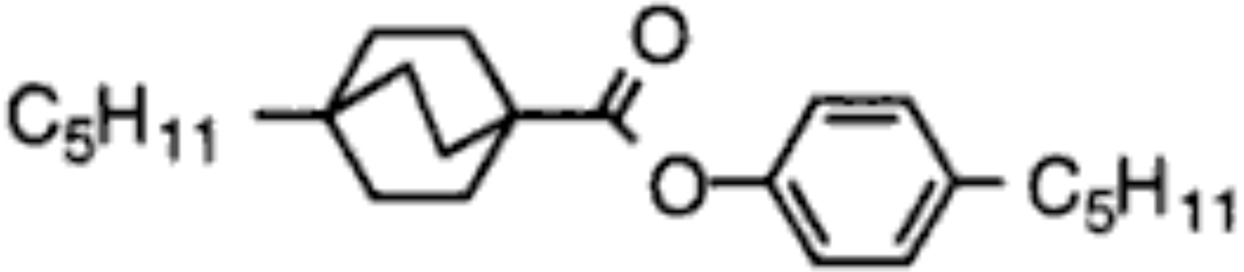
81
C 59.0 (S_A 34.0) N 108.0 I



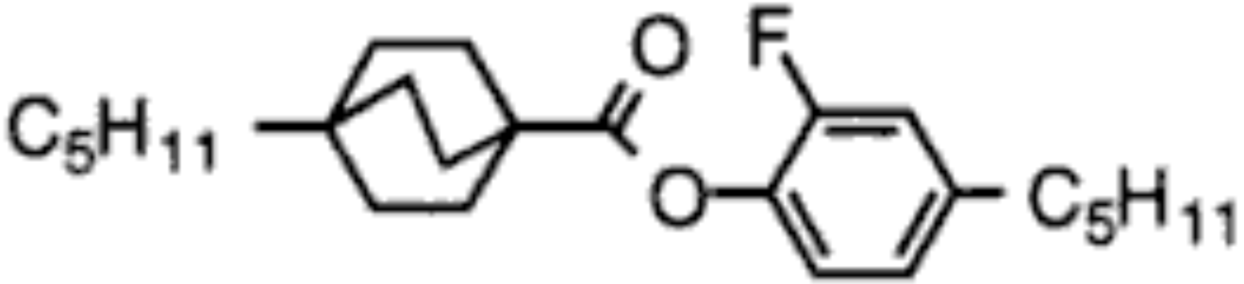
88, a = H, b = H; C 194.5 S_B 211.0 S_A 221.5 I
89, a = F, b = H; C 69.0 G 83.0 B 100.5 S_C 124.0 S_A 158.0 N 161.0 I
90, a = H, b = F; C 47.0 (J 40.0) S_I 53.5 S_C 116.5 S_A 130.0 N 155.0 I
91, a = F, b = F; C 48.5 S_C 95.0 N 141.5 I

lateral substituents

doesn’t work always:

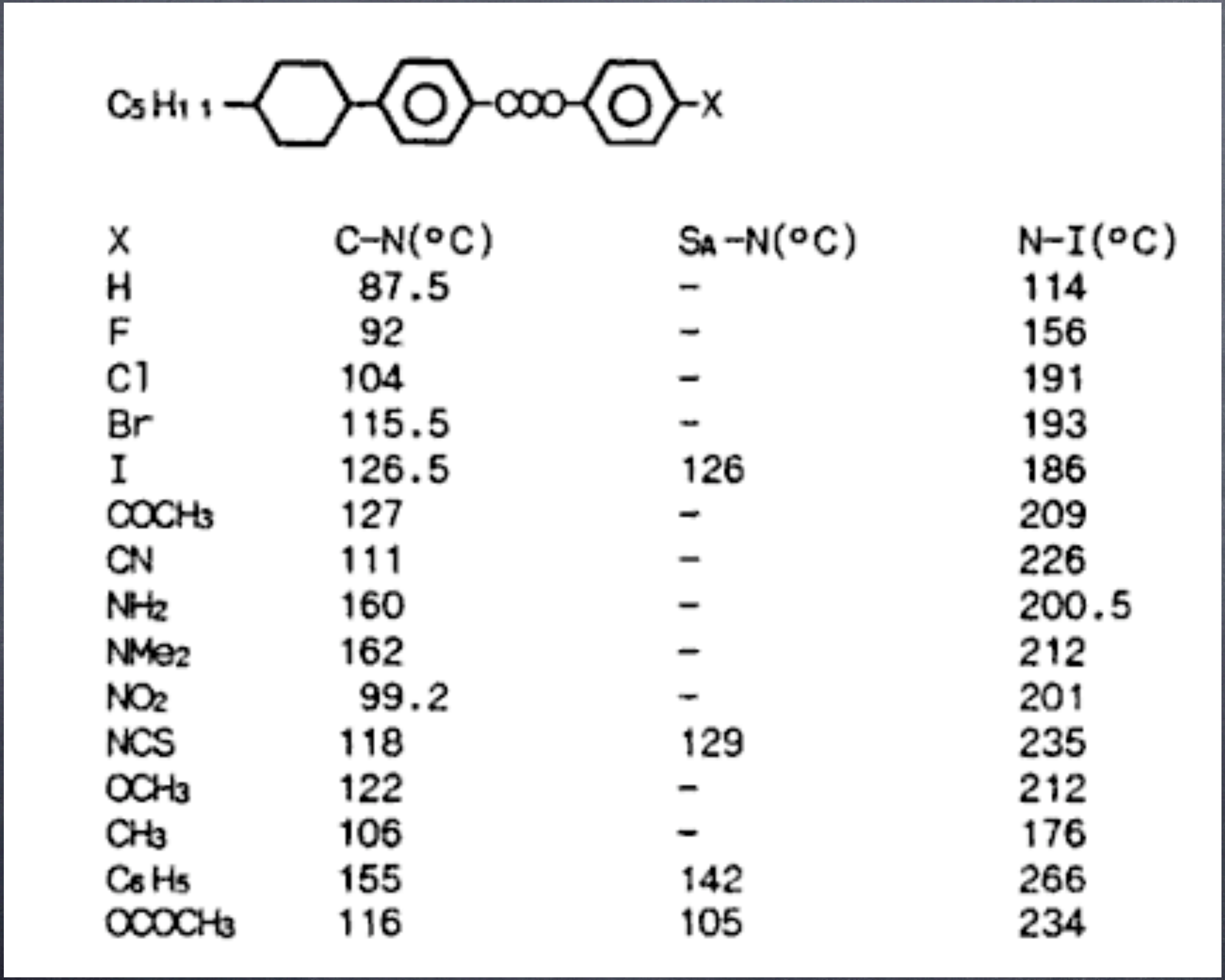


82
N 64.5 I



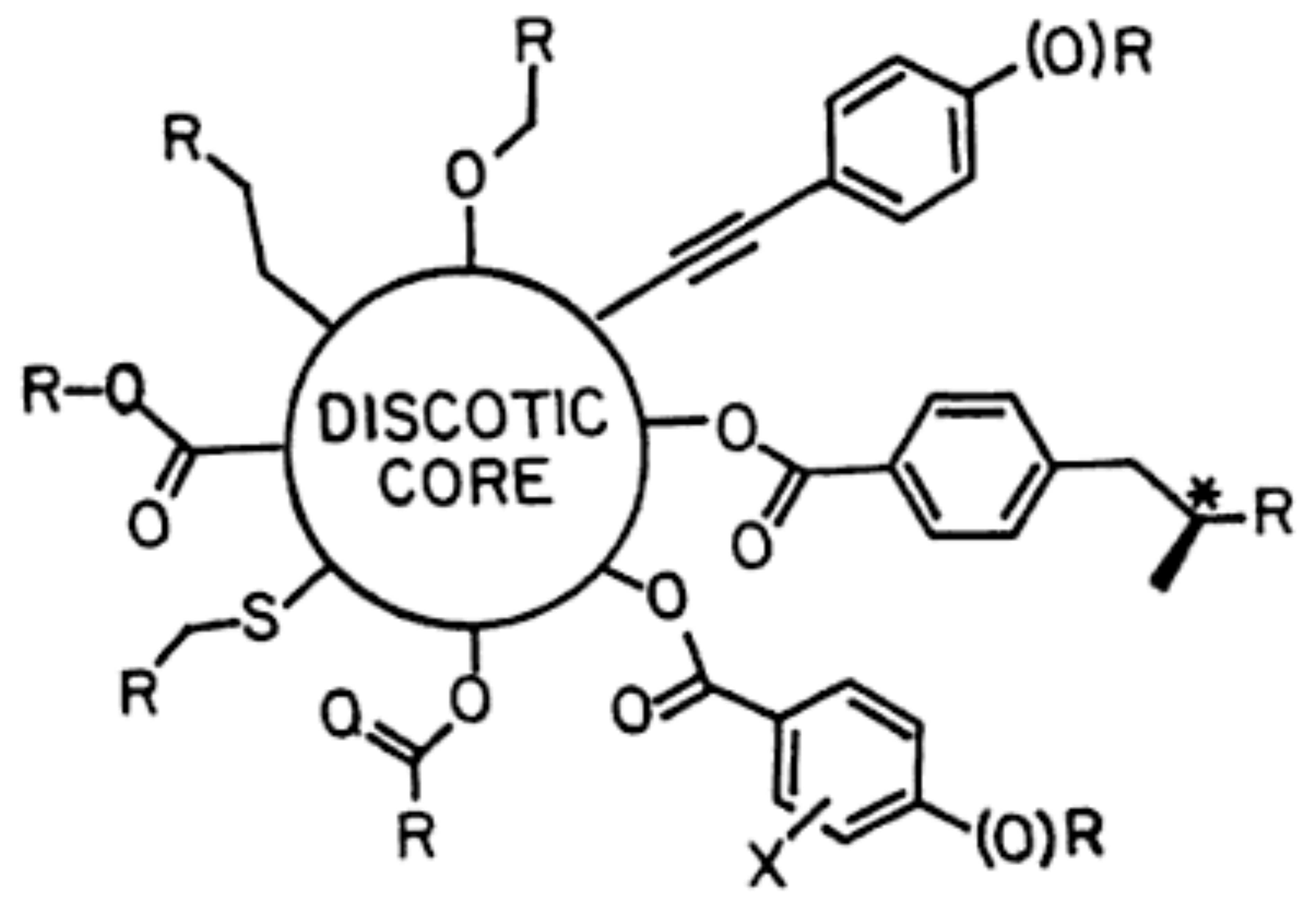
83
N 65.0 I

terminal groups



X	C-N(°C)	S_A-N(°C)	N-I(°C)
H	87.5	-	114
F	92	-	156
Cl	104	-	191
Br	115.5	-	193
I	126.5	126	186
$COCH_3$	127	-	209
CN	111	-	226
NH_2	160	-	200.5
NMe_2	162	-	212
NO_2	99.2	-	201
NCS	118	129	235
OCH_3	122	-	212
CH_3	106	-	176
C_6H_5	155	142	266
$OCOCH_3$	116	105	234

structural template for discotics



benzene based compounds

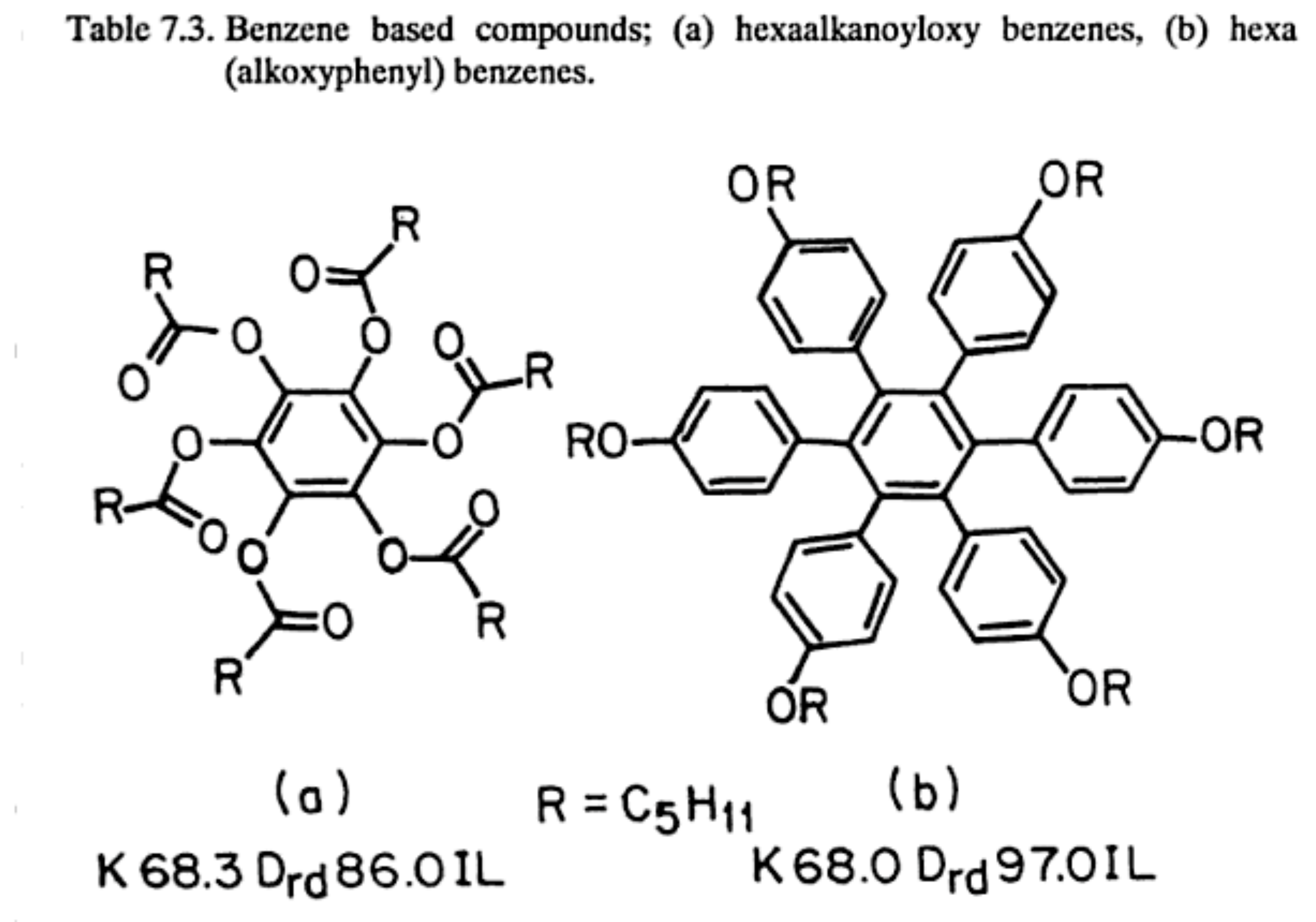


Table 7.3. Benzene based compounds; (a) hexaalkanoyloxy benzenes, (b) hexa (alkoxyphenyl) benzenes.

(a) $R = C_5H_{11}$ (b)

K 68.3 D_{rd} 86.0 IL

K 68.0 D_{rd} 97.0 IL