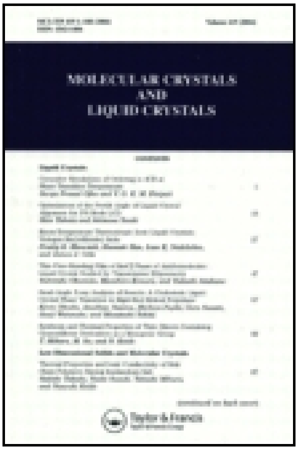

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Synthesis and Properties of Some Mesomorphic Vinyl Compounds and Their Saturated Analogs

Edward C. Hsu [a], Lee K. Lim [a], Rita B. Blumstein [a] & Alexandre Blumstein [a]

[a] Department of Chemistry, Polymer Program, University of Lowell, Lowell, Massachusetts, 01854, U.S.A.

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Synthesis and Properties of Some Mesomorphic Vinyl Compounds and Their Saturated Analogs

EDWARD C. HSU, LEE K. LIM, RITA B. BLUMSTEIN
and ALEXANDRE BLUMSTEIN

Department of Chemistry, Polymer Program, University of Lowell, Lowell, Massachusetts 01854, U.S.A.

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The synthesis of a number of mesomorphic vinyl compounds and of their saturated analogs is described. The unsaturated compounds are mostly Schiff bases with styryl, acrylic and methacrylic groups. The mesomorphic properties are studied by means of differential scanning calorimetry and polarizing microscropy. The presence of the double bond does not seem to influence the mesomorphic properties of the compounds in a consistent, predictable way. Literature data for mesomorphic compounds containing vinyl groups and their saturated analogs are also reviewed and discussed in terms of structure-property relationships.

INTRODUCTION

The influence of the nature of various terminal groups on the mesomorphic behavior and phase transition temperatures of smectogenic and nematogenic molecules has been abundantly investigated and reviewed (Refs. 1, 2 and others). Substitution of a terminal double bond, however, does not appear to have been systematically considered, although synthesis of a number of monofunctional and difunctional mesomorphic vinyl monomers has been reported recently[3–13]. Polymerization of such monomers has led to the formation of solid polymeric mesophases,[9–13] a new class of materials whose properties and supermolecular organization open a potentially fruitful new field of investigation. Monomeric liquid crystalline matrices have also been used to investigate the possibility of topochemical control of polymerization within mesophases[14–18] (influence of the mesophase on the polymerization kinetics and/or structure of the resulting polymers).

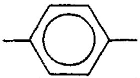
As interest in the polymerization of mesomorphic and potentially mesomorphic monomers develops, there appears a need for a comparative investigation of the mesomorphic behavior of monomers and of their more readily accessible saturated analogs. For this purpose we have synthesized a number of mesomorphic vinyl Schiff bases and of their saturated analogs.

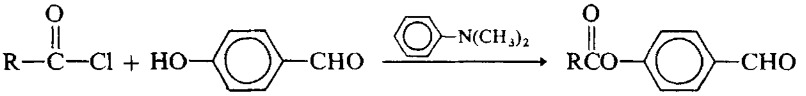
EXPERIMENTAL

1 Preparation of *p*-aminostyrene

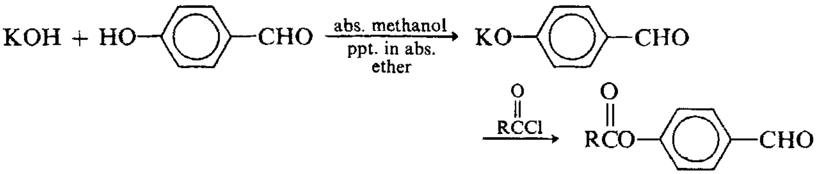
p-Aminostyrene was prepared by the modification of the method described by Sinyavskii *et al.*[29] A mixture of 200 g. *p*-aminophenethyl alcohol and 100 g. powdered potassium hydroxide was heated and distilled in 12–14 mm nitrogen atmosphere. The pressure should be maintained within the allowable range (12–14 mm). If the pressure is too high, decomposition will occur. If the pressure is too low, sublimation and clogging will result. The distillation range of *p*-aminostyrene is 85–150°C. The crude product was extracted with absolute ether and the combined extracts were dried over $MgSO_4$, filtered and concentrated at reduced pressure to give a light brown liquid. This material was redistilled under vacuum to give a colorless product (distillation range: 63–68°C/2 mm). Elemental analysis yielded the following results: Calcd. for C_8H_9N: C, 80.67%; H, 7.56%; N, 11.77%. Found: C, 80.56%; H, 7.58%; N, 11.69%.

2 Preparation of aldehyde intermediates

p-Hydroxybenzaldehyde was recrystallized three times from distilled water. Acryloyl chloride and methacryloyl chloride were distilled at reduced pressure. The products RCO_2CHO were prepared by condensation of the appropriate acid chloride with *p*-hydroxybenzaldehyde in the presence of N,N-dimethylaniline[9] or by reaction of the acid chloride with the potassium salt of *p*-hydroxybenzaldehyde,[30,31] as shown in the following general formulas:



(1)



(2)

The latter method was far superior in both yield and product quality.

The crude products of RCO_2CHO were used without further purification for the preparation of the Schiff bases.

3 Preparation of Schiff bases

(1) *Saturated derivatives* The following general procedure was used to prepare all of the saturated derivatives of Schiff's bases: Equimolar amounts of the appropriate *p*-substituted benzaldehyde and *p*-substituted amine were mixed and refluxed in a suitable medium (see Table I) for 2–4 hours (except for the use of two moles of aldehyde for diamine derivatives or two moles of monoamine for dialdehyde derivatives). All products were recrystallized from suitable solvents several times to constant melting temperatures. The expected structures of compounds were verified by elemental analysis (see Table I).

(2) *Styrene derivatives* The appropriate amounts of *p*-aminostyrene and aldehyde in absolute ethanol were reacted under nitrogen atmosphere and at room temperature (3). Because the solution is very unstable in the presence of trace oxygen, recrystallization of the products should be carried out in an inert atmosphere.

(3) *Acryloyl and methacryloyl derivatives* A mixture of the appropriate amounts of aldehyde and amine were reacted in a suitable medium for 2-4 hours at room temperature. The resulting products were recrystallized from suitable solvents several times.

(4) *Transition temperatures and phase identification* Phase transition temperatures and heats of transition were measured by means of differential scanning calorimetry with a Perkin–Elmer DSC-1B instrument. The mesophases were identified and the transition temperatures were measured by standard techniques (1) using a Leitz Ortholux POL polarizing microscope equipped with a Mettler hot stage.

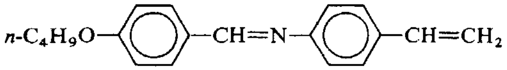
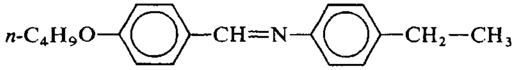
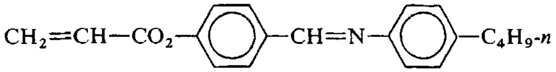
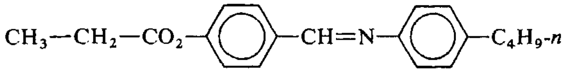
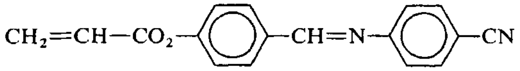
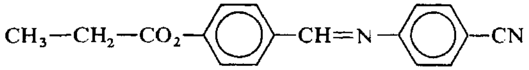
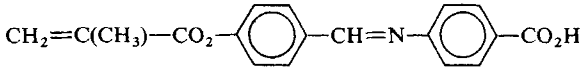
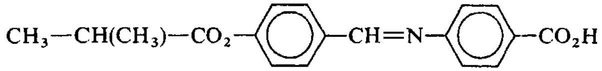
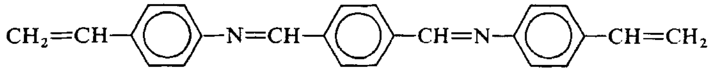
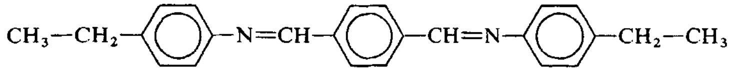
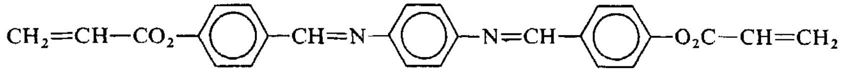
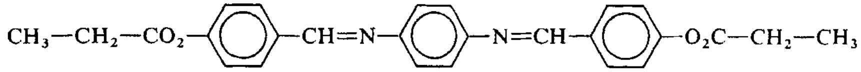
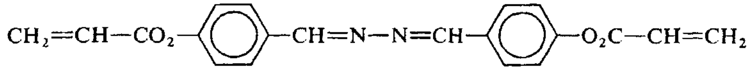
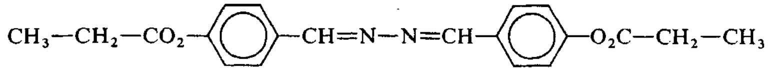
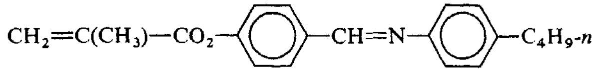
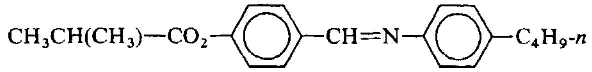
RESULTS AND DISCUSSION

A summary of the conditions of preparation of the vinyl monomers and their saturated analogs synthesized in our laboratory appears in Table I, together with the results of elemental analysis.

In Table II are listed phase transition temperatures and heats of transition for these 16 compounds, together with literature data for a few other vinyl

TABLE I

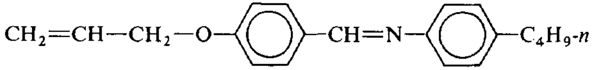
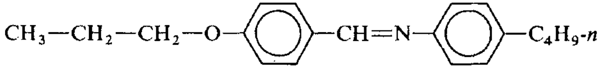
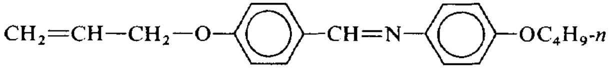
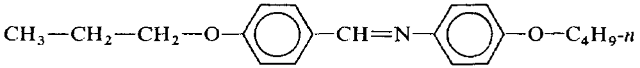
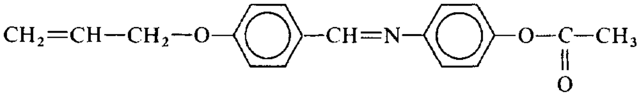
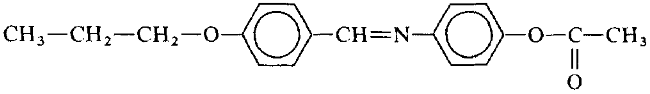
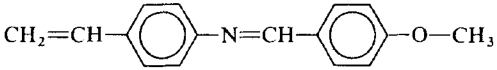
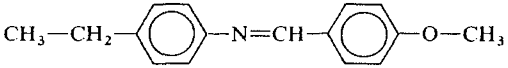
Experimental data: Synthesis of some mesomorphic monomers and saturated analogs

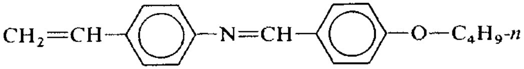
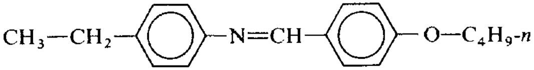
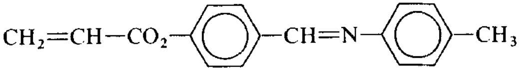
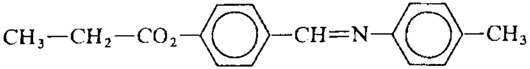
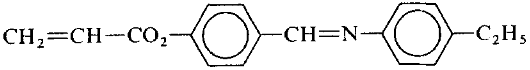
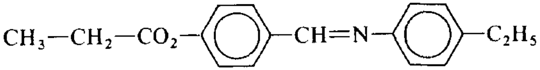
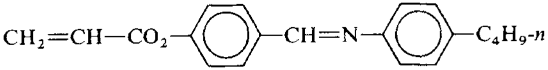
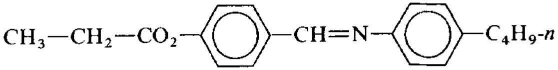
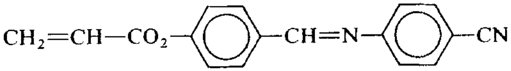
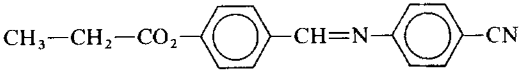
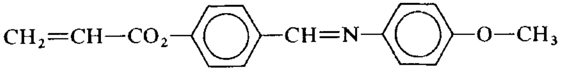
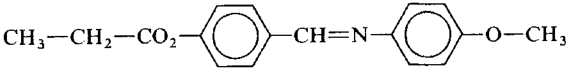
	Compound
1.	
2.	
3.	
4.	
5.	
6.	
7.	
8.	
9.	
10.	
11.	
12.	
13.	
14.	
15.	
16.	

Reaction Medium	Recrystallization Solvent	Elemental analysis: %					
		Calculated			Found		
		C	H	N	C	H	N
ethanol	acetone	81.04	7.80	5.20	80.80	7.75	5.20
ethanol	hexane/methanol	80.44	8.49	5.17	80.38	8.46	5.19
methanol	methanol/acetone	78.18	6.84	4.56	78.26	6.94	4.44
methanol	methanol/acetone	77.67	7.04	4.53	77.78	7.08	4.51
ethanol	ethanol	72.93	4.51	10.53	73.14	4.52	10.42
ethanol	ethanol	72.39	5.22	10.45	72.44	5.26	10.56
acetic acid	acetic acid/methanol	69.90	4.85	4.53	69.97	4.91	4.31
acetic acid	acetic acid/methanol	69.45	5.46	4.50	69.60	5.48	4.42
ethanol	methanol	85.71	5.95	8.33	85.85	6.06	8.34
ethanol	methanol	84.71	7.06	8.23	84.52	7.08	8.22
benzene	benzene/chlorobenzene	73.58	4.71	6.60	73.42	4.79	6.69
benzene	methanol	72.90	5.61	6.54	72.75	5.61	6.34
benzene/water	methanol	68.97	4.60	8.05	68.76	4.50	7.98
benzene/water	methanol	68.18	5.68	7.95	68.38	5.66	7.89
methanol	methanol	78.47	7.21	4.36	78.64	7.21	4.31
methanol	hexane	77.98	7.79	4.33	78.12	7.78	4.19

TABLE II

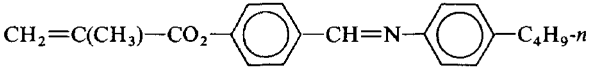
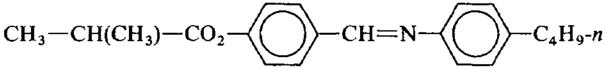
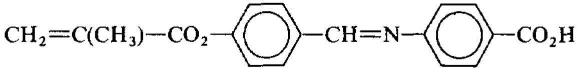
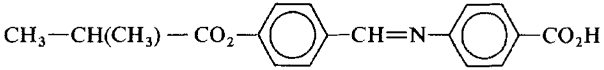
Thermodynamic data of some monomers and of their saturated analogs

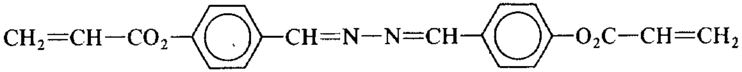
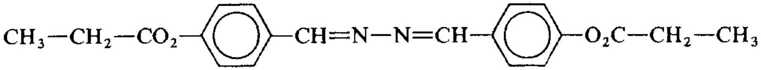
System	Structure of compound	Transition temperature (°C) and transition heats (Kcal/mole)	Ref.
1		K 49.7 N 68.5 I†	19
1′		K 41 N 58.9 I	19
2		K 114 N 119.6 I	19
2′		K 120 I (114.5 N)	20
3		K 84.5 S 110.8 N 111.4 I	19
3′		K 95 N 106 I	21
4		K 97.3 N 110.6 I	3
4′		K 56 I (32 N)	22

5	 $CH_2{=}CH{-}C_6H_4{-}N{=}CH{-}C_6H_4{-}O{-}C_4H_9\text{-}n$	$\mathrm{K}\ \frac{88.3}{1.82}\ \mathrm{N}\ \frac{120.6}{0.174}\ \mathrm{I}$‡	3
5′	 $CH_3{-}CH_2{-}C_6H_4{-}N{=}CH{-}C_6H_4{-}O{-}C_4H_9\text{-}n$	$\mathrm{K}\ \frac{39}{0.68}\ \mathrm{S}\ \frac{48}{1.97}\ \mathrm{N}\ \frac{62.5}{0.152}\ \mathrm{I}$	22
6	 $CH_2{=}CH{-}CO_2{-}C_6H_4{-}CH{=}N{-}C_6H_4{-}CH_3$	K 114 I	12
6′	 $CH_3{-}CH_2{-}CO_2{-}C_6H_4{-}CH{=}N{-}C_6H_4{-}CH_3$	K 102 I (66 N)	23
7	 $CH_2{=}CH{-}CO_2{-}C_6H_4{-}CH{=}N{-}C_6H_4{-}C_2H_5$	K 96 I	12
7′	 $CH_3{-}CH_2{-}CO_2{-}C_6H_4{-}CH{=}N{-}C_6H_4{-}C_2H_5$	K 80 I (28 N)	24
8	 $CH_2{=}CH{-}CO_2{-}C_6H_4{-}CH{=}N{-}C_6H_4{-}C_4H_9\text{-}n$	$\mathrm{K}\ \frac{48.5}{6.69}\ \mathrm{N}\ \frac{56.5}{0.069}\ \mathrm{I}$	12
8′	 $CH_3{-}CH_2{-}CO_2{-}C_6H_4{-}CH{=}N{-}C_6H_4{-}C_4H_9\text{-}n$	$\mathrm{K}\ \frac{65}{3.99}\ \mathrm{N}\ \frac{71.2}{0.176}\ \mathrm{I}$	19
9	 $CH_2{=}CH{-}CO_2{-}C_6H_4{-}CH{=}N{-}C_6H_4{-}CN$	$\mathrm{K}\ \frac{136}{5.11}\ \mathrm{N}\ \frac{164.5}{(?)}\ \mathrm{I}$	9
9′	 $CH_3{-}CH_2{-}CO_2{-}C_6H_4{-}CH{=}N{-}C_6H_4{-}CN$	$\mathrm{K}\ \frac{109.5}{5.90}\ \mathrm{N}\ \frac{124}{0.162}\ \mathrm{I}$	
10	 $CH_2{=}CH{-}CO_2{-}C_6H_4{-}CH{=}N{-}C_6H_4{-}O{-}CH_3$	K 97 N 117 I	12
10′	 $CH_3{-}CH_2{-}CO_2{-}C_6H_4{-}CH{=}N{-}C_6H_4{-}O{-}CH_3$	K 85 N 119.5 I	25

(*continued*)

TABLE II—(*continued*)

System	Structure of compound	Transition temperature (°C) and transition heats (Kcal/mole)	Ref.
11		$K \xrightarrow[4.98]{58} I$	12
11′		$K \xrightarrow[5.42]{59} I$	
12		$K_1 \xrightarrow[1.83]{182} K_2 \xrightarrow[2.14]{201} S(?) \xrightarrow[(?)]{206} N(?)$ → Polymerization	
12′		$K_1 \xrightarrow[1.36]{182} K_2 \xrightarrow[4.68]{244} S(?) \xrightarrow[(?)]{251} N(?)$ → Decomposition	
13		$K \xrightarrow[?]{\text{ca. } 180} N$ → polymerization	
13′		$K \xrightarrow[4.07]{126} S \xrightarrow[2.61]{148} N \xrightarrow[0.085]{251} I$	

14		$\mathrm{K}\xrightarrow[8.95]{180}\mathrm{S}$ → polymerization	9
14′		$\mathrm{K}\xrightarrow[3.66]{181}\mathrm{S}\xrightarrow[3.78]{187}\mathrm{N}\xrightarrow[(?)]{>315}\mathrm{I}$	26
15		$\mathrm{K}\xrightarrow[4.43]{138}\mathrm{N}$ → polymerization	11
15′		$\mathrm{K}\xrightarrow[6.76]{166}\mathrm{N}\xrightarrow[0.215]{196}\mathrm{I}$	
16	$CH_2{=}CH{-}CO_2{-}C_{27}H_{45}$	K 118 C 126 I	7
16′	$CH_3{-}CH_2{-}CO_2{-}C_{27}H_{45}$	K 102 C 116 I	27
17	$CH_2{=}C(CH_3){-}CO_2{-}C_{27}H_{45}$	K 108 C 112 I	8
17′	$CH_3{-}CH(CH_3){-}CO_2{-}C_{27}H_{45}$	K 128 I	28

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† Linear notation of Verbit.[32]

‡ $\mathrm{K}\xrightarrow[\text{transition heat}]{\text{transition temperature}}\mathrm{N}\xrightarrow[\text{transition heat}]{\text{transition temperature}}\mathrm{I}$

monomers and three *p*-allyloxybenzylidene derivatives (compounds 1, 2 and 3).

The presence of an unsaturated linkage along the major molecular axis increases the anisotropy of polarizability and should lead to higher phase transition temperatures and increased mesophase stability. Thus the thermal stability of the smectic and/or nematic mesophase in trans-*p*-*n*-alkoxycinnamic acids is considerably higher than in *p*-*n*-alkoxybenzoic acids of the same molecular length (1). Similarly, replacement of a terminal alkyl group by an alkoxy group of the same length enhances the thermal stability of the mesophase, as the non-bonded electrons of the oxygen are easily coupled to the Π-electrons of the benzene ring (2). One would then "a priori" expect that the monomers listed in Table II would exhibit higher melting points and higher mesophase clearing temperatures than would be exhibited by their saturated analogs and that this effect would be strongly enhanced in styrene derivatives in which the vinyl bond is conjugated with the aromatic moiety. Table II shows that this expectation is qualitatively fulfilled by the pairs of compounds 1–5. The influence of unsaturation in the allylic derivatives (compounds 1–3) is moderate, but replacement of an ethyl by a vinyl group increases the transition temperatures by some 50°C (compounds 4 and 5).

In the monofunctional monomers containing the acryloyloxy group (compounds 6–10 and 16) the phase transition temperatures are increased by 10-15°C, with the exception of compound 8, but the presence of unsaturation appears to suppress mesomorphism in the case of compounds 6 and 7. Introduction of a methacryloyloxy group appears to depress the phase transition temperatures (compounds 11, 12 and 17). Complete characterization of the bifunctional monomers (compounds 12–15) is difficult, as these compounds polymerize rapidly upon phase transition but it is apparent from Table II that the presence of two additional double bonds does not necessarily enhance mesophase stability.

The results of Table II show that the mesomorphic behavior of monomers cannot be reliably predicted from the mesomorphic properties of the saturated analog. Stabilization of the mesophase by the Π electrons of the monomeric double bonds may be jeopardized by unfavorable steric considerations.

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