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Mesomorphic Substances Containing Some Group IV Elements†

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Abstract—A unique series of organometallic substances has been prepared from 4′-methoxy-4-aminobiphenyl and *para*-substituted benzaldehydes. Among the substituents investigated are trimethylsilyl, trimethylgermyl, trimethyltin, trimethylsiloxy, and pentamethyldisiloxanyl. The compounds were examined for mesomorphic behavior, and the heats and entropies of the mesophase transitions were determined by differential scanning calorimetry. A majority of these compounds exhibit either a smectic or a nematic mesophase, although analogous organometallic anils derived from *p*-aminophenyl acetate or *p*-aminophenyl benzoate are non-mesomorphic. The results, taken together with data obtained from carbon-containing " isologs," indicate that the bulkiness associated with the organometallic substituent does not preclude liquid crystal formation in long molecules, especially when the electronic properties of the end groups, such as high polarizability and mesomeric interactions, are beneficial.

Introduction

Of the several thousand organic compounds which have been found to exhibit a mesomorphic phase, only a handful have contained metal atoms.⁽¹⁾ Vorlaender⁽²⁾ and Walter⁽³⁾ have demonstrated that sodium, potassium, rubidium, and thallium salts of aliphatic and aromatic carboxylic acids often display smectic phases. Urban⁽⁴⁾ and Vorlaender⁽⁵⁾ have prepared several aromatic mercurials which are nematic, and Eaborn and Hartshorne⁽⁶⁾ have reported an unclassified mesomorphic phase anomalously associated with diisobutylsilanediol.

The main purpose of this investigation was to perform a systematic study of the effect of organometallic substituents upon mesophase formation and classification. We also hoped to expand the number

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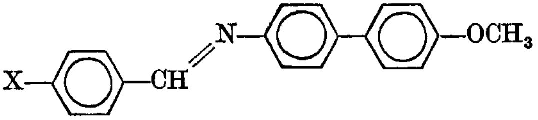
† Presented at the Third International Liquid Crystal Conference in Berlin, August 24–28, 1970.

of unique metals incorporated into mesomorphic substances and to obtain some nematic liquids with melting points near room temperature.

To this end, we synthesized a series of Schiff Bases of the following general structures,

1



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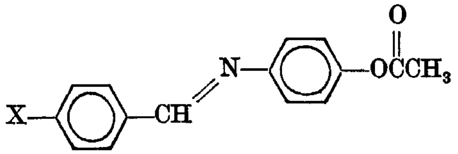

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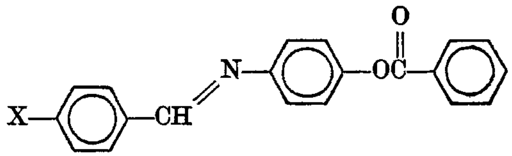


where *X* represents a substituent containing a Group IV element, i.e. silicon, germanium, tin, or lead. Two classes of substituents were proposed, one in which the metal is bonded directly to the aromatic ring [e.g., $X = (CH_3)_3Si$-, $(CH_3)_3Ge$-, $(CH_3)_3Sn$-, $(CH_3)_3Pb$-, and $(CH_3)_3Si$-O-$Si(CH_3)_2$-] and one in which some of these same groups are attached to the aromatic ring by an intermediate oxygen atom [e.g., $X = (CH_3)_3SiO$-, etc.]. For comparision, two carbon isologs were also prepared, that is $X = (CH_3)_3C$- and $(CH_3)_3CO$-. It was hoped that those materials containing the pentamethyldisiloxanyl substituent would have especially low melting points, in analogy with some siloxane-type silicone oils.

The systems *1*–*3* were chosen for several reasons. Schiff Bases are readily synthesized. Many nematic compounds of these systems ($X \neq$ organo-metallic substituent) have been reported in the literature(1,7,8) and afford a convenient basis for comparision of results. The aniline precursors of *2* and *3* were commercially available,(9) and the extremely high nematic clearing points associated with compounds of structure *1*(7) suggested some enhancement of mesophase formation in the event that the substituents were too bulky to allow the required molecular alignment in structures *2* and *3*.

Another purpose of this work was to extend the study of correlations between molecular structure, liquid crystalline properties, and the thermodynamic quantities characterizing the mesomorphic phase transitions. Transition temperatures were determined by observing the compounds under the polarizing microscope. Differential scanning calorimetry was used to measure the heats (and entropies) of transitions of all the compounds which exhibited mesophases.

Synthesis

In Fig. 1 we have shown the method of preparation of the Schiff Bases in which the silicon-containing wing groups are linked to the benzene ring through an oxygen atom. A chlorosilane is allowed to react with *p*-hydroxybenzaldehyde and the product is isolated by distillation. Initial attempts to prepare the Schiff Base by the usual methods failed, however, because the products were extremely sensitive to moisture and, in analogy with the results obtained by other synthetic chemists,(10) the products contained no silicon. This difficulty was overcome, however, by condensing the silicon-containing benzaldehyde with the appropriate aniline in dry, refluxing methylcyclohexane containing dried molecular sieves. The resulting compounds were purified and handled in an inert atmosphere to guard against hydrolysis.

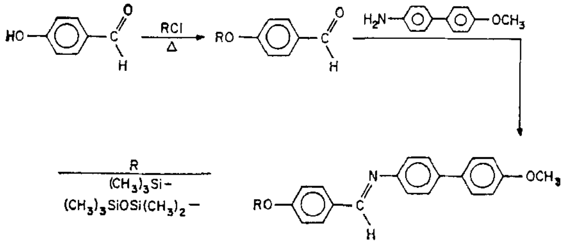


Figure 1. Synthetic route employed in the preparation of some siloxy-type anils.

Figure 2 depicts the synthesis of the derivatives in which the metal atom is bound directly to the benzene ring. The reaction of the Grignard reagent from *p*-dibromobenzene with ethyl orthoformate afforded the diethyl acetal of *p*-bromobenzaldehyde. This material gave a Grignard reagent which coupled with several of the trimethyl-metal halides to yield the organometallic acetal as shown. These compounds were directly condensed with the appropriate aniline to give the desired Schiff Base products.

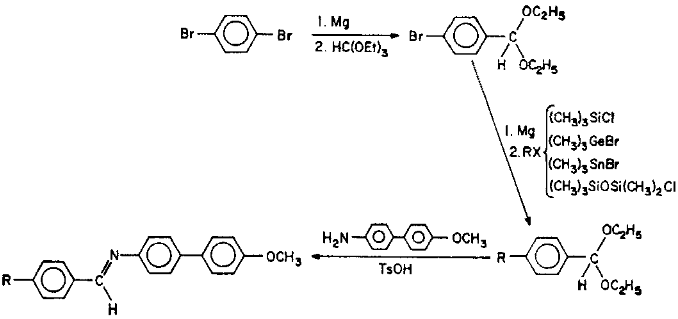


Figure 2. Reaction sequence used for the synthesis of some organometallic Schiff Bases.

Unfortunately, this last reaction was unsuccessful in the case of the organometallic acetal which contained a trimethyl-lead group in the *para*-position. Apparently, the *p*-toluenesulfonic acid, which was present in catalytic amount, was consumed by electrophilic reaction with the lead-carbon bond. Attempts are currently underway to synthesize the lead compound by an alternate route.

Figure 3 shows the synthesis of the carbon " isolog " Schiff Bases. The *t*-butoxyacetal was prepared by reaction of *t*-butyl perbenzoate with the Grignard reagent from *p*-bromobenzaldehyde diethyl acetal.(11) The *t*-butoxy compound was then condensed with an appropriate aniline in *t*-butyl alcohol to afford the desired products. The *t*-butyl derivative was prepared in the usual manner from the commercially obtained *p*-*t*-butylbenzaldehyde.

Organometallic Derivatives of *p*-Aminophenyl Acetate and Benzoate

The Schiff Base esters prepared for this investigation and their physical properties are recorded in Table 1. Also listed are some

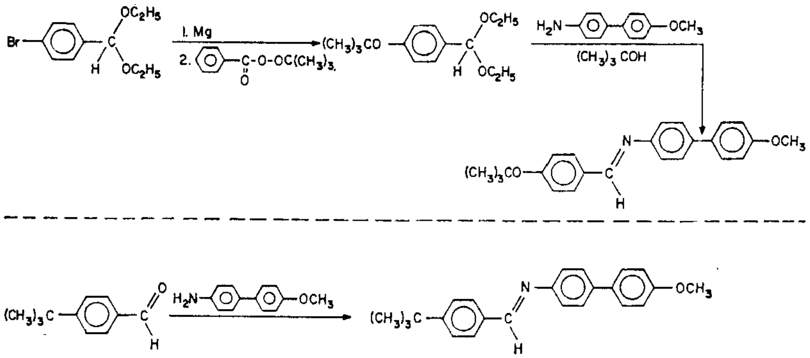
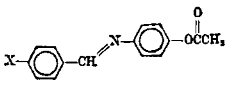
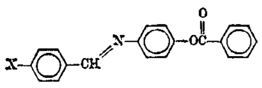


Figure 3. Synthetic route used to prepare two carbon " isolog " azomethines.

Table 1 Transition Temperatures of Some Schiff Base Acetates and Benzoates

						
X	No.	Transition	Temp.	No.	Transition	Temp.
$(CH_3)_3CO$-	*4a*	C→I	96	*4b*	C→I	121
$(CH_3)_3SiO$-	*5a*	C→I	63	*5b*	C→I	73
$(CH_3)_3Si\text{-}O\text{-}Si(CH_3)_2O$-	*6a*	C→I	37	*6b*	C→I	55
$(CH_3)_3Si$-	*7a*	C→I	80	*7b*	C→I	145
$(CH_3)_3Si\text{-}O\text{-}Si(CH_3)_2$-	*8a*	C→I	47	*8b*	C→I	64
CH_3O-	*9a*	C→N	82[a]	*9b*	C→N	119[a]
		N→I	108[a]		N→I	178[a]
C_2H_5O-		—		*10b*	C→N	144[b]
					N→I	188[b]
CH_3S-	*11a*	C→I	100[c]		—	
		N→I	82[c]			
CH_3-		—		*12b*	C→I	136[b]
					N→I	119[b]

a. From Ref. 12. b. From Ref. 13. c. From Ref. 8.

reference compounds which have been reported in the literature. As opposed to the biphenyl derivatives discussed below, neither the *t*-butoxy (*4a, 4b*) or the silicon-containing esters (*5a–8a, 5b–8b*) exhibit any mesomorphic phase. This is true despite the fact that the siloxane end-chains reduce the melting points of the Schiff Base acetates and benzoates substantially. This reduced nematic stability, in comparison with the reference compounds (*9–12*) is readily explained by considering the bulkiness of the *t*-butoxy and silicon-containing substituents. Molecular models and simple calculations based upon compilations and theories of Pauling(14) indicate that the following *para* substituents have increasing breadth:

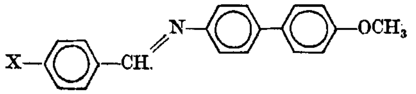
$$CH_3 < CH_3O < CH_3S < (CH_3)_3C < (CH_3)_3Si < (CH_3)_3CO < (CH_3)_3SiO.$$

It can thus be postulated that the bulkier substituents separate the neighboring molecules and hence preclude the formation of a mesophase. This might also help explain the significantly lower nematic clearing point for the thiomethyl acetate *11a* relative to the methoxy analog *9a*, despite the fact that the higher polarizability of the sulfur atom, relative to oxygen, would tend to stabilize a nematic phase.

Organometallic Derivatives of 4-Amino-4′-Methoxybiphenyl

To overcome the lack of mesomorphic properties associated with the organometallic acetate and benzoate Schiff Bases, it was necessary to prepare Schiff Bases derived from 4-amino-4′-methoxybiphenyl. The large length/breadth ratio of azomethines derived from this

TABLE 2 Mesomorphic Properties of Some Ethereal Schiff Bases.



No.	*X*	Transition	Temp[a]	ΔH[b]	ΔS[d]
13	$(CH_3)_3CO$-	C → N	143	4.83	11.62
		N → I	200	.138	.291
		S → N	130†	c	c
14	$(CH_3)_3SiO$-	C → N	140	2.65	6.42
		N → I	159	.074	.171

† Monotropic Transition.

a. In °C.

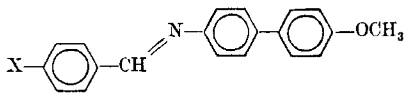
b. In Kcal/mole.

c. Crystallizes before heat of transition can be measured.

d. In cal/mole-deg.

amine leads to unusually large liquid crystalline ranges,⁽⁷⁾ or to the existence of mesophases in cases where the aldehyde component contributes little to the stabilization of the mesophase.⁽¹⁵⁾ The organometallic derivatives prepared are listed, along with their physical properties, in Tables 2–4. Clearly, the appearance of liquid crystalline phases indicates that the bulkiness associated with the organometallic moieties does not preclude mesomorphic alignment provided that the molecule is sufficiently long and has appropriately placed substituents.

TABLE 3 Mesomorphic Properties of Some Organometallic Schiff Bases.



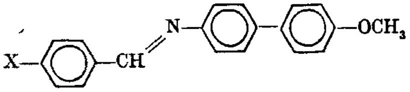
No.	*X*	Transition	Temp^a	ΔH^b	ΔS^c
15	$(CH_3)_3C$-	$C \rightarrow I$	190	—	—
16	$(CH_3)_3Si$-	$C \rightarrow S$	180	4.19	9.24
		$S \rightarrow I$	183	1.53	3.35
17	$(CH_3)_3Ge$-	$C \rightarrow I$	176	6.45	14.4
		$S_2 \rightarrow S_1$	169†	1.58	3.58
		$S_1 \rightarrow I$	175†	1.82	4.05
18	$(CH_3)_3Sn$-	$C \rightarrow S_2$	165	3.53	8.06
		$S_2 \rightarrow S_1$	171	3.60	8.08
		$S_1 \rightarrow I$	173		

† Monotropic Transition.
a. In °C.
b. In Kcal/mole.
c. In cal/mole-deg.

TRIMETHYLSILOXY AND *t*-BUTOXY WING GROUPS

Compounds *13* and *14* (Table 2) have stable nematic mesophases. It can be seen, however, that the silicon-containing substituent causes a significant decrease in both the thermal persistence (clearing point) and in the interaction energy (heat of transition) of the nematic phase. To rationalize the lower mesomorphic stability in the more highly polarizable compound, it is useful to compare these materials with some other alkoxy derivatives of the same substrate azomethine (Table 5). It is noted that as one proceeds from methoxy compound

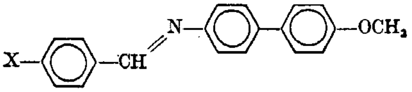
TABLE 4 Mesomorphic Properties of Some Silicon-Containing Schiff Bases



No.	X	Transition	Temp^a	ΔH^b	ΔS^c
16	$(CH_3)_3Si$-	C → S	180	4.19	9.24
		S → I	183	1.53	3.35
19	$(CH_3)_3Si\diagup^{O}\diagdown Si(CH_3)_2$-	C → S	134	3.67	9.02
		S → I	156	1.69	3.93
14	$(CH_3)_3SiO$-	C → N	140	2.65	6.42
		N → I	159	.074	.171
20	$(CH_3)_3Si\diagup^{O}\diagdown Si(CH_3)_2O$-	C → S_3	91	.89	2.45
		S_3 → S_2	124	.13	.32
		S_2 → S_1	128	1.55	3.87
		S_1 → I	133	1.44	3.54

a. In °C.
b. In Kcal/mole.
c. In cal/mole-deg.

TABLE 5 Mesomorphic Properties of Some Homologous Schiff Bases



No.	X	Transition	Temp^b
21	CH_3O	C → N	211^a
		N → I	318^a
22	C_2H_5O	C → N	190
		N → I	304
23	*i*-C_3H_7O	C → N	164^a
		N → I	256^a
13	*t*-C_4H_9O	C → N	143
		N → I	200
		S → N	130†

† Monotropic Transition.
a. From Ref. 7.
b. In °C.

21 through *t*-butoxy compound *13* by means of stepwise replacement of the hydrogens by methyl groups, the nematic clearing point drops. This lowering is most severe in the cases of the isopropoxy and *t*-butoxy derivatives *23* and *13*, and can most easily be ascribed to geometric differences (*i.e.*, increased bulkiness of the substituents).

As stated above, the trimethylsiloxy group in Schiff Base *14* is more bulky than the *t*-butoxy. Based on the reasoning of the preceding paragraph, it would be reasonable to expect that the nematic-isotropic temperature for this silicon compound would be lower than the 200° transition temperature observed for the carbon " isolog " *13*. This was observed. *A priori*, it could have been postulated that compound *14* might have a higher clearing temperature than carbon isolog *13* because of the higher polarizability of *14*, silicon being more polarizable than carbon and compound *14* having a more extensive conjugated system which includes the silicon atom. However, as is generally noted,(7) the electronic factor (*i.e.*, polarizability) plays a subordinate role to the steric factor.

AXIALLY SYMMETRIC WING GROUPS

The organometallic analogues of *p*-*t*-butylbenzylidene-4-amino-4′-methoxybiphenyl (Compounds *16–18*, Table 3) all have one or more smectic phases, even though the *t*-butyl compound itself is non-mesomorphic. This behavior differs from that of the oxygen-linked axially unsymmetric compounds discussed in the preceding section which were primarily nematic substances.

This observation extends to trimethylsilyl (as well as *t*-butyl) substituents, the often observed phenomenon that alkoxy groups effectively stabilize nematic mesophases, whereas the corresponding alkyl groups promote the stability of the smectic phase. Examples of this rule are numerous. Figure 4 illustrates this effect of methyl and methoxy groups on nematic and smectic phases of Schiff Bases derived from aminobiphenyl.(7) Table 6 demonstrates the same effect in *p*-methyl- and *p*-methoxybenzylidene-amino-cinnamic acid esters.(16,17)

We can also speculate that bulky groups, in contrast to their previously cited effect on nematic clearing points, do not similarly lower the smectic clearing points in long molecules such as the anils under discussion. This is well illustrated in Fig. 4. The methoxy

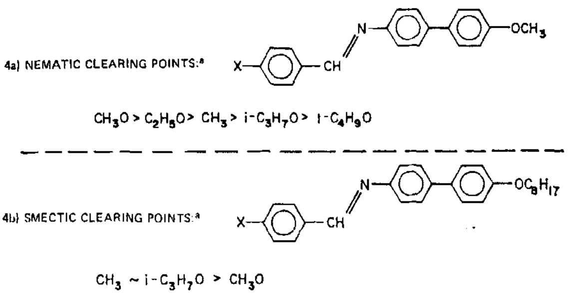
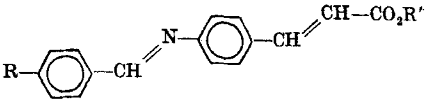


Figure 4. Substituent effects on mesophase clearing points of some biphenyl anils. a G. W. Gray *et al.*

compound (Fig. 4a) has a more thermally stable nematic phase than the isopropoxy, while in the smectic case (Fig. 4b) this order is reversed.

It is important to realize that in those examples (Fig. 4, Table 6) for which both alkoxy and alkyl compounds exhibit a nematic phase, the latter type of material regularly shows a nematic clearing point 30–50° below that of the former.(7,18) Thus, it would not be surprising, in a first approximation, to find the nematic clearing points for compounds *15* and *16* significantly below the analogous transition temperatures for the oxygen-linked compounds *13* and *14* (200° and 159° respectively). Since it is observed that the *t*-butyl and trimethylsilyl anils melt at 190° and 180° respectively, it is to be expected that neither would show a nematic phase. This is observed.

TABLE 6 Transition Temperatures of Some Cinnamic Acid Esters.a



R	m.p.	$S_2 \rightarrow S_1$	$S_1 \rightarrow N$	$N \rightarrow I$
		Methyl ester		
CH_3	151	114	129	138
CH_3O	161	—	—	183
		Ethyl ester		
CH_3	96	109	121	—
CH_3O	109	91	118	139

a. From Refs. 16 and 17.

Also, the bulkier germanium and tin compounds, *17* and *18*, should not (and do not) exhibit nematic mesomorphism.

The smectic clearing points of compounds *16–18* show only a very slightly decreasing trend as the metal atom varies from silicon through germanium to tin, namely 183°, 175° and 173°. By comparison, *p*-methyl-benzylidene-4-amino-4′-octyloxybiphenyl is smectic until 178° where it becomes nematic. Thus the bulky trimethylmetallic group, relative to methyl, does not have a strongly detrimental effect on the disappearance of the smectic mesophase. Apparently, the high polarizability associated with the metal atom is responsible for the smectogenic properties of these materials. Also, the less polarizable *t*-butyl compound *15* (mp 190°) shows no smectic phase, despite supercooling the isotropic melt to 180°.

The heats of the smectic-isotropic transitions in these organometallic Schiff Bases show only a slightly increasing trend with increasing atomic number of the metal.† The relative constancy of both the smectic clearing points and the heats of transition of materials *16–18* can be rationalized on the basis that the enhancement of smectic properties by the polarizable metals (Sn>Ge>Si)(19) is counterbalanced to some extent by steric factors, since the size of the organometallic substituents increases with increasing atomic number.

The fact that the smectic clearing points are relatively insensitive to the steric requirements of the bulky substituents suggests speculation regarding the molecular arrangement in these smectic phases. An arrangement such as that shown in Fig. 5b, where the uniaxial axis is perpendicular to the layer interface planes and neighboring molecules lie head-to-head,(20) gives rise to a relatively large intermolecular separation. This would be energetically unfavorable since molecular proximity is essential to maintain order in the mesophase. The separation can be reduced somewhat by requiring a head-to-tail molecular arrangement (Fig. 5a). A similar reduction can be achieved, however, by allowing the angle between the uniaxial axis and the layer interface planes to assume a value smaller than 90° (Fig. 5c and 5d). Such a "tilted smectic" phase has been previously proposed by Arora *et al.*,(21) but at this time we have obtained no optical or physical evidence in support of these highly simplified models.

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† We assume that the combined S_2–S_1 and S_1–I transition enthalpies of the tin compound *18* would partition in the same ratio as in the germanium coupound.

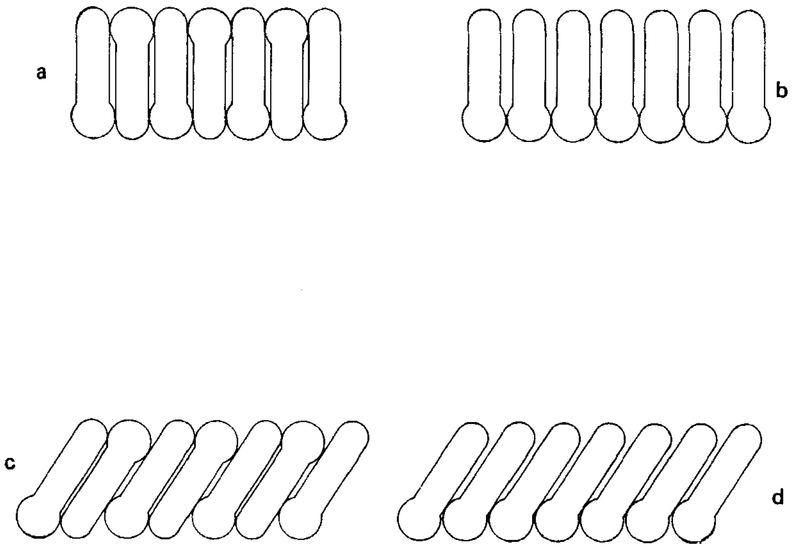

Figure 5. Schematic representation of some possible molecular arrangements of bulky-ended compounds in the smectic phase.

EXTENDED SILOXANE WING GROUPS

Returning to Table 4, it is noted that the pentamethyldisiloxanyl group, with or without an oxygen between the ring carbon and the silicon, causes smectic mesomorphism only. On the other hand, the trimethylsiloxy derivative *14* is a nematic material. These results are analogous to those obtained by Haller and Cox(22) who observed the loss of nematic phases (leaving only smectic phases) upon the insertion of oxygen atoms in the *p*-alkoxy chain of some benzylideneaminoacetophenones which had displayed both types of mesomorphism. A lowering of smectic clearing points with increasing chain length was also observed in the acetophenones with oxygen-containing end chains. This result is in accord with our observation that derivative *19* has a lower smectic persistence than the shorter trimethylsilyl material *16*.

Of the four transitions listed for the pentamethyldisiloxanyl compound *20*, the S_3–S_2 transition was not seen under the polarizing microscope, but was reproducibly detected by differential scanning calorimetry. The enthalpy change for this transition, 0.13 kcal/mole, is quite low in comparison to that of most other smectic–smectic transitions which are reported in the literature.(23) A similar observation was recently made by Arora *et al.*(20) who speculate that the transition represents a partial reordering of the molecules into a head-to-head alignment (Fig. 5b) from a random orientation.

Summary

1. A series of organometallic liquid crystals has been prepared from 4-amino-4′-methoxybiphenyl and benzaldehyde derivatives containing silicon, germanium or tin.
2. Bulky organometallic substituents at the terminus of a mesomorphic-type material do not preclude liquid crystal formation providing the aspect ratio is large enough and electronic factors are favorable.
3. The trimethylsilyl, trimethylgermyl, and trimethyltin substituents promote smectic mesomorphism in materials which might otherwise be expected to exhibit a nematic phase.
4. Bulky terminal substituents decrease the nematic thermal persistence to a greater extent than smectic thermal persistence.
5. Liquid crystals containing a terminal pentamethyldisiloxanyl groups tend to exhibit smectic mesomorphism.

Experimental

Melting points are corrected. All new compounds had satisfactory spectral properties and elemental analyses. Infrared spectra were obtained on a Perkin–Elmer 137B Infracord. Nuclear magnetic resonance spectra were obtained on a Varian HA-60-IL Spectrometer. Ultraviolet spectra were taken on a Cary 14 Spectrophotometer.

p-TRIMETHYLSILOXYBENZALDEHYDE: Using the procedure of Wolf and Hoffmann,(24) 26.7 g (0.24 mole) of trimethylchlorosilane and 15.0 g (0.12 mole) of *p*-hydroxybenzaldehyde were allowed to reflux 8 hr or until all of the aldehyde had dissolved. Fractional distillation afforded 19.4 g (81%) of the desired *p*-trimethylsiloxybenzaldehyde, bp 108° (2 mm), (lit.[24] bp 83–84° (0.3 mm)).

PENTAMETHYLDISILOXANYL CHLORIDE: The procedure of Patnode and Wilcock(25) was employed to prepare 1, 3-dichloro-1, 1, 3, 3-

tetramethyldisiloxane (*24*). Methylmagnesium chloride (0.063 mole) in 100 ml of ether was added over 1 hr to a rapidly stirred solution of 53 g (0.26 mole) of compound *24* in 100 ml of ether at room temperature. The mixture was allowed to reflux for an additional hour and was subsequently filtered. The filtrate was fractionally distilled to afford 5.5 g (48%) of pentamethyldisiloxanyl chloride, bp 120° (760 mm) (lit.[26] bp 118.6–119.6 (758 mm)).

p-PENTAMETHYLDISILOXANOXYBENZALDEHYDE: A modification of the procedure of Wolf and Hoffman(24) was employed. Pentamethyldisiloxanyl chloride (5.5 g, 0.03 mole) and *p*-hydroxybenzaldehyde in 25 ml of benzene were allowed to reflux for 16 hr. Distillation afforded 3.8 g (71%) of *p*-pentamethyldisiloxanoxybenzaldehyde, bp 110° (0.3 mm).

p-X-BENZALDEHYDE DIETHYL ACETALS (GENERAL PROCEDURE): *p*-Bromobenzaldehyde diethyl acetal was prepared from *p*-dibromobenzene according to Bergmann.(27) A solution of this acetal in dried tetrahydrofuran was added rapidly to a 10% molar excess of magnesium, and, after the initial reaction subsided, the mixture was allowed to reflux for 1 hr. After cooling to 25°, an ethereal solution of the appropriate organometallic halide was added at such a rate to maintain the reaction temperature below 35°. The mixture was stirred overnight, and hydrolyzed with saturated ammonium chloride solution. The mixture was extracted with ether and the resulting organic layer was washed with water and saturated sodium chloride solution, dried over sodium sulfate, concentrated at the water pump, and distilled *in vacuo*.

The compounds prepared by this method are the following: (a) *p*-Trimethylsilylbenzaldehyde diethyl acetal (63%); this compound was not distilled, as the crude mother liquor was sufficiently pure for subsequent reaction; (b) *p*-Trimethylgermylbenzaldehyde diethyl acetal (83%), bp 83° (0.01 mm); (c) *p*-Trimethyltinbenzaldehyde diethyl acetal (62%), bp 98–100° (0.01 mm); (d) *p*-Trimethylleadbenzaldehyde diethyl acetal (40%), bp 115° (0.01 mm); (e) *p*-Pentamethyldisiloxanylbenzaldehyde diethyl acetal (50%), bp 102–103° (0.1 mm).

p-*t*-BUTOXYBENZALDEHYDE DIETHYL ACETAL: The general procedure of Frisell and Lawesson(11) for the synthesis of *t*-butyl phenyl ether was employed in the preparation of the *t*-butoxy acetal. The

Grignard reagent from *p*-bromobenzaldehyde diethyl acetal, described above, was prepared from 5.0 g (0.019 mole) of the bromo acetal and 0.54 g (0.022 mole) of magnesium. A solution of 2.33 g (0.012 mole) of *t*-butyl perbenzoate (Matheson, Coleman and Bell) in 25 ml of ether was added to the Grignard reagent at 0° over 0.5 hr. After stirring the mixture an additional 5 min. at 0°, it was poured slowly into cold dilute hydrochloric acid. The aqueous layer was separated and extracted with ether, and the combined organic layers were washed with cold 2N sodium hydroxide solution. The ether layer was washed with water until neutral and finally dried over anhydrous sodium sulfate. Fractional distillation afforded 1.2 g (55%) of the desired product, bp 81° (0.005 mm).

SCHIFF BASES (GENERAL PROCEDURES):

(A). In order to prepare anils *7a*, *7b*, *8a*, *8b*, *16*, *17*, and *19*, equimolar amounts of the substituted benzaldehyde diethyl acetal and one of the amines (*p*-aminophenyl acetate,(9) *p*-aminophenyl benzoate,(9) or 4′-methoxy-4-biphenylamine(15)) were dissolved in a minimum amount of ethanol, and a trace of *p*-toluenesulfonic acid was added. After a 16 hr reflux period, the solutions were cooled and the precipitated crystals or oils were recrystallized from petroleum ether (bp 30–80°).

(B). The preparation of Schiff Base *18* required the use of xylene as the refluxing solvent, but otherwise the procedure was identical to (A). This method failed, however, in attempts to prepare Schiff Bases from *p*-trimethylleadbenzaldehyde diethyl acetal.

(C). To prepare azomethines *5a*, *5b*, *6a*, *6b*, *14* and *20*, equimolar amounts of the substituted benzaldehyde acetal and the amine were combined in a flask containing freshly dried methylcyclohexane and molecular sieves (#13-X). The mixture was vigorously stirred and refluxed for 16 hr, and filtered hot under nitrogen. The residue was washed with boiling methylcyclohexane, and the combined filtrates were cooled to induce crystallization. The crystals were collected under a nitrogen atmosphere, and recrystallized in like manner from methylcyclohexane.

(D). The *t*-butoxy Schiff Bases *4a*, *4b*, and *13* were prepared by combining the appropriate amine and acetal with freshly dried *t*-butanol and allowing the solution to reflux for 16 hr. Recrystallizations of the precipitated products were carried out in petroleum ether.

All of the anils prepared were recrystallized to constant melting point and until thin layer chromatography showed the presence of only one compound.

MICROSCOPY

The mesophases were identified and the transition temperatures measured by standard techniques⁽⁷⁾ on a Leitz Ortholux POL Polarizing Microscope equipped with a Koeffler Hot Stage. The temperatures were calibrated at the melting points of high purity standards, and the thermometric accuracy is estimated at ±0.5 °C.

CALORIMETRIC MEASUREMENTS

The heats of fusion and phase transitions were determined by differential scanning calorimetry on a Perkin–Elmer DSC-1B instrument as described previously.(28) The reported heats and entropies are believed to be accurate to 5%.

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