

# Stilbene Derivatives. A New Class of Room Temperature Nematic Liquids<sup>1a</sup>

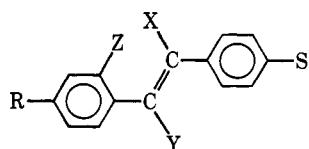
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**Abstract:** A series of planar, *trans*-stilbene derivatives of type A has been prepared. Although most of these substances exhibited nematic mesophases, all displayed melting points above 100°. In order to achieve nematic compounds with lower melting points, a series of related nonplanar stilbene derivatives (type B) was synthesized; the purpose of the methyl or chlorine group was to twist the benzene rings out of coplanarity in order to relieve steric crowding about the central double bond. As expected, these nonplanar stilbenes exhibited significantly lower melting points than their planar counterparts, although not at the expense of loss of liquid crystalline character. Ten nematic stilbenes of type B displayed melting points between 14 and 35°, and *dl*-4-(2-methylhexyl)-4'-ethoxy- $\alpha$ -chloro-*trans*-stilbene exhibited a thermodynamically stable nematic phase from 22 to 35°. In addition to being inherently interesting, these compounds show promise for utilization in physical chemical studies as well as in technology.

Scientific research devoted to liquid crystalline materials has expanded greatly during the last several years.<sup>2</sup> Of particular importance to the organic chemist is the relationship between chemical structure and mesomorphic properties of organic compounds.<sup>3</sup> One problem which has challenged chemists' ingenuities is obtaining substances which exhibit nematic mesophases at room temperature, and, simultaneously, have long-term stability under ambient conditions.

To overcome the problems of chemical instability and yellow color inherent in previously reported room temperature nematic liquids,<sup>4-6</sup> we have investigated derivatives of *trans*-stilbene (A and B). Substituted



R, S = alkyl or alkoxy groups  
A, X = Y = Z = hydrogen  
B, X, Y, or Z = methyl or chlorine

stilbenes are colorless and stable compounds under ambient conditions. Several para-disubstituted stilbenes are reported to exhibit nematic phases, although at temperatures in excess of 100°. We thus undertook the task of designing and preparing stilbenes with

significantly lower melting points while maintaining nematic order in the melt.

It is well known that molecules which possess a high degree of symmetry pack well in the solid phase and thereby exhibit relatively high melting points. Table I<sup>8,10-13</sup> enumerates the melting points of a group of

**Table I.** Transition Temperatures of Some Rod-Shaped Molecules

	Unsubstituted mp <sup>a</sup>	4,4'-Dimethoxy mp <sup>a</sup>	cp <sup>a</sup>	Geometry
<i>trans</i> -Stilbene	124 <sup>b</sup>	216 <sup>c</sup>	176 <sup>c</sup>	Planar
<i>N,α</i> -Diphenylnitron	112 <sup>d</sup>	149 <sup>e</sup>	120 <sup>e,f</sup>	?
<i>trans</i> -Azobenzene	68.5 <sup>b</sup>	165 <sup>g</sup>	110 <sup>g,h</sup>	Planar
Benzylideneaniline	49 <sup>b</sup>	146 <sup>g</sup>	99 <sup>g</sup>	Nonplanar
<i>trans</i> -Azoxybenzene	36 <sup>b</sup>	116 <sup>g</sup>	134 <sup>g</sup>	Nonplanar

<sup>a</sup> All temperatures in °C; mp represents the transition from the solid to nematic or isotropic liquid; cp represents the transition from nematic to isotropic liquid; none of the unsubstituted materials exhibits a mesophase. <sup>b</sup> From ref 10. <sup>c</sup> From ref 8. <sup>d</sup> From ref 11. <sup>e</sup> From ref 12. <sup>f</sup> Extrapolated from data obtained in binary mixtures. <sup>g</sup> From ref 13.

structurally similar elongated molecules with various degrees of symmetry. Crystal structure determinations for *trans*-stilbene,<sup>14</sup> *trans*-azobenzene,<sup>15,16</sup> and 4,4'-*trans*-azotoluene<sup>16</sup> indicate that these substances are nearly planar and belong approximately to the C<sub>2h</sub> point group. On the other hand, benzylideneaniline,<sup>17</sup> *p*-methylbenzylidene-*p*-nitroaniline,<sup>17</sup> and *p*-azoxyaniline<sup>18</sup> are nonplanar and belong to the C<sub>1</sub> point group.

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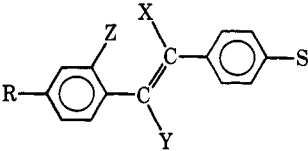
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Table II. Preparative Methods and Physical Properties for Several Substituted *trans*-Stilbenes


No.	R	S	X	Y	Z	Mp <sup>a</sup>	Cp <sup>a</sup>	CMD <sup>a</sup>	Synthesis <sup>b</sup>
1	CH <sub>3</sub> O	CH <sub>3</sub> O	H	H	H	216	176 <sup>c</sup>	-40	<i>d, e</i>
2	CH <sub>3</sub> O	CH <sub>3</sub> O	CH <sub>3</sub>	H	H	122	95 <sup>c</sup>	-27	PA <sup>f, g</sup>
3	C <sub>2</sub> H <sub>5</sub> O	C <sub>2</sub> H <sub>5</sub> O	H	H	H	209	189 <sup>c</sup>	-20	PA <sup>e, h</sup>
4	C <sub>2</sub> H <sub>5</sub> O	C <sub>2</sub> H <sub>5</sub> O	CH <sub>3</sub>	H	H	106	121	+15	PA <sup>f, g</sup>
5	<i>n</i> -C <sub>3</sub> H <sub>7</sub> O	<i>n</i> -C <sub>3</sub> H <sub>7</sub> O	H	H	H	198	<i>i</i>	<-33 <sup>i</sup>	PA <sup>e</sup>
6	<i>n</i> -C <sub>3</sub> H <sub>7</sub> O	<i>n</i> -C <sub>3</sub> H <sub>7</sub> O	CH <sub>3</sub>	H	H	109	83 <sup>c</sup>	-26	PA <sup>f</sup>
7	<i>n</i> -C <sub>4</sub> H <sub>9</sub> O	<i>n</i> -C <sub>4</sub> H <sub>9</sub> O	H	H	H	189	<i>j</i>	<-13 <sup>j</sup>	PA <sup>e</sup>
8	<i>n</i> -C <sub>4</sub> H <sub>9</sub> O	<i>n</i> -C <sub>4</sub> H <sub>9</sub> O	CH <sub>3</sub>	H	H	98	97 <sup>c</sup>	-1	PA <sup>f</sup>
9	CH <sub>3</sub> O	<i>n</i> -C <sub>8</sub> H <sub>17</sub> O	H	H	H	151	146 <sup>c</sup>	-5	<i>d, e</i>
10	CH <sub>3</sub> O	<i>n</i> -C <sub>8</sub> H <sub>17</sub> O	CH <sub>3</sub>	H	H	102	80 <sup>c</sup>	-22	FC <sup>f</sup>
11	CH <sub>3</sub> O	<i>n</i> -C <sub>8</sub> H <sub>17</sub> O	Cl	H	H	85	87	+2	FC
12	CH <sub>3</sub> O	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	Cl	H	H	40	38 <sup>c</sup>	-2	FC <sup>k</sup>
13	CH <sub>3</sub> O	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	Cl	H	H	42, 43 <sup>l</sup>	47	+5, +4 <sup>l</sup>	FC <sup>k</sup>
14	C <sub>2</sub> H <sub>5</sub> O	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	H	H	H	137			FC
15	C <sub>2</sub> H <sub>5</sub> O	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	H	H	64	59 <sup>c</sup>	-5	FC
16	C <sub>2</sub> H <sub>5</sub> O	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	Cl	H	H	29	58	+29	FC <sup>k</sup>
17	C <sub>2</sub> H <sub>5</sub> O	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	H	CH <sub>3</sub>	H	60	60 <sup>c</sup>	0	FC
18	C <sub>2</sub> H <sub>5</sub> O	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	H	Cl	H	36	56	+20	FC
19	C <sub>2</sub> H <sub>5</sub> O	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	H	H	CH <sub>3</sub>	49	44 <sup>c</sup>	-5	FC
20	C <sub>2</sub> H <sub>5</sub> O	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	Cl	H	H	52	69	+17	FC <sup>k</sup>
21	C <sub>2</sub> H <sub>5</sub> O	<i>n</i> -C <sub>8</sub> H <sub>13</sub>	Cl	H	H	34	59	+25	FC <sup>k</sup>
22	C <sub>2</sub> H <sub>5</sub> O	<i>n</i> -C <sub>7</sub> H <sub>15</sub>	Cl	H	H	36	66	+30	FC <sup>k</sup>
23	C <sub>2</sub> H <sub>5</sub> O	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	Cl	H	H	32	61	+29	FC <sup>k</sup>
24	C <sub>2</sub> H <sub>5</sub> O	2-Methylbutyl	Cl	H	H	29, 32 <sup>l</sup>	34	+5, 2 <sup>l</sup>	FC <sup>k</sup>
25	C <sub>2</sub> H <sub>5</sub> O	3-Methylbutyl	Cl	H	H	40	35 <sup>c</sup>	-5	FC <sup>k</sup>
26	C <sub>2</sub> H <sub>5</sub> O	2-Methylpentyl	Cl	H	H	32	41	+9	FC <sup>k</sup>
27	C <sub>2</sub> H <sub>5</sub> O	2-Methylhexyl	Cl	H	H	22	35	+13	FC <sup>k</sup>
28	<i>n</i> -C <sub>3</sub> H <sub>7</sub> O	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	Cl	H	H	35	37	+2	FC <sup>k</sup>
29	<i>n</i> -C <sub>4</sub> H <sub>9</sub> O	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	Cl	H	H	30	52	+22	FC <sup>k</sup>
30	<i>n</i> -C <sub>6</sub> H <sub>13</sub> O	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	Cl	H	H	33	53	+20	FC <sup>k</sup>
31	<i>n</i> -C <sub>7</sub> H <sub>15</sub> O	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	Cl	H	H	42	58	+16	FC <sup>k</sup>
32	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	Cl	H	H	14	10 <sup>c</sup>	-4	FC
33	CH <sub>3</sub> O	<i>n</i> -C <sub>8</sub> H <sub>7</sub> O	H	H	H	177 <sup>d</sup>	161 <sup>c, m</sup>	-16	<i>d, e</i>

<sup>a</sup> See Table I, footnote *a*. CMD values represent the difference between cp and mp; nonpositive values indicate that the liquid crystal is monotropic. <sup>b</sup> PA, acid-catalyzed aldehyde-phenol condensation; FC, Friedel-Crafts acylation procedure. <sup>c</sup> Monotropic transition. <sup>d</sup> Reported in ref 8. <sup>e</sup> The nmr spectrum, in benzylic-vinyl region, is identical with that depicted in ref 8, Figure 3. <sup>f</sup> The nmr spectrum, in benzylic-vinyl region, is shown in Figure 1a. <sup>g</sup> See ref 23. <sup>h</sup> See ref 24. <sup>i</sup> This material crystallized from the supercooled isotropic liquid at 165°. <sup>j</sup> This material crystallized from the supercooled isotropic liquid at 176°. <sup>k</sup> The nmr spectrum, in benzylic-vinyl region, is shown in Figure 1b. <sup>l</sup> This material exists in two different crystalline modifications. <sup>m</sup> Smectic-nematic transition temperature.

Assuming that substituents in the para positions will not grossly affect the configuration of the benzene rings and of the linkage group,<sup>19</sup> we postulated that the stilbenes and azobenzenes in Table I are planar, while the Schiff bases and azoxybenzenes are nonplanar. We further hypothesized that the relatively high degree of symmetry associated with the former substances was, to a significant extent, responsible for the higher melting points of these materials.<sup>20</sup>

In contrast to this relationship, it could be seen from Table I and from previous discussions<sup>8</sup> that no such simple affinity existed between symmetry and nematic clear points. We thus prepared several unsymmetrical derivatives of *trans*-stilbene with the hope of lowering the melting points significantly.

The introduction of asymmetry into the *trans*-stilbene molecule could be achieved by the use of unsymmetrical substituents in the para positions and/or by the replacement of  $\alpha$ ,  $\beta$ , or ortho hydrogens by small but bulkier groups such as methyl, trifluoromethyl, chlorine, or

(19) This assumption appears to be justified unless there is direct mesomeric interaction between substituents.

(20) Crystal structures of aromatic aldonitrone have not, to our knowledge, been reported.

fluorine. This would disrupt the coplanarity of the benzene rings with the ethylene linkage and should have a marked effect on the melting point. The accompanying loss of conjugation and increased breadth might, of course, have eliminated the nematic phase. Taking a cue from Chaucer,<sup>21</sup> however, we proceeded to prepare several stilbene compounds.<sup>22</sup>

In the following section, the synthetic steps for the preparation of the *trans*-stilbene derivatives are described. There then follow accounts of the various groups of such derivatives that we have made and the hypotheses motivating our synthesis of these materials.

## Results

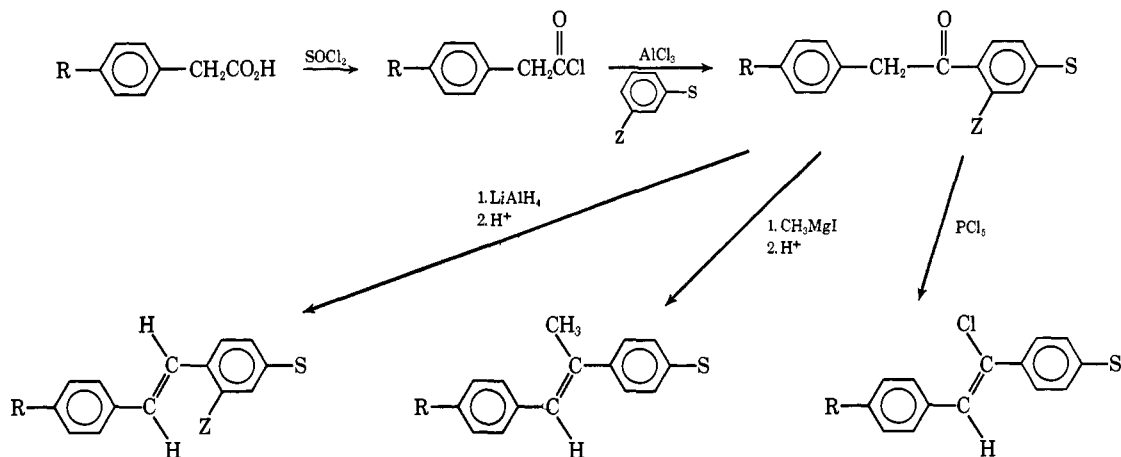
The stilbene derivatives prepared for this investigation are listed in Table II,<sup>8, 23, 24</sup> along with their physical properties and methods of preparation.

(21) G. Chaucer, "Troilus and Criseyde," Book V, line 784, 1374.

(22) A preliminary account of part of this work has been reported: *Angew. Chem.*, **83**, 399 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 410 (1971). For a study of the role of *o*-methyl groups in mesomorphic Schiff bases, see J. van der Veen, Abstracts, Third International Liquid Crystal Conference, Berlin, Aug 1970, Abstract No. S53.

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Scheme I. Preparation of Some Mesomorphic Stilbenes using a Friedel-Crafts Acylation Step



Compounds **1**, **9**, and **33** had been prepared in our laboratory previously<sup>8</sup> by means of the Wittig reaction.

**Synthesis Employing Acid-Catalyzed "Phenol-Aldehyde" Condensation.** Compounds **3**, **5**, and **7** were prepared from bromoacetal and an alkoxybenzene by the method of Al-Attar and Wizinger,<sup>24</sup> based upon the phenol-aldehyde condensation. They were identified either by melting point (**3**)<sup>24</sup> or elemental analyses plus spectral characterization (**5** and **7**). Their nmr spectra in the benzylic-vinylic proton region were identical and corresponded with that of the *trans*-stilbene **1** as depicted in Figure 3 of an earlier publication.<sup>8</sup>

The analogous  $\alpha$ -methyl-substituted stilbenes, **2**, **4**, **6**, and **8**, were prepared by a similar method of Zaheer, *et al.*,<sup>23</sup> from chloroacetone and an alkoxybenzene. The known compounds **2** and **4** were identified by their melting points<sup>23</sup> and the remaining new materials by their elemental analyses and spectral properties. The *trans* configurations were assured, since all four compounds exhibited nematic mesophases,<sup>8</sup> and, in addition, all had aromatic-vinylic absorption patterns in the nmr which were identical (group A type spectrum, shown in Figure 1a).

**Synthesis Employing the Friedel-Crafts Acylation.** The majority of the stilbene derivatives prepared for this investigation were synthesized by one of the methods shown in Scheme I. In each case, a benzyl phenyl ketone was prepared by the Friedel-Crafts acylation of a substituted benzene with a suitable phenylacetyl chloride derivative.

Fifteen of these materials (**12**, **13**, **16**, **20-31**), the 4-alkyl-4'-alkoxy- $\alpha$ -chloro-*trans*-stilbenes, can be classified as belonging to several homologous series. Each one, however, exhibits an nmr spectrum which contains an identical absorption in the vinylic-aromatic region. This absorption pattern, shown in Figure 1b, will be designated as a group B spectrum. All other spectral properties and elemental analyses were consistent with the proposed structures. In addition, the appearance of nematic properties in all of the 15 substances indicates the assigned *trans* configuration to be the correct one.

Of the remaining materials synthesized by the Friedel-Crafts acylation procedure, all exhibited a nematic phase except compound **14**. Therefore, stilbenes **10**,

**11**, **15**, **17**, **18**, **19**, and **32** must have the *trans* configuration. In addition, the aromatic regions of the nmr spectra of compounds **10**, **15**, and **17** are quite similar to the group A spectra (Figure 1a), while stilbene **18** exhibited aromatic absorption analogous to the group B compounds.

Compound **14**, a nonmesomorphic stilbene, was assigned the *trans* configuration on the basis of its infrared spectrum, which exhibited strong absorption at 977  $\text{cm}^{-1}$ , characteristic of *trans*-disubstituted ethylenes.<sup>25</sup>

All of the stilbenes **1-33** are colorless substances. The electronic absorption spectra of the stilbenes can be exemplified by the data for chlorostilbene **23**, which exhibits a  $\lambda_{\text{max}}$  at 305 nm ( $\epsilon$  28,000) in ethanol and a  $\lambda_{\text{cutoff}}$  at 370 nm (neat). End absorption of uv light at 366 nm will cause photodegradation of the material.

## Discussion

**4,4'-Dialkoxy-*trans*-stilbenes.** The centrosymmetric homologous stilbenes, **1**, **3**, **5**, and **7**, are white solids which exhibit relatively high melting points, ranging from 189 to 216°. The less symmetric, but still planar derivatives, **33** and **9**, display somewhat lower melting points, 177 and 151°, respectively. The introduction of  $\alpha$ -CH<sub>3</sub> or  $\alpha$ -Cl groups into these molecules, however, generated the nonplanar stilbenes **2**, **4**, **6**, **8**, **10**, and **11**; these substances, which are members of the C<sub>1</sub> point group, exhibit significantly lower melting points, ranging from 85 to 122°. These results are consistent with the hypothesis relating melting point and molecular symmetry discussed above.<sup>26</sup>

In order to assess the role of symmetry upon the nematic clearing points, it is useful to consider the clearing point-melting point difference (CMD), which we define as the difference between a substance's clearing point and melting point. Thus, a nonpositive CMD delineates a monotropic liquid crystal, while a positive CMD denotes an enantiotropic liquid crystal and enumerates the range over which a substance exhibits mesomorphism.

Although the data for these substances (Table II) may indicate a very slight trend toward more negative CMD values for the more highly symmetric stilbene derivatives, we are able to discern no *significant* change

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(24) Y. Al-Attar and R. Wizinger, *Helv. Chim. Acta*, **46**, 1286 (1963).

(25) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, p 45.

(26) R. T. Morrison and R. N. Boyd, "Organic Chemistry," Allyn and Bacon, Boston, Mass., 1959, p 250.

in the CMD's as the symmetry elements are varied. That is, the clearing points of these substances tend to follow the melting points. This correlation may be explained by the hypotheses that (a) highly symmetric molecules may "pack" more closely in the nematic phase, resulting in higher nematic clearing points relative to less symmetric molecules; (b) the protruding bulky group ( $\text{CH}_3$  or  $\text{Cl}$ ) may cause larger intermolecular separations, thereby lowering the clearing points of these molecules;<sup>3</sup> or (c) polarizability effects.

We feel that explanation b is the correct one. Despite the loss of conjugation in the twisted stilbenes, these nonplanar stilbenes should have virtually the same or slightly higher polarizabilities than their planar counterparts, which have lower molecular weights. Since higher polarizabilities are associated with higher clearing points,<sup>3,27</sup> possibility c can be discarded. With regard to hypothesis a, it was recently shown that the nematic clearing points of related stilbenes, azoxybenzenes, nitrones, azobenzenes, and Schiff bases do not correlate with molecular symmetry.<sup>8,9</sup> Also, Cox and Clecak have prepared the 2-methyl (34) and 2,2'-dimethyl (35) derivatives of the diethoxystilbene 3.<sup>28</sup> They have observed that melting points increase with molecular symmetry ( $34 < 35 < 3$ ), while the nematic clearing points increase with decreasing number of methyl groups ( $35 < 34 < 3$ ).

It should be noted that in comparison of different linkage groups of structurally related liquid crystals, it is expected that the nematic clearing points of the homologous stilbenes containing  $\alpha$ -methyl groups (2, 4, 6, 8, and 10), when plotted against homolog number,<sup>8</sup> would trace a curve which is parallel to those of the related stilbenes, azoxybenzenes, etc. However, while the planar stilbenes exhibit the highest clearing points of the six linkage groups (*i.e.*,  $\text{CH}=\text{CH}$ ,  $\text{N}=\text{NO}$ ,  $\text{CH}=\text{NO}$ ,  $\text{N}=\text{N}$ ,  $\text{CH}=\text{N}$ , and  $\text{CH}=\text{CCH}_3$ ), the  $\alpha$ -methylstilbenes will display the lowest clearing points. Here, the steric factors (*i.e.*, intermolecular separation) as well as polarizabilities (when steric factors are virtually equal) are responsible for the observed order.

Thus, small globular substituents on the central double bond of a *trans*-stilbene will twist the benzene rings out of coplanarity, resulting in a nematic substance with substantially lower melting point. The lowest melting dialkoxystilbene liquid crystal reported herein, however, chloro derivative 11, still exhibits a melting point that is significantly above room temperature. To overcome this problem we followed the example of Kelker and coworkers<sup>4</sup> by preparing a series of stilbenes which possess a terminal alkyl group in place of an alkoxy moiety.

**Derivatives of 4-*n*-Butyl-4'-ethoxy-*trans*-stilbene.** A series of stilbenes derived from 4-*n*-butyl-4'-ethoxy-*trans*-stilbene, compounds 14–19, was prepared. The parent compound 14 is presumably planar and melts to a normal liquid at 137°. No liquid crystalline phase was detected. In sharp contrast, the five derivatives which contain either a methyl or chloro substituent in the  $\alpha$ ,  $\beta$ , or ortho position (15–19) melt at considerably lower temperatures and exhibit nematic mesophases.

These observations are analogous to those discussed above. However, for those nonplanar stilbenes which

(27) M. J. S. Dewar and R. S. Goldberg, *J. Amer. Chem. Soc.*, **92**, 1582 (1970).

(28) R. J. Cox and N. J. Clecak, unpublished results.

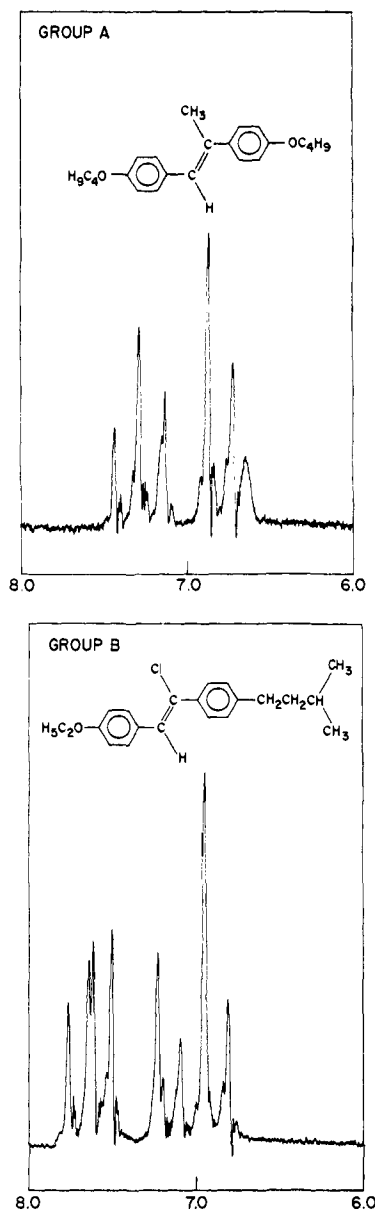


Figure 1. The aromatic-vinylic hydrogen region of the nmr spectra of stilbenes 8 (group A type spectrum) and 25 (group B type spectrum). The solvent employed was  $\text{CDCl}_3$ , and the abscissa units are ppm downfield from TMS.

contain one terminal *n*-alkoxy group and one terminal *n*-alkyl group, melting points in the vicinity of room temperature can be achieved. Thus, for example, stilbene 16 has a thermodynamically stable nematic phase between 29 and 58°.

Examination of the clearing point data for compounds 15–19 indicates that the nematic-isotropic transition temperatures do not vary greatly with the nature of the substituent ( $\text{CH}_3$  vs.  $\text{Cl}$ ). However, the ortho-substituted derivative 19 exhibits a relatively lower clearing point than the other materials, possibly because of increased molecular breadth with ortho substitution. The compounds bearing a chlorine on the central double bond (16 and 18) exhibit considerably lower melting points (and higher CMD values) than the methyl-substituted derivatives. Crystal structure data to be obtained by X-ray diffraction analysis may be helpful in rationalizing this observation.<sup>29</sup>

**Homologous Derivatives of 4-*n*-Alkyl-4'-*n*-alkoxy- $\alpha$ -chloro-*trans*-stilbenes.** Of the compounds 15–19, the chloro derivative 16 was the substance which most closely represented a room temperature nematic liquid. Consequently, it was decided to study a group of related homologous compounds, some of which might exhibit a lower melting point and/or a longer nematic range.

Three derivatives were prepared (28–30, Table II) in which the alkyl group was fixed at *n*-butyl while the alkoxy group was varied in length. Unfortunately, none of these substances exhibited a lower melting point than that of 16, while all displayed lower clearing points and CMD values.

Higher clearing temperatures, although accompanied by somewhat higher melting points, were observed for compounds 20–23, homologous derivatives of 16 in which the alkoxy group was fixed at ethoxy, and the *normal* alkyl chain was lengthened. The ethoxy-pentyl derivative 20 exhibits the highest clearing point, 69°, but also the shortest CMD of the group, 17°. The ethoxy-heptyl compound 22, on the other hand, has a nematic range of 36–66°, the longest range reported herein.

No clear-cut trend in melting points was noticed for the homologous series 16 and 20–23 as the length of the alkyl chain was regularly lengthened. However, the commonly observed<sup>3,8</sup> even/odd alternation in nematic clearing points as a function of chain length was evident in a plot of clearing temperature *vs.* homolog number. The pentyl and heptyl derivatives comprised the top branch (descending), while the butyl, hexyl, and octyl compounds comprised the bottom branch (ascending). Weygand and Gabler<sup>30</sup> reported a homologous series of Schiff bases, *p-n*-alkoxybenzylidene-*p*-ethoxyanilines, in which one end of the molecule was fixed as ethoxyl and the other end carried a *normal* alkoxy group. They observed even/odd alternation with butoxyl and hexoxyl derivatives lying on the top branch of their figure. Since butoxyl and hexoxyl groups are very similar, from a steric viewpoint, to pentyl and heptyl groups, the consistency of results between Weygand and Gabler's Schiff bases and the homologous chlorostilbenes emphasizes the role of steric factors in accounting for even/odd alternation.<sup>3</sup>

In studying binary combinations of the butyl and octyl derivatives 16 and 23, a sharply melting mixture, composed of 60 mol % 16 and 40 mol % 23, exhibited a thermodynamically stable nematic mesophase from 8 to 59°. Thus, mixtures of this kind are strong candidates for applications in electronic devices and physical science experiments requiring nematic liquids operating near room temperature.

**Derivatives of 4-Alkyl-4'-ethoxy- $\alpha$ -chloro-*trans*-stilbene Bearing Branched Alkyl Groups.** In an attempt to achieve liquid crystals with still lower melting points, several 4-alkyl-4'-ethoxy- $\alpha$ -chloro-*trans*-stilbenes (24–27, Table II) were prepared in which the alkyl groups contain a methyl branch.

From the limited amount of data, it was clear that methyl branching did not preclude the formation of nematic mesophases. Also, no regular effect upon stilbene melting points could be discerned; *i.e.*, some

(29) J. Weidenborner, A. L. Bednowitz, and W. R. Young, work in progress.

(30) C. Weygand and R. Gabler, *J. Prakt. Chem.*, **151**, 215 (1938).

derivatives exhibited higher melting points in comparison with their unbranched analogs and some lower. Of those compounds studied, the 2-methylhexyl derivative 27 exhibited a room temperature melting point and thermodynamically stable nematic phase between 22 and 35°.

A regular trend was noted in the effect of methyl branching on nematic-isotropic clearing points. The branched stilbenes always exhibited lower clearing points than their straight chain analogs. Specifically, methyl groups in the 2 and 3 positions lowered the clearing points approximately 20–30°. The interpretation of these observations will be deferred until the completion of our synthetic program which includes preparation of many additional 4-(methylalkyl)-4'-ethoxy- $\alpha$ -chlorostilbenes. These results, however, agree qualitatively with the observations of Gray and Harrison,<sup>31</sup> who made an extensive study of branched alkyl cinnamate esters.

In preparing and purifying branched alkyl derivatives such as these stilbenes, it should be kept in mind that these materials are racemic mixtures, or should be so in theory. In two preparations of the 2-methylpentyl derivative 26, small cholesteric liquid crystalline regions were observed in the nematic field under the polarizing microscope. The material effected a small but nonzero optical rotation of sodium-D light in a solution polarimeter. In addition, the material exhibited short-term memory characteristics, analogous to a cholesteric-doped nematic liquid,<sup>32</sup> when a thin film of the substance was subjected to a direct current electric field between transparent electrodes.

Pending additional work, these observations have been interpreted as a segregation of *d* and *l* forms, to a small extent, during crystallization from solution. In sampling the crystals for various tests, an equal quantity of the two antipodes was not obtained. The disparity in the concentrations of the two enantiomers resulted in the appearance of cholesteric properties.

**4-*n*-Octyl-4'-butyl- $\alpha$ -chloro-*trans*-stilbene.** This derivative, compound 32, is the only substance prepared in this investigation which contained two alkyl groups as terminal moieties. As a consequence of this structural characteristic, we believe, the material exhibited a lower melting point (14°) than the straight chain alkyl-alkoxy stilbenes. Also, it exhibited a monotropic nematic phase and, in contrast to the other stilbenes, a monotropic smectic phase with an S-N transition temperature of -5°. In order to substantiate our intuitive beliefs, the synthesis of additional dialkyl type liquid crystals in the Schiff base, azoxybenzene, azobenzene, and nitron classes, as well as stilbenes, is necessary.

## Conclusions

The investigation of substituent effects upon the physical properties of *trans*-stilbene derivatives has led to the following inferences and results. (a) The introduction of a small, globular substituent into the ortho,  $\alpha$  or  $\beta$  position of a planar *trans*-stilbene compound will disrupt the molecular planarity and significantly lower the compound's melting point; simultaneously, the existence of a smectic

(31) G. W. Gray and K. J. Harrison, *Mol. Cryst. Liquid Cryst.*, **13**, 37 (1971)

(32) G. H. Heilmeier and J. E. Goldmacher, *Proc. IEEE*, **57**, 34 (1971)

and/or nematic mesophase in these nonplanar derivatives is still possible and often observed. (b) Nematic substances with melting points in the vicinity of room temperature can be achieved by preparing stilbene derivatives bearing a chlorine atom on the central double bond plus a *para*-alkyl and a *para*'-alkoxyl group. For example, 4-*n*-butyl-4'-ethoxy- $\alpha$ -chloro-*trans*-stilbene exhibits a nematic range from 29 to 58°, while *dl*-4-(2-methylhexyl)-4'-ethoxy- $\alpha$ -chloro-*trans*-stilbene is nematic from 22 to 35°. (c) Mesomorphic stilbenes bearing a *normal* alkyl group in the *para* position will exhibit higher nematic clearing points than those with branched alkyl groups of the same length.

## Experimental Section

Melting points are corrected. All new stilbenes had satisfactory spectral properties and elemental analyses. Infrared spectra were recorded on a Perkin-Elmer 137B Infracord. The nmr spectra were obtained on a Varian HA-60-IL spectrometer. Ultraviolet spectra were taken on a Cary 14 spectrophotometer.

The mesophases were identified and the transition temperatures measured by standard techniques<sup>8</sup> on a Leitz Ortholux POL polarizing microscope, which was equipped with a Mettler FP2 hot stage controller. The powder method<sup>8</sup> was employed to uncover monotropic nematic phases in compounds exhibiting little tendency to form a supercooled liquid. The transition temperatures were calibrated at the melting points of high purity standards, and the thermometric accuracy is estimated at  $\pm 0.5^\circ$ .

**4,4'-Dialkoxy-*trans*-stilbenes.** Compounds **3**, **5**, and **7** were prepared by the reaction of bromoacetal with the appropriate alkyl phenyl ether, followed by a thermal rearrangement.<sup>24</sup>

**4,4'-Dialkoxy- $\alpha$ -methyl-*trans*-stilbenes.** Compounds **2**, **4**, **6**, and **8** were prepared by a similar reaction between chloroacetone and the alkyl phenyl ether, followed by a thermal rearrangement.<sup>23</sup>

**4-Alkoxyphenylacetic Acids.** All of the compounds **10**–**32** were prepared by the Friedel-Crafts acylation route outlined in Scheme I. The precursor phenylacetic acids were either obtained commercially or prepared by standard methods. The *p*-alkoxyphenylacetic acids were synthesized by alkylation of ethyl *p*-hydroxyphenylacetate<sup>33</sup> in alcoholic sodium ethoxide solution followed by the usual saponification technique.

**4-*n*-Butylphenylacetic Acid.**<sup>34</sup> This compound, the remaining precursor phenylacetic acid, was prepared by treating the Grignard reagent of *p*-*n*-butylbenzyl chloride<sup>35</sup> with Dry Ice, followed by the usual work-up and isolation.

**4-Alkyl- and 4-Alkoxyphenylacetyl Chlorides.** The phenylacetyl chlorides, prepared from their corresponding carboxylic acids with thionyl chloride and pyridine, were isolated by fractional distillation.

**4,4'-Disubstituted Benzyl Phenyl Ketones.** These key intermediates, as shown in Scheme I, were prepared by Friedel-Crafts acyla-

tion of a *para*-substituted phenylacetyl chloride upon an appropriately substituted benzene. The general procedure is outlined below.

To a three-neck flask fitted with mechanical stirrer and nitrogen purge were added 0.5 mol of AlCl<sub>3</sub>, 1.0 mol of an alkylbenzene (or alkoxybenzene), and 500 ml of CS<sub>2</sub>. The mixture was allowed to stir and reflux while 0.33 mol of a phenylacetyl chloride was added dropwise during 1 hr. After a 2-hr reflux period, 10% HCl was added to the cooled mixture to dissolve all of the aluminum salts. The usual work-up afforded a liquid from which excess alkylbenzene (or alkoxybenzene) was removed by distillation under high vacuum. The residual oil was recrystallized twice from 300 ml of methylcyclohexane, at  $-78^\circ$ , and the product was then sublimed in a large sublimator under high vacuum. The ketones, prepared in 20–40% yield by this technique, were sufficiently pure for use in subsequent reactions. Most of them were not characterized.

**4,4'-Disubstituted  $\alpha$ -Chloro-*trans*-stilbenes.** The benzyl phenyl ketones were converted to the  $\alpha$ -chlorostilbenes (Scheme I) with PCl<sub>5</sub> in the following manner. An appropriate benzyl phenyl ketone (0.01 mol) dissolved in 50 ml of methylene chloride was added to a reaction vessel containing PCl<sub>5</sub> (0.015 mol) dissolved in 50 ml of methylene chloride. The yellow solution was allowed to stir and reflux for 5 hr and then cooled. Additional solvent was added, and the red solution was washed with saturated NaCl and NaHCO<sub>3</sub> solutions. The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. The residual oil was eluted with benzene through a column of silica gel (25 g of silica gel per gram of oil). The benzene was removed, and the oil was recrystallized repeatedly from petroleum ether or al:ohol at  $-78^\circ$  to afford the desired chlorostilbene in 10–50% yield<sup>d</sup>

**4,4'-Disubstituted  $\alpha$ -Methyl-*trans*-stilbenes.** The benzyl phenyl ketones were reduced with methylmagnesium halide and subsequently dehydrated to prepare the  $\alpha$ -methylstilbenes (Scheme I) as follows. An ethereal solution of methylmagnesium iodide was prepared from 0.02 g-atom of magnesium and 0.025 mol of methyl iodide in 60 ml of dry ether. To this was added dropwise 0.006 mol of an appropriate benzyl phenyl ketone in 40 ml of ether. After a reflux period of 2 hr, the reaction mixture was hydrolyzed with water and dilute H<sub>2</sub>SO<sub>4</sub>. The ether layer was separated, washed, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated. The oily or semisolid residue, which contained the intermediate benzyl alcohol, was directly dehydrated in an open sublimator (without cold finger) by mixing with 0.03 mol of NaHSO<sub>4</sub> and heating to 175–200° for 20 min. The cold finger was then placed in the sublimator in the usual manner, and the crude stilbene was allowed to sublime under high vacuum. The product was recrystallized from petroleum ether at  $-78^\circ$  (charcoal treatment) to constant melting point. The yields ranged from 10 to 25%.

**4,4'-Disubstituted *trans*-Stilbenes.** Stilbenes **14** and **19** were prepared in 10–15% yield from the appropriate benzyl phenyl ketones by reduction (LiAlH<sub>4</sub>) and dehydration (Scheme I) in an analogous manner.

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