that they are SP or very nearly SP, The ^{13}C NMR spectrum of **1**, R = C_6H_5, X = O, down to −90 °C showed no change. All of the resonances remained remarkably sharp. Similarly the variable temperature ^{19}F NMR spectra of **6** showed no change on cooling to −90 °C. These negative findings do not distinguish between interconverting TPs or a SP structure.

Experimental Section

The variable temperature 220-MHz ^1H NMR spectra were recorded on a $CDCl_3$ solution of the methylcatechol sulfuranes. A maximum separation for the hydrogens of methyl groups was found to be 4 Hz at −60 °C. An apparent coalescence was found at −20 °C.

The ^{13}C NMR spectra were recorded with a Varian FT-80 spectrometer operating at 20 MHz. Unless specifically stated all spectra were obtained under conditions of complete proton noise decoupling using a 2.0-kHz noise bandwidth.

The samples, ca. 100 mg, were dissolved in deuteriomethylene chloride which also served as the internal lock. The solutions were degassed by bubbling argon through them.

In a representative experiment, the sample was pulsed 2400 times, with a spectral width of 4000 Hz and using 16K data points and an acquisition time of 2.047 s. Normally a 35° flip angle was used which corresponds to a pulse width of 5 μs. In the case of the mixture of methylcatechol sulfuranes at room temperature a flip angle of 21° was used which corresponds to a pulse width of 3 μs. The reason for this change is that the carbons bonded to oxygen have long T_1's and they were difficult to detect with the 5-μs pulse.

At ambient temperature the ^{13}C NMR spectrum of the mixture of methylcatechol sulfuranes had the following resonances, and a single off-resonance spectrum indicated that the carbons were coupled to the number of hydrogens indicated in the parentheses: 15.22 (3), 109.02 (1), 122.41 (0), 122.66 (1), 124.69 (0), 124.91 (1), 143.77 (0), 144.05 (0), 144.33 (0) ppm. At −90 °C the spectrum was quite complex. A resonance with a shoulder was found at 15.22 ppm as was one at 109.34 ppm. Broad resonances were found at 109.02, 126.37,

and 126.51 ppm. Relatively sharp resonances were found at 122.23, 122.68, 127.78, 122.96, 139.57, 139.66, 140.07, 140.17, 146.35, and 147.31 ppm.

References and Notes

(1) (a) Polytechnic Institute of Brooklyn; (b) Rutgers, The State University of New Jersey.
(2) (a) J. C. Martin and E. F. Perozzi, *Science*, **191**, 14 (1976); (b) K. C. Hodges, D. Schomberg, J. V. Weiss, and R. Schmutzler, *J. Am. Chem. Soc.*, **99**, 6097 (1977).
(3) R. Lukenbach, "Dynamic Stereochemistry of Pentaco-ordinated Phosphorus and Related Elements", Georg Thieme Verlag, Stuttgart, 1973.
(4) (a) J. A. Deiters, J. C. Gallucci, T. E. Clark, and R. R. Holmes, *J. Am. Chem. Soc.*, **99**, 5461 (1977); (b) P. Narayanan, H. M. Berman, F. Ramirez, J. F. Marecek, Y. Chaw, and V. A. V. Prasad, *ibid.*, **99**, 3336 (1977).
(5) (a) J. A. Howard, D. R. Russell, and S. Tripett, *J. Chem. Soc., Chem. Commun.*, 856 (1973); (b) M. Eisenhut, R. Schmutzler, and W. S. Sheldrick, *ibid.*, 144 (1973).
(6) G. Astrologes and J. C. Martin, *J. Am. Chem. Soc.*, **98**, 2895 (1976).
(7) G. E. Wilson, Jr., and B. J. Belkind, *J. Org. Chem.*, **42**, 765 (1977).
(8) L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley, New York, N.Y., 1972. Spectrum 161 gives the three values for the carbons of catechol as (1,2) δ 145.0, (4,5) δ 122.1, (3,6) δ 117.3.
(9) In fact the data satisfy any structure in which the carbons are not equivalent. The suggestion of TBP or nearly TBP is in line with what is known about the crystal structure of similar materials.
(10) J. A. Pople, W. G. Schneider, and H. J. Berstein, "High Resolution NMR", McGraw-Hill, New York, N.Y., 1959, p 218 ff.
(11) L. J. Adzima and J. C. Martin, *J. Org. Chem.*, **42**, 4006 (1977).

Effect of Molecular Structure on Mesomorphism. 7.[1] Enhancement of Smectic–Isotropic Transition Temperatures in Binary Mixtures of a New Liquid Crystal Series: the 4-Nitrophenyl 4'-n-Alkoxybenzoates

Anselm C. Griffin,* Richard F. Fisher, and Stephen J. Havens

Contribution from the Department of Chemistry, Box 448, Southern Station, University of Southern Mississippi, Hattiesburg, Mississippi 39401. Received March 29, 1978

Abstract: The homologous series of 4-nitrophenyl 4'-n-alkoxybenzoates has been synthesized and transition temperatures have been determined. All members of this series with three carbons or more in the alkoxy chain exhibit liquid crystalline behavior. The familiar odd–even alternation in mesophase–isotropic temperatures was found. A method for determining mesophase–isotropic temperatures in strongly supercooled samples is described. This series of nitro esters exhibits marked nonlinear thermal behavior in selected binary mesophase systems. Maxima in mesophase–isotropic transition temperatures have been determined for mixtures of each of the 4-nitrophenyl 4'-alkoxybenzoates with 4-heptyloxybenzylidene-4'-butylaniline and with 4-octyloxybenzylidene-4'-butylaniline. These maxima occur at or very near 50:50 mole percent composition of the binary mixtures. A plot of the maxima vs. alkoxy chain length of the nitro esters exhibits an odd–even alternation. In mixtures of 4-substituted-phenyl 4'-decycloxybenzoates, enhanced S_A mesophases were found for the nitro ester when mixed with methyl and methoxy esters; linear, ideal mixture behavior was found for the nitro ester when mixed with trifluoromethyl and cyano esters. A π molecular complex is proposed to account for this nonideal solution behavior.

Liquid crystalline compounds and their mixtures offer unique opportunities to examine structure-property relationships in condensed phases. In general binary mixtures of

liquid crystalline materials exhibit eutectic behavior in their solid–mesophase transition temperatures, whereas their mesophase–isotropic transition temperatures vary linearly with

composition.[2] One of us recently reported[3] that a binary system of the two mesomorphs, 4-nitrophenyl 4'-decyloxybenzoate and 4-heptyloxybenzylidene-4'-butylaniline, exhibited smectic-isotropic (S → I) transition temperatures which were strongly nonlinear with composition. It was found that S → I temperatures were enhanced[4] in regions of mixed composition. Such an increase in mesophase-isotropic transition temperatures in binary mesophase systems has been observed by others[5] and has been recently found to occur with a variety of liquid crystalline systems.[1] In fact one of the compounds need not be mesomorphic. Schroeder and Schroeder[6] observed increased smectic-isotropic transition temperatures with mixtures of 4,4'-di-*n*-hexyloxyazoxybenzene and nonmesomorphic 4-nitro-substituted anils. Park and Labes[7] likewise obtained increased nematic-isotropic transition temperatures by addition of nonmesomorphic 4-aminobiphenyl to the nematogen 4-cyano-4'-pentylbiphenyl.

Enhancement of mesophase-isotropic transition temperatures in binary systems often occurs when a mesomorph having alkyl or alkoxyl groups at both ends of the molecule is mixed with a special kind of molecule,[3] specifically, one which contains, in addition to the usual planar aromatic rings, a flexible hydrocarbon chain on one end and a small, compact, electron-withdrawing group on the other end such as in the generalized structure shown below.
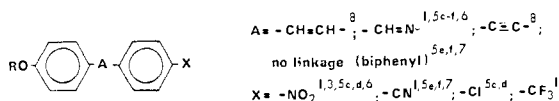
The molecular structural rationale for this positive deviation from ideal mixture behavior is not completely understood, but it is thought[1,3,6,7] that molecular complexation between unlike molecules is responsible. A π-complexed, bimolecular smectic arrangement such as that suggested[1] for the smectic A phase of pure **1** may be intimately involved. Dave[5c,d] prefers an explanation involving orientation of group dipole moments. In an effort to systematically expand the study of nonideal phase behavior in nitro-containing liquid crystals, we decided to prepare and examine the homologous series of 4-nitrophenyl 4'-*n*-alkoxybenzoates shown below.
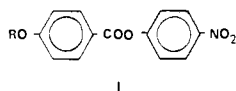
The literature contains isolated data for three of these esters, but there has been no systematic study of this series of compounds. X-ray data have been obtained[3] for the decyloxy ester and support a bimolecular smectic A phase for this compound. It was decided to examine the binary mesophase behavior of these compounds. We prepared a series of mixtures in which regular variations in alkoxyl chain length were used to probe nonideal mixture behavior. Representative binary phase diagrams were prepared to determine the dependence of nonlinear thermal behavior on the electronic nature of the terminal group.

Experimental Section

General. ^{1}H NMR spectra were obtained on a Varian A-60D spectrometer using tetramethylsilane as internal reference; infrared spectra were obtained using a Perkin-Elmer Model 257 spectrometer. Elemental analyses on all new compounds were performed by Galbraith Laboratories, Knoxville, Tenn. Suppliers for compounds which are difficult to obtain are specified. Otherwise, the compounds and reagents are commonly available and no suppliers are given. The line notation introduced by Verbit[9] is used to describe transitions and report transition temperatures. In this system the numbers between the two symbols are the temperatures (°C) of the transitions between the two states. The symbols used follow: K = crystalline solid, S_x = smectic of modification X, N = nematic, and I = isotropic liquid. Monotropic transitions are in parentheses.

Preparation of Materials. 4-Alkoxybenzoyl chlorides were prepared from the 4-alkoxybenzoic acids by heating them under reflux (12 h) with an excess of thionyl chloride. The excess thionyl chloride was removed using a rotary evaporator leaving the acid chloride as residue. The 4-nitrophenyl 4'-alkoxybenzoates (**1a-1**) were prepared by reaction of 4-nitrophenol with an equimolar amount of the appropriate 4-alkoxybenzoyl chloride in dry pyridine (25 mL of pyridine for each gram of acid chloride). After stirring overnight at room temperature the reaction mixture was added to cold, dilute hydrochloric acid which precipitated the ester. The crude product was removed by suction filtration, washed with water, and slurried for 1 h with a saturated sodium bicarbonate solution. The ester was again collected by filtration, washed repeatedly with water, air dried, and then repeatedly crystallized from ethanol or ethanol-chloroform. All new compounds gave satisfactory spectral and elemental analysis data as described below. 4-Octyloxybenzylidene-4'-*n*-butylaniline (**2a**)[10,11] and 4-heptyloxybenzylidine-4'-*n*-butylaniline (**2b**)[12] were prepared by reaction of equimolar quantities of the appropriate *n*-alkoxybenzaldehyde with 4-*n*-butylaniline in absolute ethanol. The products were isolated by suction filtration and crystallized from absolute ethanol until literature values were obtained for transition temperatures.

Transition temperatures (corrected), spectral data, and elemental analyses for new compounds are given in Table III.[13] The complete data set for one of these esters (heptyloxy, **1g**) is presented below.

4-Nitrophenyl 4'-Heptyloxybenzoate (1g). K 63.5 N (42.5) I; IR (KBr) cm^{-1} 2920, 2850, 1740, 1604, 1510, 1339, 1248, 1198, 1164, 1155, 1046; ^{1}H NMR (CCl$_4$) δ 0.91 (t, 3 H, CH$_3$, J = 6 Hz), 1.40 (broad m, 1.10–2.10, 10 H, CH$_2$), 4.00 (t, 2 H, ArOCH$_2$, J = 6 Hz), 7.45 (m, ArCOO), 7.75 (m, 4 H, ArNO$_2$).

Anal. Calcd for C$_{20}$H$_{23}$NO$_5$: C, 67.21; H, 6.49; N, 3.92. Found: C, 67.15; H, 6.40; N, 3.93.

The 4-substituted-phenyl 4'-decyloxybenzoates were prepared according to the following procedure. To 5 mmol of the appropriate phenol (Aldrich) dissolved in 10 mL of dry pyridine was added 5 mmol of 4-decyloxybenzoyl chloride and the resulting solution stirred overnight. The product ester was then precipitated by addition of the reaction mixture to 500 mL of 3 N hydrochloric acid. The resulting mixture was stirred for 30 min, filtered, washed with water, air dried, and recrystallized at least twice from 95% ethanol. Yields of pure material ranged from 20 to 40%.

4-Methylphenyl 4'-Decyloxybenzoate (3a). K 55 S (50.5) N 59 I (lit.[14] K 56 S (51) N 60.5 I); IR (KBr) cm^{-1} 2918, 2850, 1725, 1606, 1285, 1275, 1260; ^{1}H NMR (CCl$_4$) δ 0.88 (t, 3 H, CH$_3$, J = 5 Hz), 1.29 (broad m, 1.10–2.10, 16 H, CH$_2$), 2.35 (s, 3 H, ArCH$_3$), 3.97 (t, 2 H, ArOCH$_2$, J = 6 Hz), 7.06 (m, 4 H, ArCH$_3$, 6.85–7.25), 7.45 (m, 4 H, ArCOO, 6.75–8.20).

4-Methoxyphenyl 4-decyloxybenzoate (3b). K 86 S (46) N (76.5) I; IR (KBr) cm^{-1} 2915, 2845, 1730, 1607, 1247, 1192, 1152, 1070; ^{1}H NMR (CCl$_4$) δ 0.92 (t, 3 H, CH$_3$, J = 5 Hz), 1.35 (broad m, 1.10–2.10, 16 H, CH$_2$), 3.98 (s, 3 H, ArOCH$_3$), 4.20 (t, 2 H, ArOCH$_2$, J = 6 Hz), 7.33 (m, 4 H, ArOCH$_3$, 7.05–7.65), 7.92 (m, 4 H, ArCOO, 7.15–8.65).

Anal. Calcd for C$_{24}$H$_{32}$O$_4$: C, 74.97; H, 8.39. Found: C, 74.86; H, 8.37.

4-Trifluoromethylphenyl 4'-Decyloxybenzoate (3c). K 72 S (72) I; IR (KBr) cm^{-1} 2920, 2850, 1740, 1730, 1605, 1332, 1260, 1170, 1121, 1060; ^{1}H NMR (CCl$_4$) δ 0.87 (t, 3 H, CH$_3$, J = 5 Hz), 1.29 (broad m, 1.10–2.10, 16 H, CH$_2$), 4.00 (t, 2 H, ArOCH$_2$, J = 6 Hz), 7.47, (m, 4 H, ArCOO, 6.80–8.25), 7.48 (m, 4 H, ArCF$_3$, 7.15–7.80).

Anal. Calcd for C$_{24}$H$_{29}$F$_3$O$_3$: C, 68.23; H, 7.41. Found: C, 68.09; H, 7.30.

4-Cyanophenyl 4'-Decyloxybenzoate (3d). K$_1$ 39 K$_{II}$ 78 S (77.5) N 84.5 I (lit.[15] no transition temperatures reported); IR (KBr) cm^{-1} 2910, 2845, 2210, 1742, 1600, 1247, 1158, 1060; ^{1}H NMR (CCl$_4$) δ 0.88 (t, 3 H, CH$_3$, J = 5 Hz), 1.30 (broad m, 1.10–2.10, 16 H, CH$_2$), 4.01 (t, 2 H, ArOCH$_2$, J = 6 Hz), 7.46 (m, 4 H, ArCOO, 6.80–8.20), 7.47 (m, 4 H, ArCN, 7.20–7.80).

Transition Temperatures. Transition temperatures (corrected) were determined with a Thomas metal stage polarized light microscope equipped with a Thomas Model 40 heating stage. In some cases a Thomas-Hoover capillary melting point apparatus was used. The transition temperatures reported were determined in the usual manner[2] in which the solid or mesophase has completely disappeared from the microscopic field.

Maxima in the mesophase-isotropic transition temperature curves of binary mixtures were conveniently determined using capillary tube

Table I. Transition Temperatures for the
4-Nitrophenyl 4'-Alkoxybenzoates[a]

no.	no. carbons in alkoxy chain	K-I	K-S$_A$	K-N	S$_A$-N	S$_A$-I	N-I
1a	1	166[b]					
1b	2	127					
1c	3	66[c]					(34.5)
1d	4	56.5					(45)
1e	5	59.5					(40.5)
1f	6			55	(40)		57.5
1g	7	63.5					(53.5)
1h	8		49[d]		60.5		67.5
1i	10		55[e]			77	
1j	12		64			82.5	
1k	14		71			86	
1l	16		76.5			87	

[a] Monotropic transitions are in parentheses. [b] F. M. Menger and J. H. Smith, *J. Am. Chem. Soc.*, **94**, 3824 (1972), report K → I temperature of 165–166 °C. [c] Reference 18. [d] G. Pelzl and D. Demus, *Z. Phys. Chem.* (*Leipzig*), **256**, 305 (1975), report K49S62N681. [e] This compound crystallizes from the melt to a metastable solid which upon heating transforms to the stable solid at 48 °C. Thus the equilibrium phase diagrams in ref 1a should not have included this metastable transition.

Figure 1. Plots of maxima in smectic–isotropic transition temperatures vs. alkoxy chain length as obtained in binary mixtures of the 4-nitrophenyl 4'-alkoxybenzoates, 1a–l, with 4-heptyloxybenzylidene-4'-butylaniline (2a) and with 4-octyloxybenzylidene-4'-butylaniline (2b).

mixtures.[1] In this method one component is packed in a melting point capillary, fused, and cooled and the second component is placed on top of the first. Mixing occurs in the region in which the two compounds make contact. Enhancement of the mesophase is then observable at the interface of the two components when the capillary tube is heated in a Thomas-Hoover capillary melting point apparatus. However, to be easily observable, the mesophase in the mixed region must be more thermally persistent then either of the pure components.

Phase Diagrams. Phase diagrams were determined semiquantitatively using the Kofler contact method.[16,17] In this procedure the two compounds are fused between a glass slide and a cover slip, and the region in which the two compounds make contact is taken to vary in concentration with distance from the pure compounds. Accordingly, the center of the mixed region is assumed to be of approximately 50:50 mole percent composition. Using a calibrated heating stage it is possible to accurately obtain temperatures at the intersections of three phases (triple points); maxima and minima in the transition curves; but not the compositions that correspond to these temperatures. For this reason the concentration axes of the phase diagrams are not graduated. The Kofler contact method has been used on occasion by Billard[17] in the classification and identification of smectic modifications based on miscibility. Many others have also used this method when it was desirable to obtain a large amount of information with a minimum expense of time. To ensure that our phase diagrams were reasonably accurate, carefully weighed 50:50 mole percent mixtures were prepared and examined. Maxima in the smectic–isotropic transition curves were often at or very near that composition.

Results and Discussion

Transition temperatures for the 4-nitrophenyl 4'-alkoxybenzoates are given in Table I. The first two members of the series, 1a and 1b, are not mesomorphic. Van Meter and Klanderman have reported synthesis of the propyloxy ester (mp 60–62 °C)[18] but did not report a mesophase. This is not too surprising as this compound tends to quickly crystallize on slow cooling from the isotropic liquid. We first observed its nematic phase under the polarizing microscope as it appeared from the isotropic on rapid cooling. The exact nematic–isotropic transition temperature was obtained by heating the sample in a capillary tube to the isotropic phase (alcohol lamp); cooling it in air to the nematic phase, as evidenced by the opacity of the sample; and quickly placing the capillary in the Thomas-Hoover melting point apparatus preset at a temperature slightly below the estimated nematic–isotropic temperature. The nematic phase is reasonably stable once it forms and the
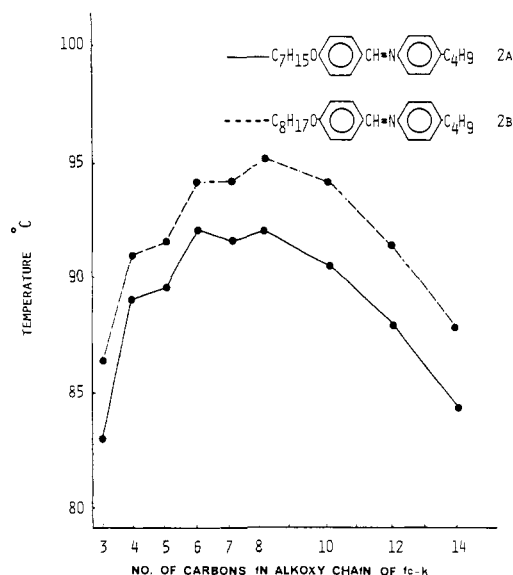
nematic–isotropic temperature is easily seen on further heating of the sample in the melting point apparatus. This again points up the importance of conceptualizing liquid crystal phase behavior in three-dimensional space, and recognizing kinetic phenomena in liquid crystal transitions.[19]

The homologous series of 4-nitrophenyl 4'-alkoxybenzoates fits a pattern in which mesophase–isotropic transition temperatures rise with increasing chain length. The lower homologues exhibit an even–odd effect, which diminishes as the number of carbons in the alkoxy groups approaches ten. Increasing transition temperatures in this type of series are attributed by Gray[20] to the fact that lateral attractions grow stronger as the alkoxy group is lengthened while the terminal attractions grow relatively weaker. The net result is a rising mesophase–isotropic curve, which levels off as the series terminates at 16 carbons. Conoscopic observations revealed a uniaxial smectic phase which is consistent with our classification of smectic A for this series.

Schiff's bases 2a and 2b were chosen as constant second

$C_7H_{15}O$—⟨⟩—CH = N—⟨⟩—C_4H_9 $C_8H_{17}O$—⟨⟩—CH = N—⟨⟩—C_4H_9

2a   2b
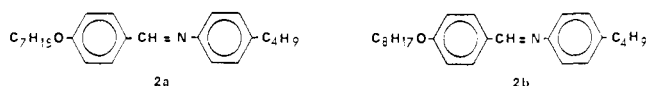
components for binary studies since they each possess a smectic A phase which has a temperature range compatible with those of the nitro esters.

Using the previously described capillary tube method (see Experimental Section), maxima in the smectic–isotropic curves of the binary mixtures of 1c–k with 2a and with 2b were conveniently determined. These maxima are given in Table II. Both sets of maxima are plotted vs. increasing chain length in Figure 1. Enhancement of the smectic A phase was so pronounced that mixtures of the lower homologues (which themselves possess only a monotropic nematic phase) with 2a and 2b exhibit a smectic phase which is more thermally persistent than either of the pure components. Although it is not obvious how one would quantitate the amount of enhancement of the smectic–isotropic transition temperature ($T_{S→I}$) for the lower homologues (these homologues have no smectic phase), it is clear that the greatest enhancement is found with lower members of the series. From Figure 1 it is seen that the intermediate length alkoxy groups (C_6–C_{10}) promote higher $T_{S→I}$,
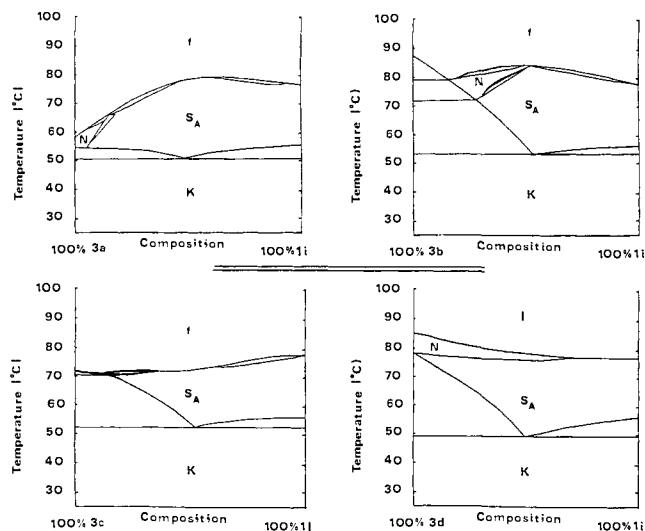
Figure 2. Binary phase diagrams obtained by the Kofler contact method for the following systems: 1i:3a; 1i:3b; 1i:3c; 1i:3d.

Table II. Maxima in Smectic–Isotropic Transition Temperatures Obtained upon Mixture of 4-Nitrophenyl 4'-Alkoxybenzoates (1a–1) with 4-Hexyloxybenzylidene-4'-butylaniline (2a) and with 4-Octyloxybenzylidene-4'-butylaniline (2b)

no.	carbon atoms in alkoxy chain	$T_{S \to I}$ (with 2a)	$T_{S \to I}$ (with 2b)
1a	1	*a*	*a*
1b	2	*a*	*a*
1c	3	83	86.5
1d	4	89	91
1e	5	89.5	91.5
1f	6	92	94
1g	7	91.5	94
1h	8	92	95
1i	10	90.5	94
1j	12	88	91.5
1k	14	84.5	88
1l	16	*a*	*a*

a Missing temperatures denote that one of the components of the mixture had a higher transition temperature than that of the mixed region. Consequently, no interfacial mesophase was seen.

with the octyloxy ester having the maximum in both Schiff's base mixtures. An even–odd alternation is found in $T_{S \to I}$ of these mixtures for lower members of the series. It is not unlikely that the methoxy and ethoxy esters could also have shown enhancement of binary smectic–isotropic transition temperatures had their melting points not been so much higher than the clearing points of 2a and 2b. The transition temperature diagram of maximum $T_{S \to I}$ vs. increasing chain length of the nitro esters 1a–1 when mixed with the hexyloxy Schiff's base (2a) is very similar in shape to the one obtained when they are mixed with the octyloxy Schiff's base (2b). As shown in Figure 1 the two plots do not intersect, the one for the hexyloxy Schiff's base (solid line) always lying several degrees below the plot for the octyloxy Schiff's base (dashed line). Any expected difference in the relative appearance of the two curves, due to the fact that one of the Schiff's bases has an even number (eight) of carbon atoms in its alkoxy chain while the other Schiff's base has an odd number (seven), was not observable. In each case the alkoxy chain of the nitro esters apparently exerts a controlling influence over the smectic–isotropic transition temperatures of the mixtures. Transition temperatures of accurately weighed mixtures showed that the maximum smectic–isotropic transition temperatures for these mixtures occurred when the composition was at or very close at 50:50 mole percent.

4-Substituted-Phenyl 4'-Decyloxybenzoate Mixtures. To further delineate structural features which promote nonideal solution behavior in liquid crystal mixtures, we synthesized a series of 4-substituted-phenyl 4'-decyloxybenzoates. The substituents used were –CH₃, –OCH₃, –CF₃, and –CN.

$X = CH_3(3a)$; $OCH_3(3b)$; $CF_3(3c)$; $CN(3d)$
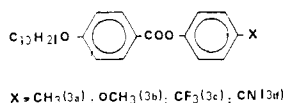
Mixtures of each of these compounds with 4-nitrophenyl 4'-decyloxybenzoate (1i) were examined. Deviation from ideal solution behavior (enhanced mesophases) in these mixtures must be due to electronic factors since all of the compounds in this study have, to a first approximation, the same molecular geometry. In Figure 2 are shown phase diagrams for the decyloxy nitro ester compound when mixed with the methyl (3a), methoxy (3b), trifluoromethyl (3c), and cyano (3d) compounds. Methyl and methoxy are two classical electron-donating substituents; trifluoromethyl and cyano, classical electron-withdrawing substituents. Differences among the

phase diagrams must have their roots in the nature of electronic interactions in these molecules. From Figure 2 it is seen that the methyl and methoxy mixed systems show enhanced mesophase–isotropic transition temperatures while the trifluoromethyl and cyano mixtures show linear, ideal solution behavior. We feel that the best explanation for this phase behavior is formation of some type of a weak molecular complex as has been variously described by Labes,[5e,7] Schroeder,[6] Cladis,[21] and ourselves.[1a] We envision a binary mesophase in which there are attractions between electron-rich molecules and electron-poor molecules ($CH_3:NO_2$, $OCH_3:NO_2$), possibly due to interaction between aromatic rings or between rings and –I substituents.[22] Mixtures of compounds which have substituents with similar electronic properties tend to show ideal solution behavior ($CF_3:NO_2$, $CN:NO_2$). Earlier work by Sackmann and Demus[5b] and by Labes[5e] has revealed congruent melting behavior in binary mesophase systems which exhibit nonlinear behavior. We[23] have also observed similar behavior in a binary mesophase which shows enhanced S → I temperatures. We feel that this is evidence of molecular complexation strong enough to overcome the normal tendency to exhibit eutectic behavior. The large majority of binary mesophase systems in which one finds enhanced mesophase–isotropic temperatures, however, do exhibit eutectic formation.

Acknowledgment. A.C.G. wishes to thank Research Corporation for generous support of this work.

References and Notes

(1) (a) For part 6 in this series see A. C. Griffin, T. R. Britt, N. W. Buckley, R. F. Fisher, S. J. Havens, and D. W. Goodman, "Liquid Crystals and Ordered Fluids", Vol. 3, R. S. Porter and J. F. Johnson, Ed., Plenum Press, New York, N.Y., 1970, p 61. (b) Taken in part from the M.S. Thesis of S. J. Havens, University of Southern Mississippi, 1978.

(2) G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals", Academic Press, New York, N.Y., 1962.

(3) A. C. Griffin and J. F. Johnson, *J. Am. Chem. Soc.*, **99**, 4859 (1977).

(4) The term "enhanced" here refers to a positive deviation in transition temperature from that calculated assuming a linear variation of mesophase–isotropic transition temperatures with concentration.

(5) (a) H. Sackmann and D. Demus, *Z. Phys. Chem. (Leipzig)*, **224**, 177 (1963); (b) ibid., **230**, 285 (1965); (c) J. S. Dave, P. R. Patel, and K. L. Vasanth, *Indian J. Chem.*, **4**, 505 (1966); (d) *Mol. Cryst. Liq. Cryst.*, **8**, 93 (1969); (e) J. W. Park, C. S. Bak, and M. M. Labes, *J. Am. Chem. Soc.*, **97**, 4398 (1975); (f) C. S. Oh, *Mol. Cryst. Liq. Cryst.*, **42**, 1 (1977).

(6) J. P. Schroeder and D. C. Schroeder, *J. Org. Chem.*, **33**, 591 (1968).
(7) J. W. Park and M. M. Labes, *Mol. Cryst. Liq. Cryst. Lett.*, **34**, 147 (1977).
(8) A. C. Griffin, unpublished work.
(9) L. Verbit, *Mol. Cryst. Liq. Cryst.*, **15**, 89 (1971).
(10) M. Sorai, T. Nakamura and S. Seki, *Pramana, Suppl. 1*, 503 (1975).
(11) (a) J. B. Flannery and W. Haas, *J. Phys. Chem.*, **74**, 3611 (1970); (b) P. R. Patel, *J. Indian Chem. Soc.*, **50**, 514 (1973).
(12) (a) J. Billard, *C. R. Hebd. Seances Acad. Sci.*, Ser. B, **280**, 573 (1975); (b) G. W. Smith and Z. G. Garlund, *J. Chem. Phys.*, **59**, 3214 (1973); (c) J. B. Flannery and W. Haas, *J. Phys. Chem.*, **74**, 3611 (1970).
(13) See paragraph at end of paper regarding supplementary material.
(14) J. S. Dave and R. A. Vora, *Pramana, Suppl. 1*, **447** (1975).
(15) A. P. Kovshik, Y. I. Denite, E. I. Ryumtsev, and V. N. Tsvetkov., *Kristallografiya*, **20**, 861 (1975).
(16) L. Kofler and A. Kofler, "Thermomikromethoden", Verlag Chemie, Weinheim/Bergstr., Germany, 1954.

(17) J. Billard, *Bull. Soc. Fr. Mineral. Cristallogr.*, **95**, 206 (1972).
(18) J. P. Van Meter and B. H. Klanderman, *Mol. Cryst. Liq. Cryst.*, **22**, 271 (1973).
(19) A. C. Griffin, *Mol. Cryst. Liq. Cryst. Lett.*, **34**, 141 (1977).
(20) (a) Reference 1, p 197 ff; (b) see G. W. Gray and P. A. Winsor, Ed., "Liquid Crystals and Plastic Crystals", Vol. 1, Ellis Horwood, Chichester, England, 1974, pp 116–121.
(21) We wish to thank Dr. P. E. Cladis for a preprint of this work.
(22) As pointed out by a referee we are unable a priori to rule out complexation through terminal groups themselves. Of interest in this regard is the fact that a mixture of cholesteryl palmitate and **1l** gives rise to a slightly enhanced $S_A \rightarrow I$ temperature. There is of course no aromatic ring in cholesteryl palmitate, but it does possess a carbonyl group which could participate in a charge transfer interaction.
(23) J. F. Johnson, G. J. Bertolini, and A. C. Griffin, Abstracts, Seventh North American Thermal Analysis Society Conference, St. Louis, Mo., Sept 1977, No. 24.

Valence Shell Electron Pair Repulsions and the Pauli Exclusion Principle

Michael B. Hall

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. Received May 2, 1977

Abstract: The basic tenet of the valence shell electron pair repulsion (VSEPR) model, that the Pauli exclusion principle determines the molecular geometry, has been examined by direct ab initio calculations on H_2O. The calculations include one-electron models, which have Pauli forces but no electron–electron repulsions, and Hartree models, which have electron–electron repulsion but no Pauli forces. The latter calculations strongly suggest that as the Pauli restriction is removed the H_2O angle decreases. This behavior, which is opposite that expected by VSEPR, indicates that the dominant Pauli repulsions in H_2O are between the bond pairs. The calculations show that the optimum hybridization is relatively independent of the H–O–H angle. Thus, the hybrids appear to have some intrinsic existence and are not formed solely to provide better O–H bonding and are not always directed toward the hydrogens. The intrinsic hybridization is shown to be controlled by the number of electrons in the valence shell. This result provides a connection between traditional localized valence concepts and Walsh's rule. The driving force for the formation of these hybrids is, of course, the system's desire to keep the lower energy 2s orbital as fully occupied as possible, i.e., as a lone pair. Thus, the stereochemical activity of the lone pairs is, in reality, the stereochemical activity of the 2s orbital. A simple model based on these concepts is useful in predicting the geometry of a variety of AH_n systems, particularly why the angles decrease so dramatically when a first-row central atom is replaced with one from the second row, i.e., from H_2O to H_2S.

Introduction

Of the two most popular models for rationalizing and predicting molecular structure, Walsh's rules[1] and valence shell electron pair repulsion (VSEPR),[2] only Walsh's rules have been subject to extensive theoretical investigation and justification.[3] Although VSEPR appears to work quite well, its physical basis is still unclear. Its basic assumption is that the Pauli exclusion principle forces electron pairs to occupy different regions of space. It is important to note that the repulsions between pairs of electrons are attributed to the Pauli principle (Pauli repulsions) and not to electrostatic repulsions. This assumption is based on the early work of Lennard-Jones, who showed that in the absence of all other forces, the Pauli principle will force particles of like spin to occupy different regions of space.[4] Recently, Thompson has presented a similar model as justification for VSEPR.[5]

For a real molecule the question is, will the Pauli principle still be the dominant factor in determining the geometry when there are other strong forces present. Several authors have justified VSEPR by comparing its predictions of the geometry with those of other models. Thus, Allen has shown that the VSEPR and Walsh's rules parallel each other.[6] The similarity between the predictions of extended Hückel theory and VSEPR has been pointed out by Bartell and Plato.[7] Schnuelle and Parr have made a connection between their valence bond

model and VSEPR,[8] while Nakatsuji has shown the equivalence of the results of his force model with VSEPR.[9] Comparisons have been made between VSEPR and accurate self-consistent field calculations with conflicting results. Trindle and Weiss, using the floating spherical Gaussian model, found that the total electron repulsion parallels the total energy.[10] They interpreted this as supporting the VSEPR model. However, Naleway and Schwartz, using a very large basis for calculations on H_2O, were not able to find an intuitively satisfying way of partitioning the total energy which would totally support VSEPR.[11]

However, none of these investigations has examined the actual physical basis of the VSEPR model itself. In the first direct study of the effect of the Pauli principle on the geometry, Bader and Preston have shown that its effect is in the opposite direction from that assumed by VSEPR, i.e., the Pauli principle has the effect of increasing the angles in H_2O and NH_3 from tetrahedral values rather than decreasing the angle as suggested by VSEPR.[12] In a recent paper, Bills and Snow have suggested that the previous work of Bader and Preston is open to ambiguous interpretation.[13] However, they agree with Bader and Preston that the Pauli principle is not responsible for the geometry of molecules. One of their key arguments is the fact that a one-electron model calculation for H_2O predicts a linear molecule. Their conclusion that one-electron models do not predict the correct geometry is at variance with the results of