Liquid Crystals. I. Stable Smectic Mixtures of 4,4'-Di-*n*-hexyloxyazoxybenzene and *p*-Nitro-Substituted Aromatic Compounds

J. P. SCHROEDER AND DOROTHY C. SCHROEDER

Department of Chemistry, The University of North Carolina at Greensboro, Greensboro, North Carolina 27412

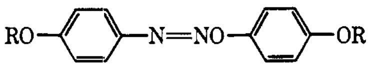
Received June 9, 1967

Mixtures of 4-nitro-substituted anils and 4,4'-di-*n*-hexyloxyazoxybenzene were found to have smectic mesophases which are much more stable than that of the pure azoxy compound. This was surprising in that the highly polar terminal nitro group would be expected to oppose rather than enhance formation of a smectic liquid crystal. The results can be explained, however, by invoking a head-to-head arrangement of the nitro-substituted molecules in the layer structure of the mixed smectic mesophase with the nitro groups adjacent to one another in the middle of each layer. For two of the nitroanils, stabilization of the mixed nematic mesophase was observed also. The molecular arrangement which is proposed to account for these phenomena is supported by the behavior of 4,4'-di-*n*-hexyloxyazoxybenzene–4-*n*-hexyloxynitrobenzene mixtures.

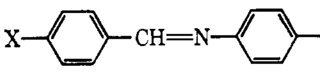
The liquid crystalline (mesomorphic) state[1,2] is a state of matter intermediate between crystalline solids and isotropic liquids. This phenomenon is exhibited by certain compounds with relatively rigid, polar, rod-shaped molecules which tend to be oriented with their long axes parallel owing to mutual attractive forces. On heating such a substance, the crystalline solid melts to an anisotropic liquid (the mesophase) in which adjoining molecules lie parallel to one another. At a still higher temperature, a sharp transition to the isotropic liquid occurs. Two common varieties of liquid crystals are the nematic and smectic types. Whereas nematic mesophases have only the parallel molecular arrangement, the molecules in smectic phases are not just constrained to be parallel but also to be arranged in layers with their long axes perpendicular to the layer planes.

This paper deals with liquid crystalline mixtures. As is true for other solids, a mesomorphic compound's melting point is depressed by addition of another substance and a mixed mesophase results in which the liquid crystalline range originates at a lower temperature. If the added substance is structurally dissimilar to the original compound, only a small amount suffices to destroy liquid crystallinity because of its disrupting effect on the mesophase.[3] If, however, it is structurally similar, liquid crystallinity may persist to a high concentration of the second component and, in fact, over all compositions if both components are mesomorphic.[4,5] This is reasonable in that rod-shaped, polar molecules, which meet the fundamental criteria for liquid crystallinity, would be expected to adapt more readily to the parallel molecular alignment in a mixed mesophase than bulky, nonpolar molecules.

In the course of studying a variety of mixed liquid crystals, it was observed that mixtures of 4,4'-di-*n*-hexyloxyazoxybenzene (Ib) with the *p*-nitro-substituted anils, 4-(4-methoxybenzylideneamino)nitrobenzene (IIa), 4-(4-nitrobenzylideneamino)anisole (IIb), and 4-(4-nitrobenzylideneamino)toluene (IIc), gave highly stable mixed smectic mesophases, much more stable, in fact, than the smectic mesophase of pure Ib. This result was unexpected. Typically, the molecule of a smectic compound is rod-shaped with polar groups along most of its length providing the lateral intermolecular attractive forces which are responsible for the parallel alignment of molecules in the mesophase but with *non*polar terminal groups. The latter have the effect of reducing end-to-end attractive forces between molecules so that, on melting, the characteristic layer structure of the smectic mesophase, in which the strata are free to move across one another, is obtained. The terminal groups are often long *n*-alkyl chains that not only provide end-to-end intermolecular "insulation" but also further enhance lateral attractive forces.[1] Ib is a good example, with polar azoxy and ether groups to provide lateral cohesive forces and nonpolar terminal *n*-hexyl groups. Thus, the observed increase in stability of the smectic mesophase on adding IIa, IIb, or IIc, compounds with a polar nitro group in the terminal position, to Ib was surprising and a more detailed examination of this phenomenon was undertaken.



Ia, R = CH_3
b, R = $n\text{-}C_6H_{13}$



IIa, X = CH_3O; Y = NO_2
b, X = NO_2; Y = CH_3O
c, X = NO_2; Y = CH_3

Experimental Section

Materials.—The *p*-nitro-substituted anils were prepared by boiling a solution of 2.0 g of amine, a 10% molar excess of aldehyde, and 10 drops of glacial acetic acid in 100 ml of absolute ethanol until half the solvent had distilled. The residue was cooled, the insoluble product separated by filtration, and recrystallized from ethanol. The results were as follows.

4-(4-Methoxybenzylideneamino)nitrobenzene (IIa) was obtained as yellow needles, mp 124.5–125°,[6] in 73% yield. This anil is sensitive to hydrolysis, recrystallization from 95% ethanol resulting in a drastic loss of material. Such behavior is reasonable in light of the weak basicity of 4-nitroaniline.

Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93. Found: C, 66.18; H, 4.74; N, 11.04.

4-(4-Nitrobenzylideneamino)anisole (IIb), yellow plates, mp 134.5–136° (lit. mp 136°,[3b] 134–135°[7]), and 4-(4-nitrobenzylidene-

---

[1] G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press Inc., New York, N. Y., 1962.

[2] G. H. Brown and W. G. Shaw, *Chem. Rev.*, **57**, 1049 (1957).

[3] (a) J. S. Dave and M. J. S. Dewar, *J. Chem. Soc.*, 4616 (1954); (b) *ibid.*, 4305 (1955).

[4] A. C. de Kock, *Z. Phys. Chem.*, **48**, 129 (1904).

[5] A. Prins, *ibid.*, **67**, 689 (1909).

[6] Reported to melt at 204–205° by J. R. Merchant, R. J. Shah, and R. M. Bhandarkar, *Rec. Trav. Chim.*, **81**, 131 (1962).

[7] O. K. Koz'minykh, *Uch. Zap. Permsk. Gos. Univ.*, **15**, (4), 111 (1958).

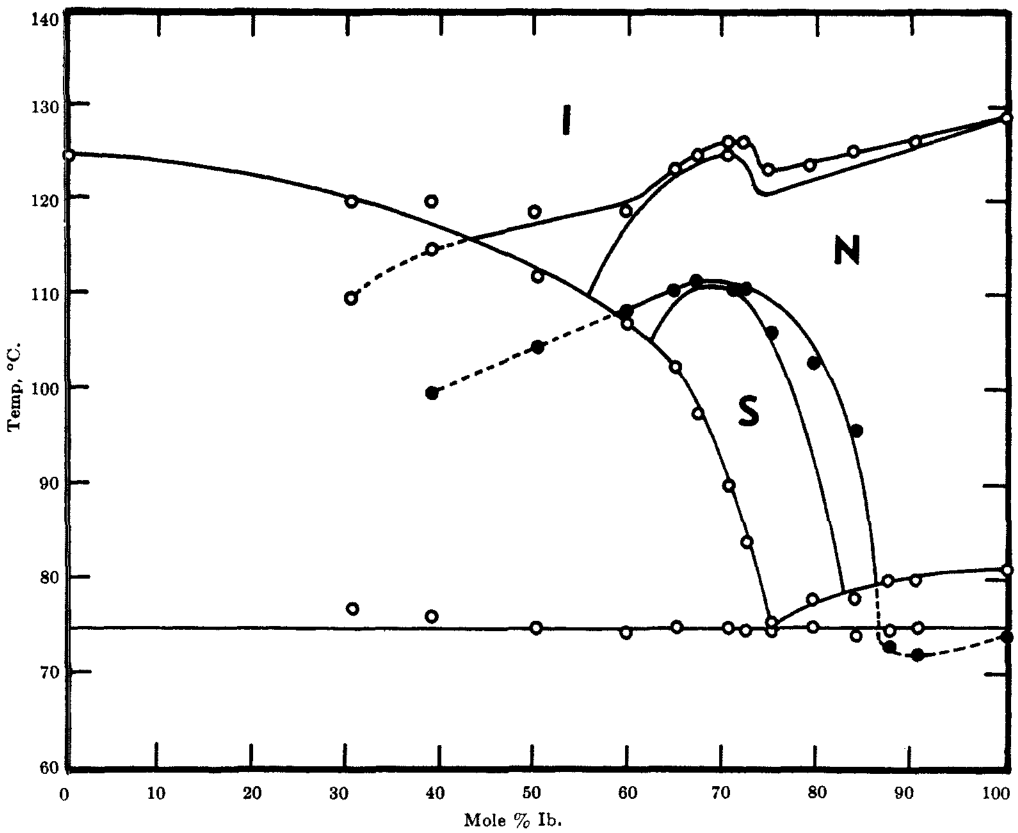


Figure 1.—Phase diagram of system 4,4′-di-*n*-hexyloxyazoxybenzene (Ib)–4-(4-methoxybenzylideneamino)nitrobenzene (IIa): I = isotropic, N = nematic, S = smectic.

amino)toluene (IIc), yellow plates, mp 123.5–124° (lit. mp 124°,[3b,8] 123.5–124.5°[9]), were obtained in yields of 93 and 95%, respectively.

4-*n*-Hexyloxynitrobenzene (IV) was prepared in theoretical yield from 4-nitrophenol and *n*-hexyl bromide by a method adapted from that of Gray and Jones.[10] After recrystallization from 95% ethanol, the product melted sharply at 25.5° (lit.[11] mp 26°).

4,4′-Di-*n*-hexyloxyazoxybenzene (Ib) was kindly provided by Professor M. J. S. Dewar and Mr. R. S. Goldberg, The University of Texas. It had been synthesized by lithium aluminum hydride reduction of 4-*n*-hexyloxynitrobenzene[12] and had the following transition temperatures: nematic → smectic, 74° (monotropic, on cooling from nematic melt), solid → nematic, 80.5–81°, nematic–isotropic, 129° (lit.[11] 72°, 81°, 127°).[13]

Procedure and Apparatus.—The mixtures for the phase studies were prepared by weighing the components accurately into a microbeaker, melting, stirring to give an intimate blend, and cooling with stirring until solidification occurred. Phase transitions were determined by observation of powdered samples on gradual heating in a Nalge-Axelrod melting point apparatus which had been calibrated against pure compounds of known melting points. In this instrument, the sample is confined between cover glasses in a metal heating block, illuminated from below by polarized light and viewed from above through a 25x microscope. There is a Polaroid analyzer in the rotatable eyepiece so that birefringence can be observed. The sample chamber takes a 22-mm-diameter cover glass whereas the viewing port is only 3 mm in diameter. An annoying tendency of the small samples to flow out of view at a crucial moment was obviated by using a small (12 mm diameter) cover glass on top which confined them to the region under the port.

The maximum heating rate was 1°/min. Smectic–nematic and nematic–isotropic transition temperatures were also studied on cooling. Most of the values obtained in this manner agreed with those determined on heating within 0.5°, but there were a few instances in which the cooling cycle value was lower by several degrees. This behavior has also been observed by Gray.[14] In particular, mixtures of Ib and IV displayed this behavior in the composition range 40–50 mole % Ib. In such instances, the higher (heating cycle) transition temperature is reported, the position being taken that we are dealing here with a metastable equilibrium condition analogous to the supercooling of a liquid below its freezing point.

Transitions from crystalline solid or mesophase to isotropic liquid were easily recognized by disappearance of birefringence. Solid–nematic transitions were obvious also because of the marked changes in birefringence and physical state. Smectic–nematic transitions were more difficult to discern but these mesophases often assume characteristic textures by which they are readily distinguished from one another and the smectic phase is always more viscous. Thus, even if both phases exhibit a homeotropic (nonbirefringent) texture, the transition can still be determined accurately because the mobile nematic liquid flashes spectacularly on agitation whereas the viscous smectic mesophase does not. The most difficult transitions to observe were solid → smectic melting points. Since solids generally soften before melting, this determination would seem to involve distinguishing between a soft solid and a highly viscous liquid, obviously a highly subjective decision. Fortunately, subtle differences in texture and birefringence made recognition of the phases possible.

Results and Discussion

Transition temperatures at various compositions for the systems Ib–IIa, Ib–IIb, Ib–IIc, and Ib–IV are listed in Table I and the phase diagrams plotted from these data are presented in Figures 1–4.

The smectic phase of Ib is stable only at 74° and below. Figures 1–3 show that, on incremental ad-

---

(8) W. Borsche and F. Sell, *Chem. Ber.*, **83**, 78 (1950).

(9) E. A. Smirnov and I. A. Korbukh, *Dokl. Akad. Nauk SSSR*, **160** (2), 373 (1965).

(10) G. W. Gray and B. Jones, *J. Chem. Soc.*, 1467 (1954).

(11) C. Weygand and R. Gabler, *J. Prakt. Chem.*, **155**, 332 (1940).

(12) M. J. S. Dewar and R. S. Goldberg, *Tetrahedron Letters*, **24**, 2717 (1966).

(13) Compounds Ib and IV are now commercially available from Frinton Laboratories.

(14) See ref 1, p 128.

TABLE I

TRANSITION TEMPERATURES OF MIXTURES OF 4,4′-DI-*n*-HEXYLOXYAZOXYBENZENE (Ib) AND *p*-NITRO-SUBSTITUTED COMPOUNDS

Compn, mole % of Ib	Transition temp, °C		
	Melting range	Smectic–nematic	Nematic–isotropic
System Ib–IIa			
0.0	124.5–125	. . .	. . .
30.2	77–120; *100.5, 105*[a]	. . .	(109.5)[b]
38.7	76–120; *104.5, 109*	(99.5)	(115)
49.9	75–112; *103.5, 109.5*	(104.5)	119
59.5	74.5–107; *104.5*	108	117–119
64.5	75–102.5	110–110.5	122.5–123.5
67.0	*c*; 97.5	111–111.5	124–125
70.3	75–90	109.5–110.5	124–125, 126.5
72.1	74.5–84	109.5–111	125.5–126.5
74.8	74.5–75.5	101.5–106	121–123.5
79.2	75–78	96–103	123–124
83.7	74–78	78–96	124.5–125.5
87.3	74.5–80; *78*	(73)	*c*
90.3	75–80; *78.5*	(72)	124.5–126.5
100.0	80.5–81	(74)	129
System Ib–IIb			
0.0	134.5–136	. . .	[91][d]
30.6	75–129.5; *c, 119*	. . .	(117.5)
39.5	74–126; *113, 118*	(106.5)	(118)
50.4	74.5–121; *111, 119*	(117.5)	126.5
58.9	74.5–117; *114*	118	124.5–127.5
70.1	75–110.5	116–118	128.5–129.5
75.7	74.5–105	110.5–112	129–129.5
80.4	73.5–83.5	103.5–105	129.5–130
82.1	74.5–79	79–104.5	*c*
83.4	75–77.5	79–98	*c*
84.9	75–78; *77*	(73)	129–129.5
92.2	75–80; *78*	Cr 73[e]	128.5–129
System Ib–IIc			
0.0	123.5–124	. . .	[57]
29.4	75–119; *108, 108*	. . .	. . .
39.4	75–112; *107, 108*	(103.5)	(109)
49.5	73–104	107–109.5	108–118
58.8	73–92	108.5–110.5	116–118.5
70.7	73	106–108.5	122–123.5
79.5	73–77	78–101	125.5–127.5
81.3	73–78; *77*	95.5	*c*
83.9	73–79; *78*	(73)	*c*
91.5	73–81; *77*	(72)	127.5–128.5
System Ib–IV			
0.0	25.5	Cr 10	Cr 10
4.8	24–25	. . .	. . .
10.4	24–45	Cr 35	Cr 35
19.9	24–68	Cr 63	Cr 63
30.0	69[f]	Cr 56	(58)
34.4	70.5	Cr 65	(68.5)
40.1	71	73[g]	74[g]
46.2	71.5	75	90.5[g]
55.3	74	76	85–95
65.3	76	78	84–105.5
74.3	79	(78)	104–110.5
82.6	79	(74)	110–116.5
90.2	80	Cr 72	118–121
94.6	80	Cr 76	123–126

[a] Figure in italics are the temperatures at which nematic and isotropic liquid first appeared in the melt. [b] Figures in parentheses refer to monotropic transitions observed only on cooling. [c] Not determined. [d] A number in brackets represents the virtual transition temperature of the compound obtained by extrapolation of the transition curve from the data of Dave and Dewar[3b] for its mixtures with 4,4′-dimethoxyazoxybenzene (Ia). [e] Entries of this type mean that the melt crystallized on cooling to the indicated temperature and, therefore, the pertinent monotropic transition could not be observed. [f] Because of the difficulty of operating at subambient temperature, the initial appearance of liquid was not measured for this and succeeding mixtures. [g] The smectic ranges in this system proved to be narrow and complex, involving the coexistence of smectic with nematic and/or isotropic liquids. The exact delineation of these combinations was beyond the precision of the experimental method. Therefore, only the temperatures for complete transition of the smectic to the nematic phase are given. For the same reason, two of the nematic–isotropic transitions are similarly reported.

dition of IIa, IIb, or IIc to Ib, the upper temperature limit of the mixture's smectic range at first drops slightly but then increases markedly at a higher concentration of anil (*ca.* 15 mole %) and passes through a maximum at approximately 30–40 mole % anil. These maxima in mesophase stability occur at 110–118°, much higher than the top temperature at which the smectic phase of pure Ib is stable.

An explanation of these unexpected results was not immediately apparent. As indicated earlier, a typical smectic compound has nonpolar end groups which "insulate" adjoining molecules, situated end to end, from one another and thus favor layer formation. The highly polar nitro substituent is, therefore, a most unlikely terminal group for a smectic compound and, to our knowledge, no compound with a nitro group in this position has ever been reported to be smectic. The enhancement of smectic phase stability in Ib by the *p*-nitro-substituted anils becomes understandable, however, on considering the relative lengths of the molecules in the mixtures and the dipolar interactions resulting from various steric arrangements.

The maxima in the smectic–nematic transition curves in Figures 1–3 suggest some sort of complex formation between Ib and the nitroanils in the smectic liquid by analogy with the familiar maxima in melting point curves of binary mixtures corresponding to compound formation in the solid state.[15] This concept is further supported by the sharpness of the transitions at the maxima relative to the gradual nature of the transitions for neighboring compositions. A reasonable molecular alignment for the mixed smectic mesophases which would provide an opportunity for such complexing is one in which the anil molecules are parallel to those of Ib in a head-to-head orientation with the nitro groups adjacent to one another in the middle of each layer. This arrangement is shown on p 594 in an idealized manner for the anil IIa; the other two cases are, of course, similar.

In this arrangement, the requirements for a stable smectic mesophase are realized; *i.e.*, there is an array of relatively rigid, rod-shaped, parallel molecules with polar substituents providing lateral attractive forces and nonpolar terminal groups which discourage end-to-end intermolecular attraction. The polar anil "dimer" apparently enhances the lateral attractive forces and a smectic mesophase which is more stable than that of pure Ib results.

This dimeric species is a logical postulate. Dipolar interactions of nitro compounds with one another and with other compounds have been well known for many

---

(15) A. Findlay, A. N. Campbell, and N. O. Smith, "The Phase Rule," 9th ed, Dover Publications, Inc., New York, N. Y., 1951, p 144 ff.

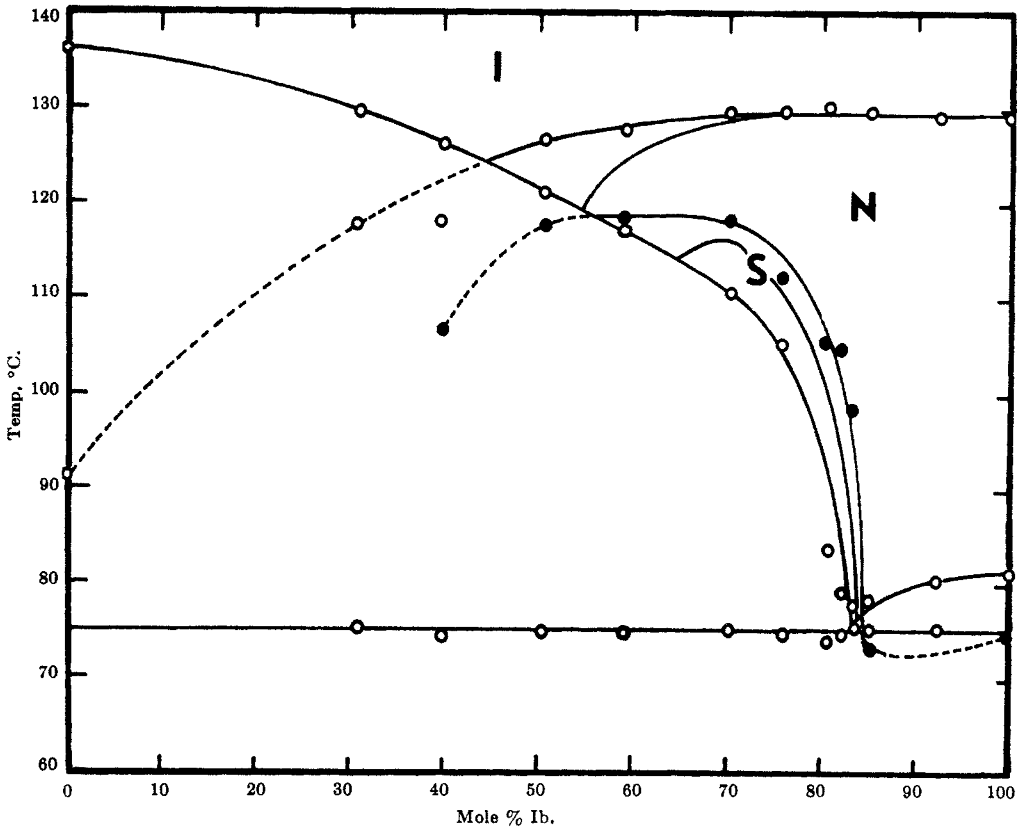
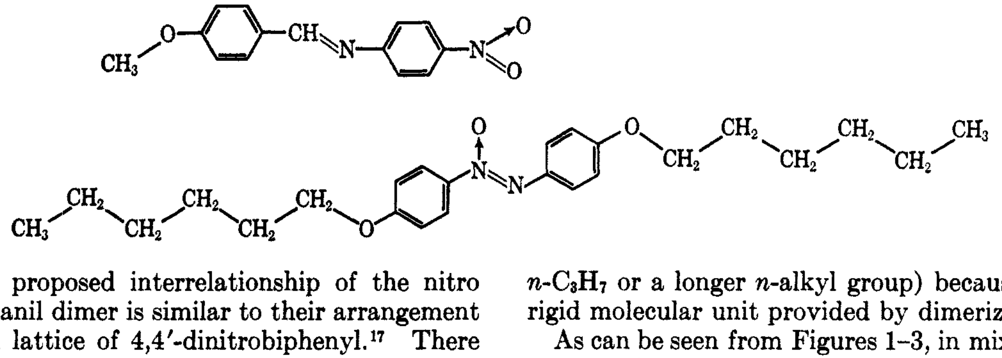
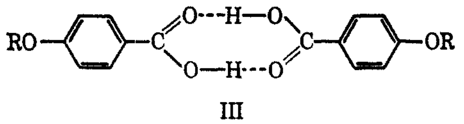


Figure 2.—Phase diagram of system 4,4′-di-*n*-hexyloxyazoxybenzene (Ib)–4-(4-nitrobenzylideneamino)anisole (IIb): I = isotropic N = nematic, S = smectic.



years.[16] The proposed interrelationship of the nitro groups in the anil dimer is similar to their arrangement in the crystal lattice of 4,4′-dinitrobiphenyl.[17] There is also an analogy between the nitroanil dimers and carboxylic acids which exhibit liquid crystallinity. A good example is the homologous series of *p*-*n*-alkoxybenzoic acids (III) which are mesomorphic (when R is *n*-C_3H_7 or a longer *n*-alkyl group) because of the long, rigid molecular unit provided by dimerization.[18]



III

As can be seen from Figures 1–3, in mixtures with Ib, the anils have a disrupting effect on the smectic mesophase at low concentrations, probably because they do not form the linear, head-to-head dimer appreciably under these conditions. The presence of single anil molecules interspersed among molecules of Ib would be expected to disrupt the mesophase owing to their dissimilar lengths. Apparently, as the anil concentration is increased, the polar dimeric structure is formed and acts to buttress the smectic mesophase. Then an optimum composition is attained beyond which mesophase stability decreases, reflecting the inability of the

---

(16) N. V. Sidgwick, T. W. J. Taylor, and W. Baker, "The Organic Chemistry of Nitrogen," Oxford University Press, London, 1942, p 264.

(17) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961, p 176.

(18) G. W. Gray and B. Jones, *J. Chem. Soc.*, 4197 (1953).

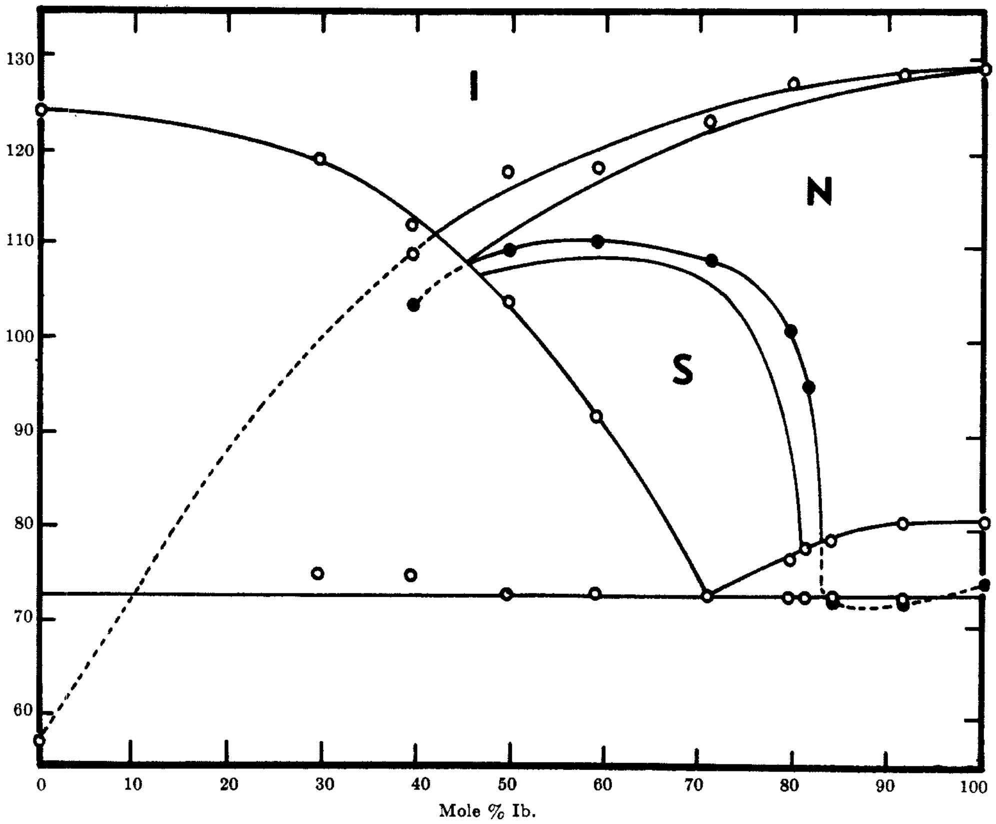
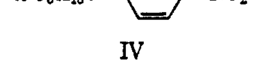


Figure 3.—Phase diagram of system 4,4′-di-*n*-hexyloxyazoxybenzene (Ib)–4-(4-nitrobenzylideneamino)toluene (IIc): I = isotropic, N = nematic, S = smectic.

anil to sustain a smectic molecular arrangement on its own. Thus, both the anil and Ib contribute synergistically to the high mesophase stability at the optimum composition. As indicated above, the contribution of the anil is undoubtedly to increase lateral intermolecular attractive forces. That of Ib would appear to be twofold: provision of a molecular matrix in which the anil dimer is formed readily and the insulating effect of its terminal *n*-hexyl groups.

In order to gain a better insight into the nature and relative importance of these influences and to test the above explanation for the behavior of Ib–nitroanil mixtures further, a simpler system was studied. By our hypothesis, the head-to-head linear dimeric form of 4-*n*-hexyloxynitrobenzene (IV) should have properties similar to those of Ib, including a smectic mesophase of comparable stability, because of their close structural resemblance. IV has a melting point (25.5°) which is much lower than that of Ib and does not exhibit mesomorphism even on supercooling the isotropic melt to 10°, which is consistent with our expectation that there would be little, if any, dimer in the pure compound. In mixtures of IV with Ib, however, we would expect the latter to provide a molecular matrix conducive to the formation of dimeric IV and, in some optimum composition range, a mixed smectic mesophase with much the same properties as smectic Ib should result. On constructing the Ib–IV phase diagram (Figure 4), we were somewhat surprised to find that the components are not readily miscible, as shown by the very gradual decrease in melting point with increasing IV, but gratified to see that they form a mixed smectic mesophase which is similar in stability to that of pure Ib as predicted.



IV

The results are in complete accord with the postulated molecular arrangement. The slightly greater stability of the mixed smectic mesophase at the optimum composition, which is again about 30–40 mole % of the nitro compound, relative to smectic Ib reflects the enhanced lateral attractive forces provided by the nitro groups. The much greater stabilizing effect of the nitroanils demonstrates that the benzylidenamino moiety makes the major contribution to the powerful dipolar interactions which are responsible for the marked mesophase stabilization by these compounds. Apparently, the role of the nitro groups is mainly to position the dimer properly in the mesophase by dipolar interaction with the azoxy linkage in Ib.

In Figure 1 (system Ib–IIa), it will be seen that there is also a peak in the nematic–isotropic curve and the transitions in this region are sharp. These phenomena indicate complex formation between Ib and IIa in the *nematic* liquid. Furthermore, since this peak and the maximum in smectic mesophase stability occur at the same composition, it appears that the same complex is responsible for both. However, there must be some sort of disaggregation on passing from the viscous smectic to the more fluid nematic mesophase. We propose that the smectic → nematic transition at the peak composition involves the breakdown of the layer structure into bundles of parallel molecules with their ends still constrained to be in line (the proposed com-

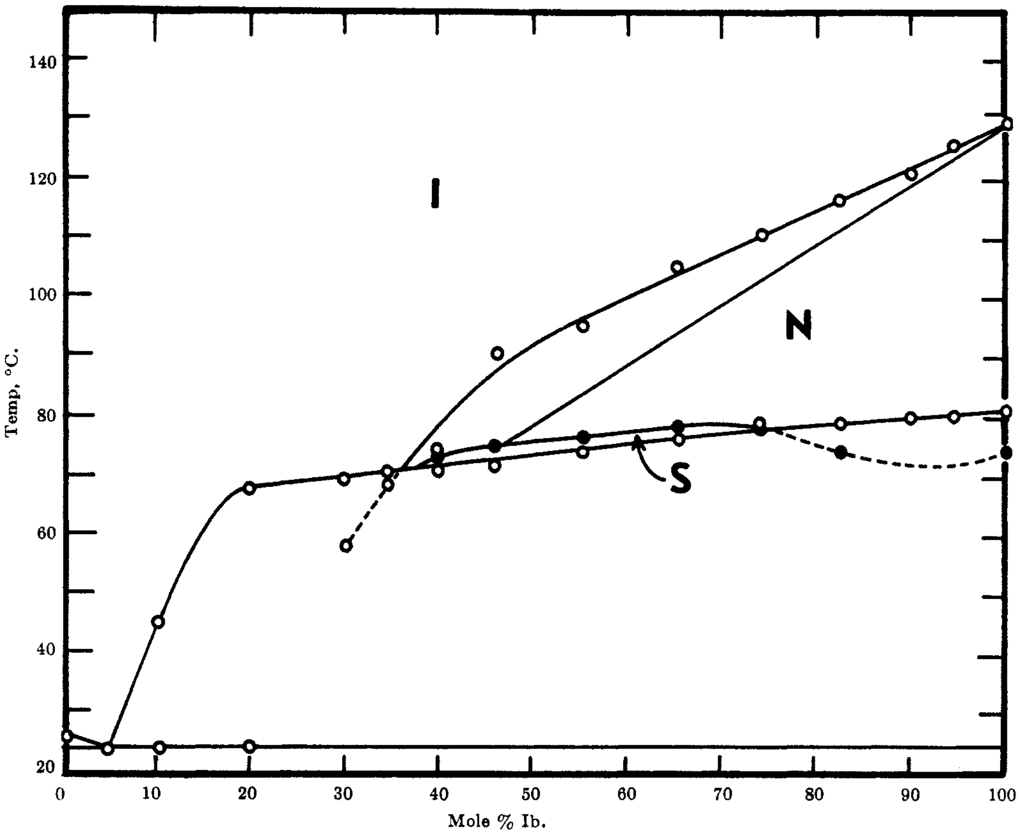
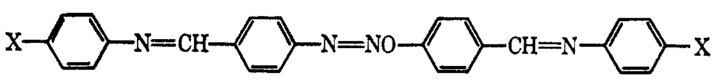


Figure 4.—Phase diagram of system 4,4′-di-*n*-hexyloxyazoxybenzene (Ib)-4-*n*-hexyloxynitrobenzene (IV): I = isotropic, N = nematic S = smectic.

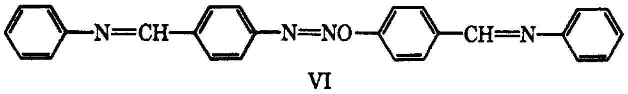
plex could not survive movement of the molecules with respect to each other in the direction of their long axes). The molar composition of this mixture suggests also that each bundle consists of four to five molecules of Ib parallel to and clustered around a linear dimer of IIa. Presumably, the rod-shaped bundles are oriented with their long axes parallel just as are the individual molecules in a conventional nematic mesophase.[19] The nematic → isotropic transition, then, can be pictured as the disruption of the bundles into randomly oriented molecules. No clear-cut peak in the nematic–isotropic curve was obtained for the other systems which were studied but a very broad maximum can be discerned at about 80 mole % Ib in Figure 2.

Maxima in the smectic–nematic transition curves of mixtures have been observed before by Sackmann and his associates in their extensive investigation of binary liquid crystalline systems.[20] In these instances, both components of the systems were mesomorphic (smectic and nematic) and, although no explanation for the maxima was offered, they must also be due to enhanced lateral intermolecular attractive forces in the mixtures compared with those available in either pure component; *e.g.*, the binary systems Va–Vb and Va–Vc were found by these authors[20b,d] to have phase diagrams with a marked maximum in the smectic–nematic transition curve at the equimolar composition. A plausible explanation for this behavior is that the electron-withdrawing Cl substituents in Va make the aromatic rings to which they are attached positive with respect to the analogous rings in Vb or c. The resulting interaction between these rings would encourage an end-opposite-end, *i.e.*, a smectic molecular arrangement. The Va–Vc system had the more stable mixed smectic mesophase and its melting point curve showed compound formation (undoubtedly a charge-transfer molecular complex) whereas the Va–Vb system's did not. These facts are consistent with the presence of the electron-donating CH_3 groups in Vc which would enhance the intermolecular attraction.

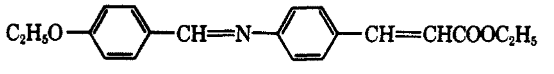


Va, X = Cl
b, X = H
c, X = CH_3

One of the systems (VI–VII) described by Sackmann and his collaborators[20b] exhibited maxima in *both* the smectic–nematic and nematic–isotropic transition curves



VI



VII

---

[19] It would be interesting to measure the viscosity of the nematic liquid at this composition which should be higher than that of a "normal" nematic mesophase owing to the bulky multimolecular unit. Actually, such a liquid can be thought of as a smectic–nematic hybrid since its molecular organization has features resembling both types of mesophase.

[20] (a) H. Arnold and H. Sackmann, *Z. Phys. Chem.*, **213**, 137 (1960), and subsequent papers, in particular, H. Sackmann and D. Demus, *ibid.*, (b) **224**, 177 (1963); (c) **227**, 1 (1964); (d) **230**, 285 (1965).

at the same composition, a situation similar to that in Figures 1 and 2. While we have no detailed explanation for this, it is interesting that the peak composition is about 80 mole % VI which at least allows for the possibility of a molecular bundle unit in the nematic mesophase similar to the one that we have proposed in which four molecules of VI are clustered around one of VII.

Several other features of our data merit comment. There has been disagreement as to whether nematic-isotropic transitions of binary systems occur sharply or over a temperature range.[21] The question is incidental to the main theme of this paper, but our results indicate a significant temperature range for such transitions so clearly in most cases that it must be mentioned here. The range becomes larger as the concentration of the nonmesomorphic component increases except at a maximum in the transition curve. The data also show that the smectic-nematic transitions are not sharp with the same exception. Other workers have obtained similar results.[20]

The nematic-isotropic transition curves in Figures 2 and 3 extrapolate nicely to the virtual transition temperatures for pure IIb and IIc provided by analogous data for mixtures of these anils with 4,4′-dimethoxyazoxybenzene (Ia) reported by Dave and Dewar.[3b]

In the system Ib-IIb (Figure 2), a second smectic phase was found for mixtures in the composition range 80.4-84.9 mole % Ib. The monotropic smectic-smectic transitions, which were observed on cooling the melts to 73-79°, are not included in the phase diagram because of the congestion of data points in this region.

Registry No.—Ib, 15450-65-4; IIa, 15450-66-5; IIb, 5455-87-8; IIc, 703-39-2; IV, 15440-98-9.

Acknowledgments.—This work was supported in part by a grant-in-aid from The University of North Carolina at Greensboro Research Council. The elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

---

[21] See ref 1, p 127 ff.

The Preparation and Properties of Cyclic Six-Membered Silicon Compounds[1]

ROBERT A. BENKESER, STANLEY D. SMITH, AND JAMES L. NOE

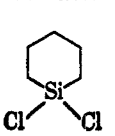
Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received July 6, 1967

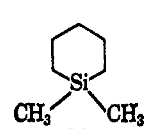
The reaction of 1,1-dichlorosilacyclohexane and 1,1-dimethylsilacyclohexane with sulfuryl chloride was studied. The chlorination of 1,1-dichlorosilacyclohexane caused little opening of the ring which was extensive during the chlorination of 1,1-dimethylsilacyclohexane. The distributions of isomers obtained from these cyclic silanes were compared with those obtained by chlorination of *n*-alkylchlorosilanes. Chlorine atoms on silicon disfavor free-radical chlorination on carbon atoms directly attached to such a silicon both in linear and cyclic silanes. Dehydrohalogenation was carried out on the monochlorinated 1,1-dichlorosilacyclohexanes with quinoline, ferric chloride, and pyrolysis.

In a continuation of our studies concerned with the preparation and properties of cyclic sila olefins,[2] the free-radical chlorination of 1,1-dichloro- and 1,1-dimethylsilacyclohexane was studied to obtain workable quantities of monochlorinated intermediates which would lend themselves to the formation of silacyclohexenes by dehydrohalogenation.

Our attention was first directed to the chlorination of 1,1-dichlorosilacyclohexane (I) since reports concerning the chlorination of 1,1-dimethylsilacyclohexane (II) had already appeared,[3] although the results were still somewhat unclear.

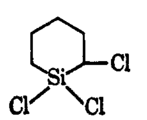


I

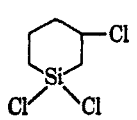


II

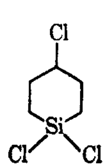
Treatment of I with sulfuryl chloride and benzoyl peroxide resulted in a good yield of monochlorinated product. Complete separation of the isomers by vpc was not achieved completely, despite the use of many different analytical columns[4] and conditions. It was possible by this analytical method, however, to estimate that the 2-chloro isomer[4] (III) comprised about 19% of the reaction product. This value was corroborated by the nmr spectrum[5] of a reaction mixture consisting of compounds III, IV, and V. By comparison of the relative peak areas of the methine hydrogens in these three compounds, a value of 22% for III was obtained. Indirect methods were devised to determine the relative percentages of IV and V.



III



IV



V

Direct titration of a redistilled sample of the monochlorinated isomers for hydrolyzable chlorine gave a value of 58% for compound IV. This value is based on the assumption that only the β isomer (IV) will provide 3 equiv[6] of hydrochloric acid, while III and V will pro-

---

[1] Part V of a series on cyclic silicon compounds. Part IV: R. A. Benkeser and R. F. Cunico, *J. Org. Chem.*, **32**, 395 (1967).

[2] (a) R. A. Benkeser, Y. Nagai, J. L. Noe, R. F. Cunico, and P. H. Gund, *J. Am. Chem. Soc.*, **86**, 2446 (1964); (b) R. A. Benkeser, J. L. Noe, and Y. Nagai, *J. Org. Chem.*, **30**, 378 (1965); (c) R. A. Benkeser and R. F. Cunico, *J. Organometal. Chem.*, **4**, 284 (1965).

[3] R. Fessenden and F. J. Freenor, *J. Org. Chem.*, **26**, 2003 (1961); R. J. Fessenden and J. S. Fessenden, *ibid.*, **28**, 3490 (1963).

[4] Approximately 20 different columns were tried. The best separation which could be achieved resulted in two peaks. The first peak was pure 1,1,2-trichlorosilacyclohexane and the second was a mixture of 1,1,3- and 1,1,4-trichlorosilacyclohexanes.

[5] The methine hydrogen of III is quite characteristic at about τ 6.41 and lies upfield from the methine hydrogens of IV and V.

[6] L. H. Sommer and F. C. Whitmore, *J. Am. Chem. Soc.*, **68**, 485 (1946).