THERMOTROPIC LIQUID CRYSTALS IN THE HETEROCYCLIC SERIES (REVIEW)

V. V. Titov and A. I. Pavlyuchenko

UDC 532.783:547.7/8

The available literature data on mesomorphic compounds that contain heterorings are correlated, and a brief account of the general concepts of liquid crystals and their types and properties is given. The liquid crystal properties of mesogenic derivatives of six-membered nitrogen-containing heterocycles are compared with the properties of their benzene analogs. The chief requirement for the potentially mesogenic molecule, viz., a high degree of geometrical "anisotropy," is illustrated in the case of five-membered and condensed heterocycles.

Compounds that, in the fused state over a certain temperature range, partially retain the elements of orderliness that are peculiar to crystals are called thermotropic liquid crystals, as well as mesomorphic or mesogenic compounds (see [1] for a detailed discussion). This orderliness is displayed only in microparticles of the liquid crystal, the chaotic location of which in the mass imparts the form of a turbid liquid to it. A liquid "single crystal" with anisotropy of all of the physical properties, the control of which by external forces constitutes the basis of numerous applications of liquid crystals, is formed only in thin, specially oriented layers of the substance.

The properties of liquid crystals that determine their practical usefulness and should be taken into account in purposeful searches include the type of mesophase, the temperature of the phase transitions, the sign and magnitude of the dielectric anisotropy, the electric field frequency at which this sign undergoes inversion, the optical anisotropy, and a number of other properties that are specific for a certain form of application.

Heterocyclic liquid crystals may play a large role in ensuring these properties, and in the present paper we have set out to not only correlate the literature data on heterocyclic mesogens, but also to attract the attention of chemists engaged in research on heterocycles.

General Properties of Liquid Crystals

One of the general characteristics of thermotropic liquid crystals is their thermal stability. The clarification temperature, i.e., the point at which a phase transition from the mesomorphic state to an isotropic liquid occurs, may serve as a measure of this thermal stability. In most of the known liquid crystals, which are called enantiotropic liquid crystals, the clarification temperature lies above the melting point (or the formation of a mesophase). In this case the temperature range over which the mesophase exists, which varies from units to hundreds of degrees Celsius, is an important characteristic of liquid crystals that determines their practical usefulness. When the thermal stability of the mesophase lies below the melting point (when it is determined by the reproducible temperature of the formation of the mesophase during supercooling of the melt), the liquid crystal is called monotropic. For practical use one usually looks for liquid crystals with as low a melting point as possible (below 20°C) and relatively high thermal stability of the mesophase (above 60°C). Individual compounds with such characteristics are extremely rare, and mixtures of them are therefore most often used. One usually looks for a eutectic composition with the minimal melting point. Since the clarification temperature of the mixture is approximately a linear function of its composition, monotropic liquid crystals can also be used in a mixture with thermally stable components.

Another important property of liquid crystals that is responsible for the realization of various electrooptical effects (see [2] for details) is their dielectric anisotropy ε_a (or $\Delta\varepsilon$), which is defined as the difference in the dielectric constants of the liquid crystal parallel to the direction of the molecules (or, more precisely, their long axes or the

---

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 3-18, January, 1980. Original article submitted May 17, 1979.

"director") in the oriented layer ($\varepsilon_\parallel$) and perpendicular to it ($\varepsilon_\perp$). Depending on the type of electrooptical effect, liquid crystals with either negative dielectric anisotropy (NDA) ($\varepsilon_a < 0$) or with positive dielectric anisotropy (PDA) ($\varepsilon_a > 0$) or a mixture of them are necessary. The sign and magnitude of the dielectric anisotropy depend on the direction and magnitude of the dipole moment constant of the mesogenic molecule, and these characteristics can be changed deliberately by incorporating polar groups in the molecule.

Sometimes it is necessary to know such characteristics of liquid crystals as the anisotropy of the refractive index, the viscosity, the optical transmittance, and the wavelength of the selective reflection of light and its temperature dependence (for cholesteric liquid crystals) and be able to change them deliberately.

Classification of Liquid Crystals

Nematic, cholesteric, smectic, and discoidal liquid crystals differ with respect to the manner and degree of orderliness of the molecules. In addition to the latter type, a principal general requirement for the potential formation of a mesomorphic state is a high degree of geometrical "anisotropy" of the molecule that ensures its rod-shaped form.

Nematic liquid crystals (NLC) are characterized by an approximately parallel orientation of the molecules in the "single crystal," which move freely in all three directions with retention of the direction of the "director" and rotate about the long molecular axis. Nematic liquid crystals with negative dielectric anisotropy are used in electrooptical devices that operate on the principle of dynamic light scattering (turbulent motion of aggregates of the molecules under the influence of an electric current) and for the creation of other types of materials. Nematic liquid crystals with positive dielectric anisotropy are widely used in devices that utilize field orientation effects.

Cholesteric liquid crystals (CLC) are a modification of nematic liquid crystals and are formed by optically active molecules. The orientation of the molecules in CLC can be represented as approximately parallel in a monomolecular layer with turning of the "director" in each successive layer at a certain angle with respect to the preceding layer such that the layers form a helix with a pitch (P), the magnitude of which depends on the nature of the CLC and may change under the influence of the temperature, pressure, fields, etc. If the P value is comparable to the wavelength of light in the visible region, a change in it is accompanied by a change in the wavelength of the selectively reflected light, and such liquid crystals are used in color thermography. The electrooptical effects of CLC that are realized in materials with selective reflection of light in the UV and IR regions have also found application.

Smectic liquid crystals (SLC) (eight types) consist of freely sliding parallel layers with a thickness of one or two molecules that are oriented orthogonally to the plane of the layer or inclined toward it.

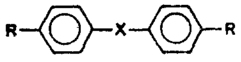
Within a layer the molecules may either move freely relative to one another in two directions (smectics A and C) or form a hexagonal lattice (B and H). Smectic liquid crystals may also have a cubic lattice (D) or form more nearly perfect packings of the molecules (F, G, and E). The inclined smectic forms (C and H) formed by chiral molecules have layers that are turned along the spiral relative to one another at a certain angle and have Seignette-electrical properties. Functional groups that reinforce the side-chain intermolecular interactions promote the formation of SLC. Of the SLC, mesophase A, which is used for the realization of a thermooptical effect in controllable transparencies and an electrothermooptical effect in matrix screens of the television type, has found practical application.

Discoidal liquid crystals are formed by hexasubstituted benzene [3] or triphenylene [4] derivatives and are stacks of discoidal molecules, which in turn form a hexagonal structure.

Heterocyclic Liquid Crystals

As compared with the thousands of known liquid crystals of the benzene series, the several hundred known heteroanalogs clearly are not sufficiently representative of the possibilities of the chemistry of heterocyclic compounds. The presence of a heteroatom may have a strong effect on the polarity and polarizability of the molecule, the angle of rotation between its fragments, and thereby on the temperatures of the phase transitions. In addition, the heteroatoms may participate in intermolecular interactions and affect the type of mesophase. Finally, by influencing the direction and magnitude of the dipole moment constant of the molecule, the heteroatom may affect the sign and magnitude of the dielectric anisotropy of the liquid crystal.

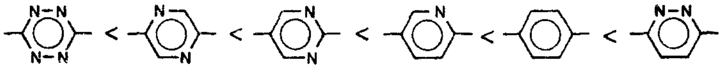
Let us compare liquid crystal compounds that contain six-membered nitrogen heterorings with their benzene analogs. The effect of replacement of the benzene ring by a heterocyclic ring was studied by Gray [9, 65], while Schubert [6] made a detailed comparison of the properties of compounds with general formula I, where R is an alkyl group, and X is a pyridine,



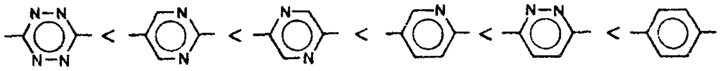
I

pyrimidine, pyridazine, pyrazine, or tetrazine ring. The changes in the thermal stabilities of the mesophases of these compounds cannot be interpreted by a change in the diameter of the molecules or the dipole constant or by the angle of rotation between the rings. Compounds that contain a pyridine or pyrimidine ring differ from the other systems with respect to their greater tendency to form smectic mesophases, and they have the lowest relative melting points. In these compounds one of the phenyl rings occupies the β position relative to the heteroatom, in which the π interaction between the rings decreases because of the repulsion between the ortho protons [7] with an attendant decrease in the molecular polarizability and the thermal stability of the crystal lattice.

For the indicated series of compounds the thermal stabilities of the smectic mesophases decrease in the following order of central fragments:

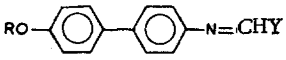


The thermal stabilities of the nematic mesophases decrease in the following order of central fragments:



The difficulties in the prediction of the thermostability of the mesophase are not simplified for pyridine. Both the temperatures of the phase transitions and the ability to form a smectic or nematic phase change as a function of the position and nature of the substituents in the pyridine or benzene ring of the two-ring mesogens, as well as of the nature of the central grouping between the rings.

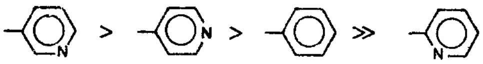
Attempts have been made [7, 8] to analyze the effect of the pyridine ring on the mesomorphism of compounds of the II type (Fig. 1). It is apparent from Fig. 1 that the nematic



II

R = alkyl, Y = phenyl or pyridyl

and smectic thermal stabilities of these compounds decrease in the order



Nash and Gray [7] and Young and co-workers [8] explain the low thermal stabilities of 2-substituted pyridines by means of interaction of the electron pair of the heteroring nitrogen atom with the electrons of the azomethine bond; this weakens the π interaction and increases the angle between the CH=N bond and the heteroring. As a consequence of this, the smectogenic properties vanish, and a decrease in the polarizability of the molecule leads to low stability of the nematic phase. The low melting points of these derivatives are also explained by turning of the heteroring. The lower stabilities of the mesophases of 4-pyridine derivatives as compared with 3-pyridyl derivatives were explained by intermolecular repulsion between the electron pair of the heteroatom of one molecule and the electron pair of the oxygen atom of the methoxy group of the other. This effect is smaller for the octyloxy derivative because of the large separation between the nitrogen and oxygen atoms.

In the case of the analogous Schiff bases obtained for benzidine, a mesophase is completely absent for the 4-pyridyl derivative [7]; this might have been expected because of the maximal electrostatic repulsion between the ends of adjacent molecules. A mesophase is also absent in the case of 2-substituted pyridine.

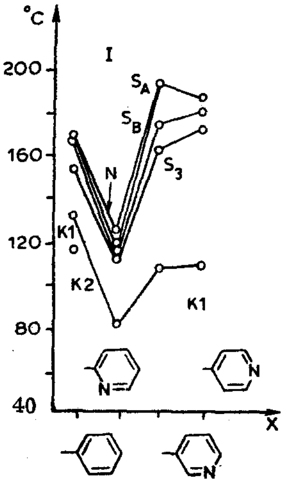
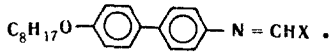
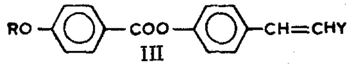
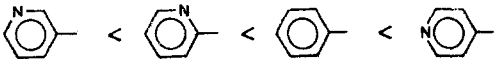


Fig. 1. Temperatures of the phase transitions of  .

Different regularities in the order of the increase in the thermal stability of the nematic phase are observed when a vinyl residue is the central grouping [7]. Thus for compounds with formula III


III

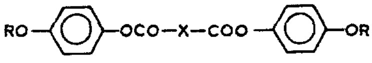
the nematic thermal stability decreases in the order



One's attention is directed to the very low nematic and crystalline thermal stabilities of the 3-pyridyl derivatives. It is assumed [7] that the introduction of a heteroatom in the 3 position leads to a decrease in the conjugation of the terminal ring with the remainder of the molecule, thereby decreasing the overall polarizability. This effect was not observed in the case of Schiff bases, in which it is known that the aromatic rings are not coplanar.

The use of six-membered nitrogen heterorings in the mesogenic molecule changes the geometry of the molecules only slightly as compared with the benzene analogs. However, the position of the heteroatom has a substantial effect on the polarizability of the molecule, the dispersion forces, the dipole moment constant of the molecule, and, consequently, on the dielectric properties of the liquid crystal. Thus, the dielectric anisotropy of the liquid crystal may have positive and negative values, depending on the position of the heteroatom in the mesomorphic derivatives. When the direction of the dipole moment makes an angle of close to 90° with the long molecular axis, the liquid crystal has negative dielectric anisotropy (e.g., in the case of mesomorphic derivatives of pyridazine). Molecules with a dipole directed along the molecular axis form a liquid crystal with positive dielectric anisotropy (e.g., pyrimidines). Of course, in this case one must also take into account the group dipole moments of the remaining fragments of the molecule.

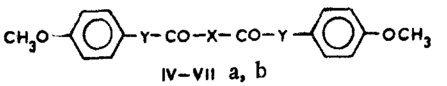
It has been assumed [9] that an increase in the polarity and polarizability of the central fragment of an elongated molecule should lead to an increase in the thermal stability of the mesophase due to intensification of the side-chain interactions. However, a comparison of a large number of mesomorphic compounds provides evidence that geometrical "anisotropy" (the ratio of the long and short axes of the molecule) is the most important factor in the determination of the stability of the mesophase and that the degree of unsaturation and polarity play only a secondary role. Thus in the series of compounds



R = alkyl, X = p-phenylene, 2,5-pyridylidene, trans-1,4-cyclohexylidene

the temperatures of the transitions from the nematic state to the isotropic liquid were found to be close [10, 11, 66].

In confirmation of this conclusion, it is interesting to compare benzenoid liquid crystals with the analogous furan (IVa, b and Va, b) and thiophene (VIa, b and VIIa, b) derivatives, in which the molecule undergoes "broadening" due to deviation of angle θ between the terminal fragments of the molecule from 180° (θ is, respectively, 137, 160, 148, and 140°), and the geometrical "anisotropy" consequently decreases [11]. The thermal stability of the mesophase of these compounds is determined primarily by the geometry of the molecules and



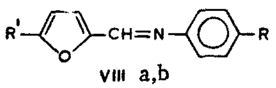
IV–VII a, b

IV X= 2,5-furylidene, V X=2,4-furylidene, VI X=2,5-thienylidene; VII X=2-4-thienylidene ; a Y=O, b Y=S

decreases as θ deviates from 180°. Of course, the polarizability of the heteroatom also makes a certain contribution, which is manifested in the higher thermal stabilities of thiophene derivatives (VI) as compared with furan derivatives (V), which have somewhat larger θ values. As a result of a large degree of deviation of the molecule from a linear structure (IV and VII), the thermal stabilities of the mesophases formed by them lie below their melting points.

Let us examine other data on heterocyclic liquid cyrstals after systematization with respect to the classes of heterocycles.

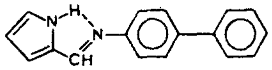
Furan, Thiophene, and Pyrrole. In connection with the nonlinearity of the molecules, only a few derivatives of five-membered heterocycles, particularly furan, form a liquid crystal state when they are melted. Thus N-furfurylideneanilines (VIIIa), which are analogous to the classical benzenoid mesogenic structures [12], have mesomorphic properties. Lengthening of the VIIIb molecule also does not lead to positive results [7].



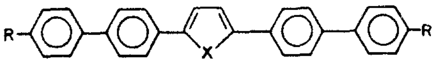
VIII a,b

VIII a R = alkyl, b R=4-R''OC$_6$H$_4$

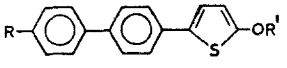
As a result of the smaller deviation of 2,5-disubstituted thiophenes from linearity, one observes the formation of a mesophase in the case of three-ring Schiff bases [8]. Similar pyrrole derivatives have even a greater tendency for the formation of a mesophase; in the opinion of Young and co-workers [8], this is due to stabilization of the state most favorable for the formation of a linear structure as a consequence of the presence of an intramolecular hydrogen bond:



Unfavorable deviations from linearity in the structure of a mesogenic molecule may be partially compensated by an increase in its overall length or by location of the heteroring at the end of the molecule. Thus, whereas 2,5-bis(p-alkylphenyl)furans and -thiophenes are not mesomorphic, of the biphenyl analogs IX the thiophene derivatives (X = S) are thermally stable nematic liquid crystals; a smectic mesophase also begins to appear commencing with R = C_4H_9 [13]. A high-temperature smectic phase is realized in the case of X, even though it has a narrow (up to 10°C) temperature range [14].

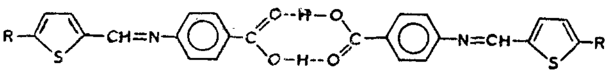


IX



X

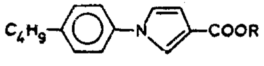
4-(5-Alkylthenylideneimino)benzoic acids, which, like other mesomorphic acids, form linear dimers XI, display nematic liquid crystal properties over a broad temperature range and a smectic mesophase appears commencing with the seventh member of the homologous series [14].

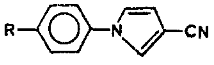


XI

trans-β-(5-Alkyl-2-thienyl)acrylic acids also have mesomorphic properties [19]. The mesomorphism of N,N'-bis(5-alkylthenylidene)benzidines, which form nematic liquid crystals, as well as smectic liquid crystals commencing with the fourth member of the series, is also similar [14].

Mesomorphic compounds were recently obtained in the case of 1-substituted pyrroles (XII, XIII) [15]. The first compounds have low melting points (−3°C for R = CH_3) and small posi-


XII


XIII

tive dielectric anisotropies ($\varepsilon_a \sim 0.5$), whereas the positive dielectric anisotropies of the second compounds ($\varepsilon_a = 10-12$) are comparable to the values for the corresponding biphenyl derivatives. Mesomorphic compounds that contain thiophene and furan rings in addition to a pyridine or pyran ring have also been synthesized [20, 21].

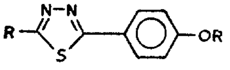
Imidazole. The interrelationship between the linearity of the molecule and the liquid crystal behavior has been investigated in detail in the case of various azoles [16]. It is possible that one may find liquid crystals among 2,4(5)- or 1,4-disubstituted imidazoles. Physicochemical studies demonstrated that imidazole derivatives that contain a proton attached to the heteroatom form associates both in solution and in the fused state; this should hinder a parallel orientation of the molecules. In fact, compounds with mesomorphic properties could not be obtained in any of the systems that contain a monosubstituted or 2,4-disubstituted imidazole [16, 17]. p,p'-Disubstituted 2-(p-phenylbenzoyl)-4-(p-biphenylyl)-imidazoles, in which the carbonyl group simultaneously hinders intermolecular association and "straightens out" the molecule, constitute an exception to this. The existence of a stable smectic mesophase has been noted in the case of 1,3-didodecylimidazolium bromide [16, 17].

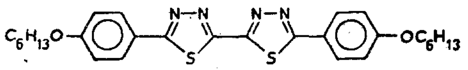
Oxazole and Thiazole. These heterocycles do not form associates but give rise to a large deviation from linearity that prevents the formation of a mesophase. Mesogenic compounds are therefore not observed among 2,4- and 2,5-di(p-alkylphenyl)oxazoles and 2,4-di-(p-alkylphenyl)thiazoles [16]. At the same time, one cannot exclude the possibility that lengthening of the molecule due to additional p-phenylene groups or straightening out of the molecule by the incorporation of "compensating" fragments may lead to the development of mesomorphic properties. 2,5-Di(p-alkyl)thiazoles form a liquid crystal state, and all of the homologs up to the nonyl compound are exclusively nematogens [16].

1,3,4-Thiadiazole. From a geometrical point of view, 1,3,4-thiadiazole is the most favorable of the five-membered heterocycles for the "construction" of the mesogenic molecule owing to the greater length of the C—S bond as compared with the other bonds in the ring and thereby to the smallest deviations of the 2,5-disubstituted derivatives from linearity. In addition, the absence of protons in the 1, 3, and 4 positions promotes a smaller overall width of the molecule. In fact, 2,5-bis(p-alkylphenyl)-1,3,4-thiadiazoles form a thermally stable nematic mesophase; a smectic phase also appears for higher homologs [16]. Unsymmetrical derivatives have lower melting points and, consequently, a broader temperature range over which the mesophase exists. The nematic phase is retained even if one of the phenyl fragments is unsubstituted, whereas the corresponding pyridazines do not form liquid crystals [5].

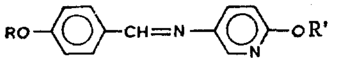
Like the corresponding biphenyl derivatives, 2-alkyl-5-(p-alkoxyphenyl)-1,3,4-thiadiazoles (XIV) form only a smectic phase, which, however, as a consequence of the high melting points, develops over a narrow temperature range or is monotropic [16].

Heteroanalogs of quaterphenyl (XV), which are yellow and have a mesophase that exists over a broad range, have also been obtained.


XIV

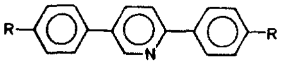

XV

Pyridine. Schiff bases obtained from 2-, 3-, and 4-formylpyridines and p-alkoxy-p'-aminobiphenyls [7, 8] or benzidine [7] were discussed above. Mesomorphic Schiff bases obtained from aminopyridines have considerably wider representation. Thus 2-alkoxy-5-(4-alkoxybenzylideneamino)pyridines (XVI) form primarily smectic A and B phases; however, a nematic mesophase is also observed when R = CH_3 and C_2H_5 [22, 23]. A typical dependence of the temperatures of the phase transitions on the length of the alkyl chain is presented in Fig. 2, in which the irregular character of the change in the melting points, even-odd alternation of the temperature of the transition from smectic B to smectic A ($S_B - S_A$), and a monotonic increase in the thermal stability of mesophase A ($S_A - I$) are clearly apparent. As a rule, the tempera-

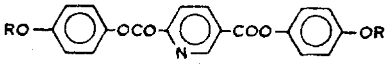

XVI

tures of the phase transitions of XVI are lower than in the case of their benzene analogs; this is explained by a decrease in the symmetry of the molecules, whereas the increased (as compared with the benzene analogs) tendency for the formation of smectic mesophases is explained by an increase in the transverse component of the dipole constant. As compared with XVI, 2-alkyl-5-(4-alkoxybenzylideneamino)pyridines melt at lower temperatures and form a nematic phase along with a smectic phase; the methoxy derivatives, for which primarily a monotropic nematic mesophase is noted [24, 25], constitute an exception to this. High-melting liquid crystal Schiff bases from terephthalaldehyde and aminopyridines [7, 26] and smectic liquid crystals from 2-methoxy-5-aminopyridine and p-acyloxybenzaldehydes [22] have been obtained.

The pyridine analogs of liquid crystal derivatives of terphenyl are interesting. In contrast to the latter, XVII (R = alkyl and alkoxy) form a nematic mesophase along with a smectic phase and melt ~50°C lower, whereas the thermal stability of the mesophase decreases to a lesser extent [6]. The mesomorphic esters of pyridine-2,5-dicarboxylic acid (XVIII)



XVII

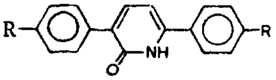


XVIII

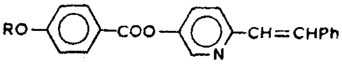
and the corresponding thioesters also melt at lower temperatures than their benzene analogs [11].

Liquid crystals, the temperatures of the phase transitions in which are close to the characteristics of their benzene analogs, have been obtained in the case of p-substituted phenyl esters of 5-alkoxypicolinic acids, whereas the isomeric esters of 6-alkoxynicotinic acids have a mesophase with a lower thermal stability [7, 28]. 6-Alkoxynicotinic acids also have liquid crystal properties; however, they have a mesophase with a relatively lower stability than p-alkoxybenzoic acids. This is evidently due to the fact that, in addition to the formation of linear dimers, one observes partial disruption of the nematic order as a consequence of the formation of an intermolecular hydrogen bond with the participation of the pyridine nitrogen atoms. 5-Alkoxypicolinic acids, which form an intramolecular hydrogen bond, did not display mesomorphic properties at all [29].

Pyridine analogs that are important for the practical utilization of liquid crystals of the p-cyanobiphenyl type are also known [30]. 3,6-Diaryl-2-pyridones (XIX), which form a high-melting stable (to 360°C) smectic phase [27], and XX [7] may also be noted.



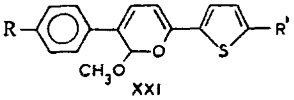
XIX



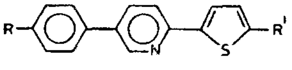
XX

High-melting (~140°C) smectic liquid crystals with a narrow-range mesophase are formed by p-alkoxyphenyl esters of pyridone-2-carboxylic acid [31]. It is assumed that they exist in the form of dimers. The formation of smectic liquid crystals by 4-(p-alkoxyphenyl)-2-pyridones is also explained by the formation of dimers [6].

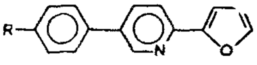
5-Alkyl-2-(p-alkoxyphenyl)pyridines, which display smectic and nematic properties with low melting points and a rather broad temperature range of existence of the mesophase, were recently synthesized. Isomeric 2-alkyl-5-[p-alkyl(or alkoxy)phenyl]pyridines display exclusively smectogenic properties [20]. The intermediates for the preparation of the latter, viz., 2-thienyl-5-aryl-6-methoxypyrans (XXI) and 2-thienyl-5-arylpyridines (XXII), also have liquid crystal properties; the first compounds are nematic liquid crystals over a narrow temperature range, while the second compounds are pure smectics with a rather low temperature of formation of the mesophase and high thermal stability of this phase. 2-Furyl-5-arylpyridines (XXIII) also have mesomorphic properties.



XXI



XXII



XXIII

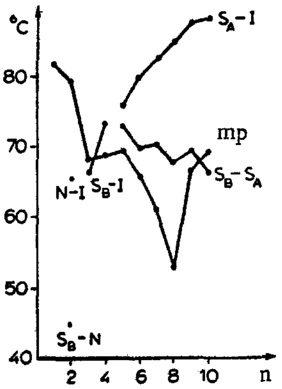
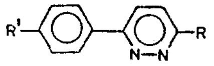


Fig. 2. Temperature of the phase transitions of XVI (R = C_nH_{2n+1}, R' = CH_3).

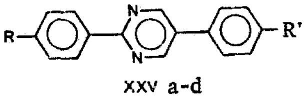
Pyridazine. The development of negative dielectric anisotropy from liquid crystal pyridazine derivatives might have been expected, since the dipole moment of this heterocycle is perpendicular to the major axis of the molecule, which passes through the 3 and 6 positions of the heteroring. However, the search for practically useful liquid crystals has been carried out only among nematics, whereas pyridazine derivatives form almost exclusively a smectic mesophase when they melt; this is evidently due to interaction of the transverse dipoles of the molecules. Thus, 3-alkoxy-6-arylpyridazines (XXIV) [32, 33] form a monotropic phase (R' = alkyl) and a narrow enantiotropic smectic C phase (R' = alkoxy) at ∿80-100°C. 3-Hydroxy and 3-chloro derivatives XXIV form smectic phase A.



XXIV

p,p'-Disubstituted 3,6-diphenylpyridazines have high melting points, and many of them form (at 200-260°C) a narrow-temperature-range nematic mesophase in addition to a smectic phase [5, 34]. Even in this rather elongated system the absence of at least one of the substituents leads to the loss of mesomorphic properties [5]. Mesomorphic pyridazine analogs of quaterphenyl derivatives have also been described [67].

Pyrimidine. Pyrimidine derivatives are currently the most representative group of heterocyclic liquid crystals. Like pyridine derivatives, they may compete seriously with the benzenoid analogs that are used in technology. In contrast to the corresponding smectogenic biphenyl derivatives, many 2-(p-alkoxyphenyl)-5-alkylpyrimidines [35, 36] form a nematic mesophase with positive dielectric anisotropy (in addition to a smectic phase for the higher homologs), and, although the thermal stability of the mesophase also decreases, it remains sufficient (60-70°C) for practical use. Although their alkylthio analogs also melt at low temperatures and have a rather stable mesophase (up to 75°C), they form exclusively smectic mesophase A [37, 68]. On the other hand, replacement of the alkoxy substituents by alkanoyloxy groups leads to more pronounced nematogenic properties, although the thermal stability of the mesophase decreases rapidly in this case, and the melting point increases, so that many derivatives are monotropic smectic liquid crystals (C and A) [38]. Mesomorphic 2-substituted 5-arylpyrimidines are known [68]. Lower temperatures of formation of the mesophase than in the case of the corresponding terphenyl derivatives are also observed for 2,5-diarylpyrimidines (XXV). Although these compounds form primarily smectic liquid crystals of the A type, a nematic phase is encountered more frequently here than in the case of terphenyl derivatives. Some compounds of this type display complex polymorphism up to the formation of four smectic phases (A, C, F, and G) [40]. High-melting polymorphic smectic liquid crystals have been found among 2,5-bis(p-alkoxyphenyl)-3-hydroxypyrimidines [39].



XXV a-d

a R= alkoxy, R'=H; **b** R=H, R'= alkoxy; **c** R= alkyl, R'=H; **d** R=H, R'= alkyl

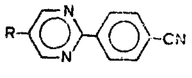
A study of the structures of polymorphic pyrimidine derivatives led to the discovery of two new types of smectic mesophases, viz., F and G, which were first observed for 2-(p-pentylphenyl)-5-(p-pentyloxyphenyl)pyrimidine, along with the previously known smectic phases A and C [41, 42].

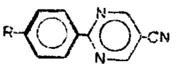
Since the presence of thermal groups is necessary in the benzenoid series for the formation of a mesophase, their effect in pyrimidine derivatives was investigated in the case of XXVa-d [18].

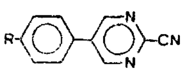
Compounds XXVa form only a nematic mesophase with a narrow range of existence (up to 15°C); this nematic mesophase is observed commencing only with the butyl homolog [35, 39]. The isomeric XXVb form exclusively smectic mesophase A with a range of existence of up to 70°C. Alkyl derivatives XXVd behave similarly, whereas liquid crystals are not observed in the case of XXVc. The authors found that the mesogenic properties increase as the dipole moments of the compounds increase. The dipole moment constants are virtually independent of the length of the alkyl chain and are 1.7, 2, 2.5, and 3.1D for XXVc, XXVa, XXVd, and XXVb, respectively. Liquid crystal derivatives are not observed in the corresponding pyridazine derivatives, in which the dipole moments are lower [5].

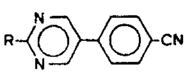
Compounds XXV have been successfully used in the nematic or smectic state as the stationary phase in gas chromatography [43, 44] and have made it possible to separate isomers (e.g., m- and p-bromotoluenes) that were separated poorly or not at all in other phases.

Interesting dielectric properties might have been expected from mesogenic compounds that simultaneously contain a pyrimidine ring and a thermal cyano group, since they make a contribution exclusively to the longitudinal component of the dipole moment of the molecule (the group dipole moments are 2 and 4D, respectively). Four series of pyrimidine analogs of 4-cyanobiphenyls (XXVIa-d) were synthesized with this in mind [45].


XXVIa


XXVIb

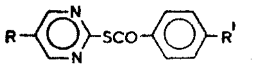

XXVIc

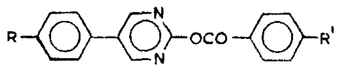

XXVId

Compounds XXVIc, d (R = alkyl) were found to be nonmesomorphic, whereas XXVIa were found to be primarily monotropic nematic liquid crystals with higher melting points and a certain increase in thermal stability as compared with the corresponding cyanobiphenyls. Compounds XXVIc (R = alkoxy) display mesomorphic properties [69], whereas XXVIb (R = alkyl, alkoxy, and acyloxy) were found to be more thermally stable nematic liquid crystals than biphenyls. They display smectic properties even when the alkyl chains are shorter (C_6H_{13}) than in the case of the cyanobiphenyls. As expected, additive character of the group dipole moments in XXVIa leads to larger positive dielectric anisotropies (ε_a up to 20) comparable to those of p-cyanophenyl esters of p-alkylbenzoic acids, whereas their opposite directions in XXVIb lead to a decrease in ε_a (3.4 for R = C_5H_{11}, 7.0 for R = C_4H_9O, and 3.0 for R = C_4H_9COO) as compared with cyanobiphenyls [46].

Four series of mesomorphic analogs of 4-alkyl-4"-cyanoterphenyls that contain a pyrimidine ring in the central and terminal parts of the three-ring system were recently synthesized. These compounds have high temperatures of formation of the mesophase and high stability of the latter; the lower members of the series also form a nematic phase [47].

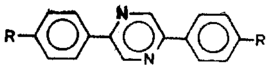
Mesomorphic thioesters (XXVII) and esters (XXVIII) that contain a pyrimidine ring are also known [48].

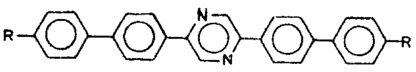

XXVII

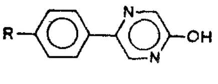

XXVIII

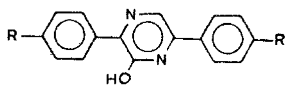
Pyrazine. Four series of mesomorphic pyrazine derivatives, viz., 2,5-diarylpyrazines (XXIX) [49], 2,5-di-(p-biphenylyl)pyrazines (XXX) [6, 50], 2-(p-alkylphenyl)-5-hydroxypyrazines (XXXI) [6, 51], and 2,5-diaryl-3-hydroxypyrazines (XXXII) [52], are presently known.

In contrast to the terphenyl analogs, XXIX (R = alkyl) have a stable nematic mesophase (R = C_2H_5–C_5H_{11}) in addition to smectic A (C_5H_{11}-C_8H_{17}) and C (from C_4H_9) phases. The tem-


XXIX


XXX

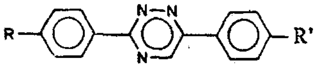

XXXI


XXXII

peratures of the phase transitions increase with R = alkoxy, and a nematic phase is observed up to the heptyl derivatives. Stable smectic mesophase B was noted for R = C_6H_{13}–C_8H_{17}.

Pyrazine analogs of quinquiphenyl (XXX, R = alkyl) have an extremely high degree of polymorphism. Thus when R = C_7H_{15}, two plastic phases with formation temperatures 116 and 142°C, four smectic phases (191, 287, 310, and 403°C), and a nematic phase (above 410°C) are observed. Compounds XXXI form only a narrow smectic phase. In contrast to XXIX, their hydroxy derivatives XXXII do not form a nematic mesophase, whereas smectic phases C and A appear at higher temperatures.

1,2,4-Triazine. Triazine derivatives (XXXIII) have approximately the same mesomorphic properties, and substituents have approximately the same effect on these properties as in the case of other azines [53]. In analogy with pyrimidine derivatives, it was expected that they would have smectic polymorphism; however, only smectic phases A and C were observed. Mesomorphic triazine derivatives that contain nitro, cyano, and pentylthio groups have also been obtained.

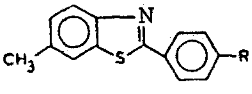


XXXIII

R and R'=H, alkyl, alkoxy.

1,2,4,5-Tetrazine. Outside of the case of a liquid crystal with a tetrazine fragment at the end of the molecule [7], only 3,6-diaryl-1,2,4,5-tetrazines that form an extremely narrow (1-10°C) mesophase of the nematic type when terminal alkyl groups are present are known; in the case of alkoxy substituents the range of its existence expands to 30°C, while the hexyloxy and subsequent homologs also have smectogenic properties [6, 54].

Benzoxazoles and Benzothiazoles. Several high-temperature liquid crystal derivatives of benzothiazole XXXIV that form exclusively a nematic phase were obtained in the twenties, but information regarding them became available only recently [55, 56].

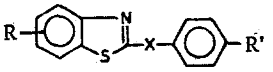


XXXIV

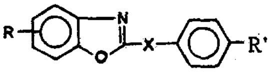
R = alkoxy, acylamino, and benzylideneamino

Almost half a century later, three other mesomorphic benzazoles, viz., 2-(p-cyanostyryl)-5-phenylbenzoxazole, 2,6-bis(5-phenyl-2-benzoxazolyl)naphthalene, and N,N'-terephthalylidene-bis)2-amino-6-ethoxybenzothiazole), which form only a stable (up to 410°C for the second compound) nematic phase, were reported [57].

A large number of mesogenic derivatives of benzothiazole (XXXV) and benzoxazole (XXXVI) were synthesized [29], and the effect of the geometry of the molecule and central grouping X on the mesomorphic properties of these compounds was investigated.



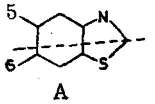
XXXV



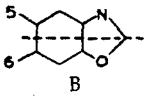
XXXVI

X=N=CH, CH=CH, COO, N=N, single bond; R=5- and 6-alkoxy, R'= alkyl or alkoxy; X=CH=CH or single bond; R=5-or 6-alkoxy; R'= alkyl or alkoxy

Like the corresponding Schiff bases, 5-methoxy-substituted styrylbenzothiazoles are not mesomorphic, whereas both series of 5- and 6-substituted benzoxazoles form a nematic phase; the 5-substituted derivatives have higher thermal stabilities of the mesophase than in the case of their 6-substituted isomers. This difference in the mesomorphic properties is due to the difference in the geometry of the molecules, as represented schematically by structures A and B:



A



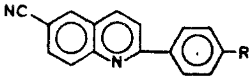
B

(the dashed line indicates the direction of the major molecular axis)

It is easy to imagine that the deviation of the substituent in the 5 or 6 position from this axis increases in the order 6-R-benzothiazoles < 5-R-benzoxazoles < 6-R-benzoxazoles < 5-R-benzothiazoles. This correlates with the decrease in the thermal stabilities of the mesophases formed by them. A comparison of liquid crystals of the XXXV series that differ with respect to the central X grouping shows that the thermal stabilities of the mesophases decrease in the order CH=CH > N=CH > single bond > COO.

Most of the benzazoles indicated above have a small degree of positive dielectric anisotropy.

Quinoline. Liquid crystal 2-(p-alkylphenyl)-6-cyanoquinolines (XXXVII) were unexpectedly obtained instead of the corresponding Schiff bases in the reaction of p-alkylbenzaldehydes with p-aminobenzonitrile in the presence of boron trifluoride etherate and alcohol [58].



XXXVII

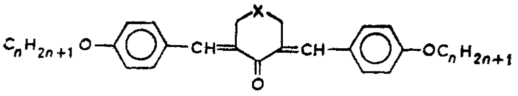
Under the reaction conditions, the latter evidently is oxidized to acetaldehyde, which then undergoes the Doebner–Miller reaction. Compounds XXXVII form a nematic mesophase with a monotonic decrease in its formation temperature as the length of the alkyl chain increases and even-odd alternation of the clarification temperature. The maximum temperature range (91.8-135.5°C) was noted for the derivative with R = C_5H_{11}.

Quinoxaline. Homologous series of alkyl and alkoxy derivatives of 2-(p-biphenylyl)-quinoxaline [59] form primarily a smectic A mesophase, and the melting points of the mesogens decrease monotonically as the length of the alkyl chain increases. Alkoxy derivatives form two smectic mesophases (E and A) and have higher (∿30°C) temperatures of the phase transitions.

Thiazolo[5,4-d]thiazole. The synthesis of mesomorphic 2,5-bis(p-alkylphenyl)thiazolo-[5,4-d]thiazoles, the linearity of the molecules of which is ensured by a condensed system of two five-membered heterocycles, has been reported [60]. In addition to nematic liquid crystals that are stable up to 220-270°C, these compounds also form smectics C and E.

Hydrogenated Heterocycles. Little attention has been directed to the search for mesogens among partially or completely hydrogenated heterocycles. However, interest in them should increase, since a number of mesomorphic derivatives of cyclohexane that have extremely valuable (in a practical respect) properties (low viscosities, low degrees of anisotropy of the refractive indexes, and transmittance in the UV region up to 200 nm) have recently been obtained.

Bis(benzylidene) derivatives of γ-pyrone, γ-thiopyrone, and N-methyl-4-piperidone (XXXVIII) are mesogenic compounds (primarily nematic liquid crystals) with atypical methylidyne bridges between the rings. In contrast to five-membered heterocycles, the great length of the C-S bond in tetrahydrothiopyrone decreases the linearity of the mesogen molecules, and this leads to a decrease in the thermal stability of the mesophase of these compounds as compared with the oxygen analogs (Fig. 3). The weakening of the mesomorphic properties of N-methylpiperidone derivatives, in which the methyl group attached to the nitrogen atom "widens" the molecule, is even more significant: the derivatives with n = 1-3 do not have



XXXVIII

X=O,S,NCH_3

liquid crystal properties at all. Smectic properties were noted in addition to nematic properties in the case of XXXVIII (X = O, n = 5-10) [61].

A plastic phase that exists over a range exceeding 100°C was observed for N,N'-bis(p-alkylphenyl)piperazines; this range is narrowed significantly on passing to the alkoxy analogs [62]. A narrow-range nematic phase has been noted for piperazine derivatives with long molecules [for example, Schiff bases from 1,4-bis(p-aminophenyl)piperazine] [63].

Mesomorphic XXXIX, which contain a tetrahydropyran ring as the terminal group, were recently obtained [64]. These compounds are primarily monotropic nematic liquid crystals

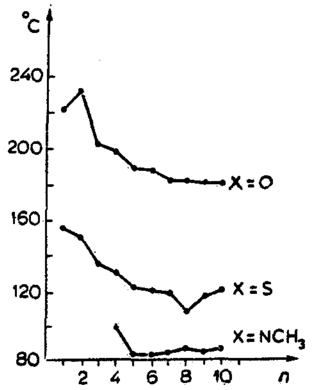
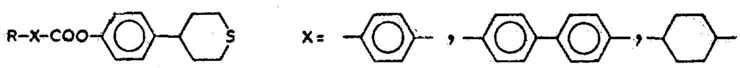


Fig. 3. Thermal stability of the mesophase of XXXVIII.

with a low degree of positive dielectric anisotropy ($\varepsilon_a \sim 1.5$). Oxidation of cyclic sulfides to the corresponding sulfoxides and sulfones leads to the development of smectogenic properties with an increase in the positive dielectric anisotropies ($\sim$10 for sulfoxides).



XXXIX

The information regarding heterocyclic liquid crystals presented above shows that it is still difficult to make a correlation between the properties of mesogens of this type and their structure; further efforts in this direction are necessary to ensure the purposeful search for practically useful heterocyclic mesogens.

LITERATURE CITED

1. E. I. Kovshev, L. M. Blinov, and V. V. Titov, Usp. Khim., 46, 753 (1977).
2. L. M. Blinov, Electro- and Magnetooptics of Liquid Crystals [in Russian], Nauka, Moscow (1978).
3. S. Chandrasekhar, B. H. Sadashiva, and K. A. Suresh, Résumés du 7 Congrès International sur les Cristaux Liquides, Bordeaux (1978), p. AP5.
4. C. Destrade, M. C. Mondon, and J. Malthête, Résumés du 7 Congrès International sur les Cristaux Liquides, Bordeaux (1978), p. AP5.
5. C. Weygand and W. Lanzendorf, J. Prakt. Chem., 151, 221 (1938).
6. H. Schubert, Wiss, Z. Univ. Halle, Math. Naturwiss, R., 19, 1 (1970).
7. I. A. Nash and G. W. Gray, Mol. Cryst. Liq. Cryst., 25, 299 (1974).
8. W. R. Young, J. Haller, and L. Williams, in: Liquid Crystals and Ordered Fluids, Vol. 2, J. P. Johnson and R. S. Porter (eds.), New York—London (1973), p. 383.
9. G. W. Gray, Molecular Structure and the Properties of Liquid Crystals, Academic Press, New York (1962).
10. M. J. S. Dewar and A. C. Griffin, J. Am. Chem. Soc., 97, 6662 (1975).
11. M. J. S. Dewar and K. M. Riddle, J. Am. Chem. Soc., 97, 6658 (1975).
12. Nguyen Dinh Triêu and Pham Trung Can, Hõa Hoc, No. 4, 13 (1976); Liq. Cryst. Abstr., 02864 (1978).
13. H. Schubert, I. A. Sagitdinov, and J. V. Svetkin (Swetkin), Z. Chem., 15, 222 (1975).
14. I. A. Sagitdinov and H. Schubert, Zh. Org. Khim., 14, 1060 (1978).
15. V. B. Kozhevnikov, V. P. Sevost'yanov, T. I. Gnilomedova, and V. N. Ryzhov, Summaries of Papers Presented at the Fourth All-Union Conference on Liquid Crystals and Their Practical Application [in Russian], Ivanovo (1977), p. 117.
16. H. Schubert, in: Acht Arbeiten über Flüsige Kristalle, MLU, Halle (Saale) (1976), p. 5.
17. H. Schubert, Giesemann, P. Steffen, and I. Bleichert, J. Prakt. Chem., 18, 192 (1962).
18. H. Zaschke and H. Schubert, J. Prakt. Chem., 315, 1113 (1973).
19. I. A. Sagitdinov and H. Schubert, Zh. Obshch. Khim., 49, 476 (1979).
20. A. I. Pavlyuchenko, V. V. Titov, and E. I. Kovshev, Summaries of Papers Presented at the Second All-Union Conference on Nitrogen-Containing Heterocycles [in Russian], Vol. 2, Riga (1979), p. 83.
21. A. I. Pavlyuchenko (Pavluchenko), N. I. Smirnova, and V. V. Titov, Abstracts of the Third Liquid-Crystal Conference of the Socialist Countries, Budapest (1979), p. G-9.
22. D. L. Fishel and P. R. Patel, Mol. Cryst. Liq. Cryst., 17, 139 (1972).
23. C. S. Oh, Mol. Cryst. Liq. Cryst., 19, 95 (1972).

24. R. A. Champa, Mol. Cryst. Liq. Cryst., 16, 175 (1972).
25. R. A. Champa, Mol. Cryst. Liq. Cryst., 19, 233 (1973).
26. S. L. Arora and J. L. Fergason, J. Chem. Soc., Faraday Div., 97 (1971).
27. K.-D. Münzner, Dissertation, Halle (1969); D. Demus, H. Demus, and H. Zaschke, Flüssige Kristalle in Tabellen, Leipzig (1974).
28. V. V. Titov, A. I. Pavlyuchenko (Pavluchenko), N. I. Smirnova, and E. I. Kovshev, Résumes du 7 Congrès International sur les Cristaux Liquides, Bordeaux (1978), p. A05.
29. A. I. Pavlyuchenko (Pavluchenko), N. I. Smirnova, V. V. Titov, E. I. Kovshev, and K. M. Dyumaev (Djumaev), Mol. Cryst. Liq. Cryst., 37, 35 (1976).
30. V. T. Grachev, B. E. Zaitsev, E. M. Itskovich, A. I. Pavlyuchenko (Pavluchenko), N. I. Smirnova, V. V. Titov, and K. M. Dyumaev (Djumaev), Résumés du 7 Congrès International sur les Cristaux Liquides, Bordeaux (1978), p. AP24.
31. S. Hoffmann, W. Witkowski, G. Bormann, and H. Schubert, Z. Chem., 18, 403 (1978).
32. H. Zaschke, C. Hyna, and H. Schubert, Z. Chem., 17, 333 (1977).
33. C. Hyna, H. Zaschke, and H. Schubert, 1 Flüssigkristallkonferenz sozialistischer Länder, Kurzereferate, Halle (1976), p. 26.
34. H. Schubert, R. Roch, and C. Weinbrecher, Z. Chem., 6, 467 (1966).
35. H. Zaschke, H. Schubert, F. Kuschel, F. Dinger, and D. Demus, East German Patent No. 95892 (1972); Chem. Abstr., 32446 (1974).
36. H. Zaschke, J. Prakt. Chem., 317, 617 (1975).
37. H. Zaschke, S. Arndt, V. Wagner, and H. Schubert, Z. Chem., 17, 293 (1977).
38. H. Zaschke and R. Stolle, Z. Chem., 15, 441 (1975).
39. H. Schubert and H. Zaschke, J. Prakt. Chem., 312, 494 (1970).
40. H. Zaschke, A. Wiegeleben, L. Richter, and D. Demus, Abstracts of the Second Conference of Socialist Countries on Liquid Crystals, Sunny Beach (1977), p. 262.
41. H. Kresse, P. Schmidt, and D. Demus, Phys. Stat. Sol., 32, 315 (1975).
42. D. Demus, S. Diele, M. Klapperstück, V. Link, and H. Zaschke, Mol. Cryst. Liq. Cryst., 15, 161 (1971).
43. G. Kraus, K. Seifert, H. Zaschke, and H. Schubert, Z. Chem., 11, 22 (1971).
44. G. Kraus and A. Kolbe, J. Chromatogr., 147, 17 (1978).
45. A. Boller, M. Cereghetti, M. Schadt, and H. Scherrer, Mol. Cryst. Liq. Cryst., 42, 215 (1977).
46. G. W. Gray, J. Phys., 36, C1-337 (1975).
47. A. Boller, M. Cereghetti, and H. Scherrer, Z. Naturforsch., 33, 433 (1978).
48. H. Zaschke, A. Isenberg, and H. Schubert, Abstracts of the Second Conference of Socialist Countries on Liquid Crystals, Sunny Beach (1977), p. 260.
49. H. Schubert, R. Hacker, and K. Kindermann, J. Prakt. Chem., 37, 12 (1968).
50. I. Herrmann, Dissertation, Halle (1970); D. Demus et al. [27].
51. H. Heberer, Diplomarbeit, Halle (1967); D. Demus et al. [27].
52. H. Schubert, I. Eissfeldt, R. Lange, and F. Trefflich, J. Prakt. Chem., 33, 265 (1966).
53. H. Zaschke, K. Nitsche, and H. Schubert, J. Prakt. Chem., 319, 475 (1977).
54. W. Schliemann, Diplomarbeit, Halle (1968); D. Demus et al. [27].
55. W Lützkendorf, Dissertation, Halle (1922); D. Demus et al. [27].
56. W. Weisswange, Dissertation, Halle (1925), D. Demus et al. [27].
57. H. Kelker and H. Schreurle, J. Phys., 7, C4-104 (1969).
58. V. V. Titov, E. I. Kovshev, L. A. Karamysheva, P. V. Purvanetskas, and V. K. Daukshas, Khim. Geterotsikl. Soedin., No. 10, 1364 (1975).
59. I. Herrmann, H. Schubert, B. Grossman, L. Richter, L. Vogel, and D. Demus, Z. Phys. Chem., 257, 563 (1976).
60. W. Weissflog and M. Süsse, Z. Chem., 19, 24 (1979).
61. K. Hanemann, Dissertation, Halle (1972); D. Demus et al. [27].
62. K. R. Kuppe, Diplomarbeit, Halle (1969); D. Demus et al. [27].
63. R. Kühnemann, Dissertation, Halle (1924); D. Demus et al. [27].
64. L. A. Karamysheva, K. V. Roitman, S. I. Torgova, and E. I. Kovshev, Abstracts of the Third Liquid Crystal Conference of Socialist Countries, Budapest (1979), p. G-11.
65. G. W. Gray, in: Advances in Liquid Crystals, Vol. 2, Academic Press (1976), p. 1.
66. M. J. S. Dewar, A. C. Griffin, and R. M. Riddle, in: Liquid Crystals and Ordered Fluids, Vol. 2, J. P. Johnson and R. S. Porter (eds.), New York-London (1973), p. 733.
67. H. Schubert, H. J. Lorenz, R. Hoffmann, and F. Franke, Zh. Chem., 6, 337 (1966).
68. H. Zaschke, 1 Flüssigkristallkonferenz sozialistischer Länder, Kurzreferate, Halle (1976), p. 25.
69. H. Zaschke, Z. Chem., 17, 63 (1977).