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# GEOMETRY AND MESOMORPHIC PROPERTIES OF NEW SCHIFF BASES CONTAINING THIAZOLE RING

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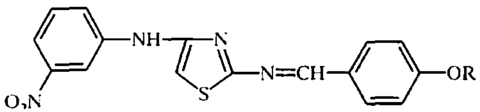
*New liquid-crystalline azomethines – 2-(4-alkoxybenzylideneamino)-4-(3-nitrophenylamino)thiazoles – displaying nematic mesomorphism at 42-137°C have been synthesized. The structure of these compounds was studied by the MNDO LCAO MO method. A correlation was found between the geometric parameters and liquid crystal properties.*

The rapid development of liquid crystal research is related to the unique optical properties of these substances, which have led to their wide application in the data processing industry [1]. The orienting properties of liquid crystals are used in nuclear magnetic and electron paramagnetic resonance spectroscopy, in the orientation of pleochroic dye molecules, and the preparation of ferromagnetic suspensions in liquid crystals. Furthermore, the unique properties of these substances are used for the orientation and structure formation of polymers [2, 3].

In this work, we synthesized 2-(4-alkoxybenzylideneamino)-4-(3-nitrophenylamino)thiazoles.



Ia–j

I a R = $CH_3$; b R = $C_2H_5$; c R = $C_3H_7$; d R = $C_4H_9$; e R = $C_5H_{11}$; f R = $C_6H_{13}$;
g R = $C_7H_{15}$; h R = $C_8H_{17}$; i R = $C_9H_{19}$; j R = $C_{10}H_{21}$

Products Ia-j were obtained by the chloroacetylation of starting *m*-nitroaniline in diethyl ether. The resultant N-chloroacetyl-*m*-nitroaniline (II) was treated with thiourea in absolute ethanol. The condensation of the obtained N-(2-amino-4-thiazolyl)-3-nitroaniline (III) with *p*-alkoxybenzaldehydes in dry tetrahydrofuran in the presence of catalytic amounts of piperidine gave products Ia-j.

The composition and structure of all obtained products were confirmed by elemental analysis data (see Table 1) and PMR spectroscopy. The PMR spectra of Schiff bases Ia-j were similar; in them signals at 0.5-0.9 (t, $CH_3$), 1.2-1.9 (m, $CH_2$), 3.5-4.2 (d, $CH_2O$), 4.3-4.5 (s, NH), 6.5-8.4 (m, $C_6H_4$), 7.2-7.3 (s, $H_{thiazole}$), and 9.8-9.9 ppm (s, N=CH) were present.

Compounds Ia-j display nematic mesomorphism in different temperature ranges (42-137°C). Table 1 shows that the clarification temperature ($T_{N-I}$) undergoes discontinuous change with the increase of length of the aliphatic chain in the benzylidene component while propyloxy (Ic) and hexyloxy (If) derivatives have a broad meso phase temperature range relative to the other derivatives.

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TABLE 1. Characteristics of Compounds Synthesized

| Compound | Empirical formula | Found, %<br>Calculated, % |  |  | $T_{C\text{-}N}$*, °C | $T_{N\text{-}I}$, °C | Yield, % |
|---|---|---|---|---|---|---|---|
|  |  | C | H | N |  |  |  |
| Ia | $C_{17}H_{14}N_4O_3S$ | 57.56<br>57.62 | 3.82<br>3.98 | 15.64<br>15.81 | 120 | 137 | 53 |
| Ib | $C_{18}H_{16}N_4O_3S$ | 58.50<br>58.68 | 4.28<br>4.38 | 15.02<br>15.21 | 50 | 119 | 71 |
| Ic | $C_{19}H_{18}N_4O_3S$ | 59.52<br>59.67 | 4.56<br>4.74 | 14.48<br>14.65 | 42 | 118 | 75 |
| Id | $C_{20}H_{20}N_4O_3S$ | 60.42<br>60.79 | 5.18<br>5.08 | 14.02<br>14.13 | 86 | 116 | 72 |
| Ie | $C_{21}H_{22}N_4O_3S$ | 61.20<br>61.44 | 4.98<br>5.40 | 13.48<br>13.65 | 55 | 127 | 63 |
| If | $C_{22}H_{24}N_4O_3S$ | 62.06<br>62.24 | 5.58<br>5.70 | 13.02<br>13.20 | 47 | 123 | 68 |
| Ig | $C_{23}H_{26}N_4O_3S$ | 62.82<br>62.99 | 5.74<br>5.98 | 12.56<br>12.78 | 59 | 110 | 62 |
| Ih | $C_{24}H_{28}N_4O_3S$ | 63.52<br>63.69 | 6.08<br>6.24 | 12.14<br>12.38 | 84 | 122 | 73 |
| Ii | $C_{25}H_{30}N_4O_3S$ | 64.12<br>64.35 | 6.36<br>6.48 | 11.86<br>12.01 | 56 | 119 | 69 |
| Ij | $C_{26}H_{32}N_4O_3S$ | 64.84<br>64.97 | 6.54<br>6.71 | 11.48<br>11.66 | 90 | 129 | 65 |
| III | $C_9H_8N_4O_2S$ | 45.64<br>45.76 | 3.28<br>3.41 | 23.48<br>23.71 | 140 | 141 | 81 |

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* $T_{C\text{-}N}$ is the temperature of transition of the crystalline phase to the nematic liquid-crystalline phase, and $T_{N\text{-}I}$ is the temperature of transition of the nematic liquid-crystalline phase to the isotropic phase.

Enantiotropic mesomorphism is characteristic of all compounds Ia-j. The three-dimensional molecular structure has a great effect on the meso phase characteristics [3]. The –N=CH– bond is not absolutely rigid, and the physicochemical data indicate a noncoplanar configuration of compounds containing this bond. The pronounced tendency to exist in the mesomorphous state is attributed to the nonplanar structure of azomethines [4].

Semiempirical MNDO LCAO MO calculations [5] with complete optimization of geometry were carried out for a detailed study of these compounds. The major geometric parameters, bond orders, and atomic charges are given in Tables 2-4. The geometry of the thiazole ring linked to the benzene azomethine group holds interest for these products, which display mesomorphism in a broad temperature range. Thus, in the compound Ia (see Table 2) the $C_{(4)}$–$C_{(2)}$ (1.386 Å), $C_{(2)}$–$N_{(2)}$ (1.404 Å), and $N_{(2)}$–$C_{(3)}$ bonds (1.336 Å) are somewhat elongated, but the $C_{(3)}$–S (1.689 Å) and S–$C_{(4)}$ bonds (1.674 Å) are shortened; the lengths of the corresponding bonds in unsubstituted thiazole are 1.355, 1.376, 1.327, 1.701, and 1.719 Å, respectively [6]. Analogous changes are found for the bond angles (see Table 3). On the whole, the thiazole ring is virtually planar as indicated by the dihedral angle values given in Table 3.

The plane of the phenyl ring of the benzylidene component forms an angle of acoplanarity $\theta_c$ with the plane of the thiazole ring. While $\theta_c$ = 40-70° for the stable molecular conformation of azomethines containing only phenyl rings [7]; in the compounds examined, in which the thiazole ring has a greater effect on configuration, $\theta_c$ = 16-32°, in some cases (If-h), $\theta_c$ = 1-9°. Table 5 shows that the minimum value of $\theta_c$ (1.8°) is found for the compound If, which has the broadest range of the mesomorphous state. Apparently, the minimum angle between the thiazole and phenyl rings in the present case corresponds to the most compact molecular packing, although there is no correlation of the geometric parameters. Most of the data for the compounds Ia-e correlate well. Thus, the temperature for the existence of the nematic meso phase decreases and the range of the meso phase expands with the increase of $\theta_c$ (Tables 1 and 5).

TABLE 2. Calculated Bond Lengths (Å) and Bond Orders in the Compounds Ia-j

| Bond | Compound | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Ia | Ib | Ic | Id | Ie | If | Ig | Ih | Ii | Ij |
| | | | | | Bond lengths | | | | | |
| $C_{(1)}$-$N_{(1)}$ | 1.441 | 1.441 | 1.443 | 1.443 | 1.443 | 1.431 | 1.441 | 1.441 | 1.441 | 1.441 |
| $N_{(1)}$-$C_{(2)}$ | 1.417 | 1.418 | 1.423 | 1.423 | 1.423 | 1.420 | 1.418 | 1.418 | 1.419 | 1.419 |
| $C_{(2)}$-$N_{(2)}$ | 1.404 | 1.403 | 1.404 | 1.404 | 1.404 | 1.401 | 1.404 | 1.404 | 1.404 | 1.404 |
| $N_{(2)}$-$C_{(3)}$ | 1.336 | 1.336 | 1.336 | 1.336 | 1.336 | 1.351 | 1.336 | 1.336 | 1.336 | 1.336 |
| $C_{(3)}$-S | 1.689 | 1.690 | 1.690 | 1.691 | 1.690 | 1.734 | 1.681 | 1.690 | 1.690 | 1.689 |
| S $C_{(4)}$ | 1.674 | 1.674 | 1.674 | 1.674 | 1.674 | 1.653 | 1.674 | 1.674 | 1.674 | 1.674 |
| $C_{(4)}$ $C_{(2)}$ | 1.386 | 1.386 | 1.385 | 1.385 | 1.385 | 1.404 | 1.386 | 1.386 | 1.386 | 1.386 |
| $C_{(3)}$ $N_{(3)}$ | 1.393 | 1.393 | 1.393 | 1.393 | 1.393 | 1.398 | 1.392 | 1.392 | 1.392 | 1.394 |
| $N_{(3)}$ $C_{(5)}$ | 1.303 | 1.307 | 1.306 | 1.306 | 1.306 | 1.298 | 1.304 | 1.304 | 1.304 | 1.302 |
| $C_{(5)}$-$C_{(6)}$ | 1.477 | 1.422 | 1.423 | 1.423 | 1.423 | 1.465 | 1.476 | 1.476 | 1.477 | 1.480 |
| | | | | | Bond orders | | | | | |
| $C_{(1)}$-$N_{(1)}$ | 0.972 | 1.972 | 0.975 | 0.975 | 0.975 | 0.985 | 0.973 | 1.973 | 0.973 | 0.973 |
| $N_{(1)}$-$C_{(2)}$ | 1.018 | 1.018 | 1.003 | 1.001 | 1.001 | 1.020 | 1.016 | 1.015 | 1.014 | 1.013 |
| $C_{(2)}$-$N_{(2)}$ | 1.165 | 1.167 | 1.163 | 1.163 | 1.163 | 1.239 | 1.166 | 1.166 | 1.166 | 1.166 |
| $N_{(2)}$-$C_{(3)}$ | 1.578 | 1.575 | 1.581 | 1.581 | 1.581 | 1.511 | 1.575 | 1.575 | 1.575 | 1.579 |
| $C_{(3)}$-S | 1.097 | 1.098 | 1.094 | 1.093 | 1.094 | 1.135 | 1.098 | 1.098 | 1.098 | 1.099 |
| S-$C_{(4)}$ | 1.099 | 1.102 | 1.107 | 1.107 | 1.108 | 1.190 | 1.101 | 1.101 | 1.101 | 1.104 |
| $C_{(4)}$ $C_{(2)}$ | 1.602 | 1.601 | 1.616 | 1.618 | 1.618 | 1.498 | 1.601 | 1.602 | 1.603 | 1.604 |
| $C_{(3)}$ $N_{(3)}$ | 1.064 | 1.067 | 1.064 | 1.065 | 1.065 | 1.064 | 1.066 | 1.066 | 1.066 | 1.061 |
| $N_{(3)}$ $C_{(5)}$ | 1.785 | 1.776 | 1.783 | 1.776 | 1.779 | 1.796 | 1.777 | 1.778 | 1.778 | 1.799 |
| $C_{(5)}$ $C_{(6)}$ | 1.006 | 1.024 | 1.021 | 1.026 | 1.024 | 1.019 | 1.010 | 1.009 | 1.009 | 0.994 |

TABLE 3. Calculated Bond and Dihedral Angles (deg) in the Compounds Ia-j

| Angle | Compound | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Ia | Ib | Ic | Id | Ie | If | Ig | Ih | Ii | Ij |
| | | | | | Bond angle | | | | | |
| $C_{(1)}-N_{(1)}-H_{(1)}$ | 109.6 | 109.6 | 109.5 | 109.5 | 109.5 | 110.5 | 109.8 | 109.7 | 109.7 | 109.6 |
| $N_{(1)}-C_{(2)}-N_{(2)}$ | 117.7 | 117.9 | 118.6 | 118.7 | 118.7 | 121.8 | 117.8 | 117.9 | 117.9 | 118.0 |
| $C_{(2)}-N_{(2)}-C_{(3)}$ | 108.9 | 108.9 | 108.9 | 108.9 | 108.9 | 109.2 | 108.9 | 108.9 | 108.9 | 108.9 |
| $N_{(2)}-C_{(3)}-S$ | 115.2 | 115.2 | 115.2 | 115.2 | 115.2 | 114.1 | 115.2 | 115.2 | 115.2 | 115.2 |
| $C_{(3)}-S-C_{(4)}$ | 91.3 | 91.3 | 91.3 | 91.3 | 91.3 | — | — | — | — | |
| $C_{(2)}-C_{(4)}-H_{(2)}$ | 128.5 | 128.5 | 128.5 | 128.5 | 128.5 | 124.4 | 128.6 | 128.5 | 128.6 | 128.5 |
| $N_{(2)}-C_{(3)}-N_{(3)}$ | 126.1 | 126.5 | 126.2 | 126.2 | 126.3 | 129.2 | 126.6 | 126.6 | 126.7 | 126.4 |
| $C_{(3)}-N_{(3)}-C_{(5)}$ | 123.5 | 123.6 | 123.6 | 123.6 | 123.6 | 122.6 | 123.8 | 123.8 | 123.8 | 123.6 |
| $N_{(3)}-C_{(5)}-H_{(3)}$ | 124.3 | 123.2 | 123.2 | 123.1 | 123.2 | 123.6 | 124.3 | 124.3 | 124.3 | 124.9 |
| $N_{(3)}-C_{(5)}-C_{(6)}$ | 120.4 | 121.0 | 120.9 | 121.1 | 121.0 | 122.7 | 120.4 | 120.4 | 120.4 | 119.9 |
| | | | | | Dihedral angles | | | | | |
| $C_{(1)}-N_{(1)}-C_{(2)}-N_{(2)}$ | -129.3 | -127.6 | 111.5 | 108.8 | 109.0 | -129.9 | -128.1 | -126.9 | -126.3 | -123.1 |
| $N_{(2)}-C_{(2)}-N_{(2)}-C_{(3)}$ | -174.3 | -174.2 | 175.4 | 175.6 | 175.6 | -174.7 | -174.3 | -174.4 | -174.4 | -174.5 |
| $C_{(2)}-N_{(2)}-C_{(3)}-S$ | -0.6 | -0.7 | 0.6 | 0.6 | 0.6 | -0.9 | -0.7 | -0.7 | -0.6 | -0.7 |
| $N_{(2)}-C_{(3)}-S-C_{(4)}$ | 0.7 | 0.7 | -0.7 | -0.7 | -0.7 | — | — | — | — | — |
| $N_{(2)}-C_{(2)}-C_{(4)}-H_{(2)}$ | -179.3 | -179.5 | 179.1 | 179.1 | 179.1 | — | — | — | — | — |
| $C_{(2)}-N_{(2)}-C_{(3)}-N_{(3)}$ | -177.1 | -178.7 | 176.6 | 176.6 | 176.7 | 179.8 | -179.4 | -179.3 | -179.2 | -178.4 |
| $C_{(3)}-N_{(3)}-C_{(5)}-H_{(3)}$ | -1.6 | -1.1 | 1.2 | 1.2 | 1.1 | 0 | -0.5 | -0.8 | -0.5 | -1.0 |
| $C_{(3)}-N_{(3)}-C_{(5)}-C_{(6)}$ | 179.1 | 179.7 | -178.8 | -178.9 | -178.9 | -179.8 | 179.7 | 179.6 | 179.7 | 179.8 |
| $N_{(3)}-C_{(5)}-C_{(6)}-C_{(7)}$ | 163.7 | 151.4 | 147.8 | 152.7 | 150.2 | 178.2 | 173.6 | 172.0 | 171.2 | 14.8 |

TABLE 4. Calculated Charges (a. u.) on Atoms in the Compounds Ia-j

| Atom | Compound | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Ia | Ib | Ic | Id | Ie | If | Ig | Ih | Ii | Ij |
| $C_{(1)}$ | 0.021 | 0.020 | 0.021 | 0.021 | 0.021 | 0.011 | 0.024 | 0.024 | 0.024 | 0.023 |
| $N_{(1)}$ | -0.214 | -0.214 | -0.207 | -0.206 | -0.206 | 0.193 | -0.214 | -0.213 | -0.213 | -0.212 |
| $C_{(2)}$ | 0.093 | 0.091 | 0.077 | 0.075 | 0.075 | 0.014 | 0.093 | 0.092 | -0.092 | 0.088 |
| $N_{(2)}$ | -0.268 | -0.267 | -0.268 | -0.269 | -0.269 | -0.175 | -0.270 | -0.270 | -0.269 | -0.266 |
| $C_{(3)}$ | -0.034 | -0.037 | -0.039 | -0.038 | -0.038 | -0.206 | -0.033 | -0.033 | -0.033 | -0.040 |
| S | 0.385 | 0.388 | 0.384 | 0.383 | 0.383 | 0.597 | 0.386 | 0.386 | 0.386 | 0.390 |
| $C_{(4)}$ | -0.337 | -0.333 | -0.310 | -0.307 | -0.307 | -0.512 | -0.336 | -0.334 | -0.333 | -0.328 |
| $N_{(3)}$ | -0.263 | -0.259 | -0.258 | -0.261 | -0.260 | -0.162 | -0.267 | -0.267 | -0.267 | -0.254 |
| $C_{(5)}$ | 0.206 | 0.200 | 0.203 | 0.205 | 0.204 | 0.041 | 0.207 | 0.206 | 0.206 | 0.198 |
| $C_{(6)}$ | -0.152 | -0.133 | -0.147 | -0.153 | -0.152 | -0.125 | -0.150 | -0.149 | -0.148 | 0.124 |
| $C_{(7)}$ | 0.013 | 0.003 | 0.012 | 0.017 | 0.016 | 0.068 | 0.012 | 0.011 | 0.011 | -0.006 |

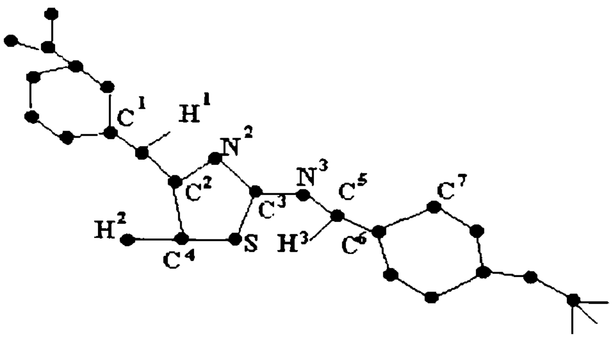

Fig. 1. Structure of the compound Ia obtained by complete optimization of geometry in MNDO calculation.

TABLE 5. Energies of Formation, Total Dipole Moments, and Acoplanarity Angles for the compounds Ia-j

| Compound | $E_{form.}$, kcal/mole | $\mu_{total}$ | $\theta_c$, deg |
|---|---|---|---|
| Ia | 81.49 | 4.05 | 16.3 |
| Ib | 79.41 | 4.89 | 28.6 |
| Ic | 73.86 | 7.24 | 32.2 |
| Id | 69.13 | 7.52 | 27.3 |
| Ie | 65.09 | 7.46 | 29.8 |
| If | 63.01 | 4.93 | 1.8 |
| Ig | 54.89 | 5.00 | 6.4 |
| Ih | 50.86 | 4.99 | 8.0 |
| Ii | 46.23 | 4.99 | 8.8 |
| Ij | 41.18 | 5.03 | 32.2 |

The anomalously high total dipole moments are also a consequence of the acoplanarity of azomethines. The mesomeric effects arising due to conjugation of the unshared electron pair of the azomethine group nitrogen atom with the phenyl ring of the benzylidene moiety influence the degree of acoplanarity of azomethines [7]. The maximum values of the meso phase temperature range of compounds Ic and Id may be also attributed to the extreme values of dipole moments found for these compounds (Table 5). Shortening of the $N_{(1)}$–$C_{(2)}$ and $C_{(3)}$–$N_{(3)}$ bonds is observed for the compounds, while the corresponding increase in the orders of these bonds (Table 2) is related to the slight transfer of electron density from the thiazole ring to the aniline (to a greater extent) and benzylidene components. The negative charge on $N_{(2)}$ atom decreases, while the charges on $N_{(1)}$ and $N_{(3)}$ atoms increase. These shifts probably have an great effect on the molecular polarizability and the capacity of these molecules to exist in the mesomorphous state.

## EXPERIMENTAL

The PMR spectra were taken on a Bruker WP-200 spectrometer at 200.13 MHz in chloroform with HMDS as the internal standard. The phase transition temperatures were determined on an MIN-10 polarizing microscope with a heating unit. The purity of all the studied compounds was checked by thin-layer chromatography on alumina plates with toluene–chloroform as the eluent.

The MNDO LCAO MO calculation was carried out on a COMPAQ-386/25 computer using the standard AMPAC program.

**N-Chloroacetyl-*m*-nitroaniline (II)** was synthesized according to the procedure [8].

**N-(2-Amino-4-thiazolyl)-3-nitroaniline (III).** Solution of the compound II (14.2 g, 0.06 mol) and thiourea (4.6 g, 0.06 mol) in absolute ethanol (100 ml) was heated at reflux for 8 h. The solvent was distilled off and the residue was neutralized by adding 20% aqueous solution of sodium carbonate. The precipitate of product III was filtered off and crystallized from water.

**2-(4-Alkoxybenzylideneamino)-4-(3-nitrophenylamino)thiazoles (Ia-j).** Mixture of the compound III (1 g, 0.042 mol) and corresponding *p*-alkoxybenzaldehyde (0.0042 mol) in dry tetrahydrofuran (30 ml) was heated at reflux for 4 h in the presence of catalytic amount of piperidine. The solvent was distilled off and the residue was crystallized from ethanol.

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