# SYNTHESIS AND QUANTUM-CHEMICAL

STUDY OF LIQUID-CRYSTAL

DERIVATIVES OF THIAZOLE

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New liquid-crystall derivatives of thiazole with smectic mesomorphism over the range 5-85°C have been synthesized. Data on the spatial structure of the compounds synthesized have been obtained by quantum-chemical calculations. The effect of geometric anisotropy of the molecules of substituted thiazoles on their mesomorphic properties has been investigated.

Keywords: liquid crystals, Schiff's bases, thiazoles, quantum-chemical calculations, mesomorphism.

We have previously prepared thiazole derivatives with liquid-crystal properties [1, 2]. In a continuation of the investigation of the structures of substituted thiazoles on their mesomorphic properties we have synthesized the following compounds:

1–10
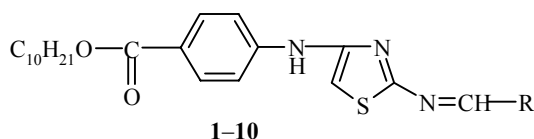
1 R = p-CH$_3$OC$_6$H$_4$; **2** R = p-NO$_2$C$_6$H$_4$; **3** R = p-(CH$_3$)$_2$NC$_6$H$_4$; **4** R = p-HOC$_6$H$_4$;
5 R = p-BrC$_6$H$_4$; **6** R = o-HOC$_6$H$_4$; **7** R = o-Br, o'-HOC$_6$H$_3$; **8** R = m-NO$_2$C$_6$H$_4$;
9 R = o-CH$_3$OC$_6$H$_4$; **10** R = o,p-(CH$_3$O)$_2$C$_6$H$_3$

Compounds **1-10** were obtained by esterification of 4-aminobenzoic acid with decyl alcohol in the presence of H$_2$SO$_4$. (4-Decyloxycarbonyl)aniline (**11**) was chloroacetylated in diethyl ether with subsequent treatment of the formed N-chloroacetyl(4-decylooxycarbonyl)aniline (**12**) with thiourea in absolute ethanol. The synthesized 2-amino-4-[(4-decyloxycarbonyl)anilino]thiazole was condensed with aromatic aldehydes in absolute THF in the presence of a trace of piperidine.

The composition and structures of the products obtained were confirmed by elemental analysis and ^{1}H NMR spectroscopy.

The following proton signals were present in the ^{1}H NMR spectra of compounds **1-10**: 0.8-1.6 (t, CH$_3$), 1.9-3.2 (m, CH$_2$), 2.6-4.3 (m, CH$_2$O), 4.9-6.0 (s, NH), 6.4-7.8 (m, C$_6$H$_4$), 8.2-8.6 ppm (s, N=CH).

Compounds **1-10** show monotropic mesomorphism of smectic type in the region of 5-85°C. Compounds containing m'-NO$_2$ and p-(CH$_3$)$_2$N groups showed the greatest mesophase temperature range.

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TABLE 1. Yields and Characteristics of the Compounds Synthesized

Com-pound	Empirical formula	Found, % Calculated, %			T_c^*, °C	$T_{K\text{-}I}^{*2}$, °C	ΔT^*, °C	Yield, %
		C	H	N				
1	$C_{28}H_{35}N_3O_3S$	67.93 68.15	7.04 7.10	8.36 8.52	8	34	26	41
2	$C_{27}H_{32}N_4O_4S$	65.56 65.85	6.29 6.50	10.79 11.38	5	36	31	54
3	$C_{29}H_{38}N_4O_2S$	67.04 66.67	7.58 7.28	11.06 10.73	10	54	44	44
4	$C_{27}H_{33}N_3O_3S$	67.42 67.64	6.75 6.89	8.52 8.77	75	83	8	43
5	$C_{27}H_{32}BrN_3O_2S$	59.64 59.67	5.72 6.08	7.56 7.73	9	31	22	41
6	$C_{27}H_{33}N_3O_3S$	67.46 67.64	6.82 6.89	8.54 8.77	6	35	29	45
7	$C_{27}H_{32}BrN_3O_3S$	57.66 58.06	5.62 5.73	7.44 7.53	74	85	11	46
8	$C_{27}H_{32}N_4O_4S$	63.48 63.78	5.96 6.30	10.84 11.02	8	47	39	36
9	$C_{28}H_{35}N_3O_3S$	68.02 68.15	6.94 7.10	8.40 8.52	7	26	19	50
10	$C_{29}H_{37}N_3O_4S$	66.42 66.54	6.84 7.07	7.95 8.03	61	72	11	52
11	$C_{17}H_{27}NO_2$	73.24 73.60	9.84 9.75	5.21 5.05	—	42	—	60
12	$C_{19}H_{28}ClNO_3$	64.34 64.50	7.75 7.92	3.82 3.96	—	59	—	78
13	$C_{20}H_{29}N_3O_2S$	63.84 64.00	7.58 7.73	10.88 11.20	—	38	—	60

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* Temperature at which the smectic phase is formed.

*^{2} Transition temperature into an isotropic liquid.

We carried out quantum-chemical analyses on the thiazoles **1-10** using the semiempirical AM1 method in order to investigate the effect of substituents on the molecular spatial structure and to estimate the relationship between the molecular structure and the properties which give rise to substances capable of forming the liquid crystal mesophase. In calculations of the molecules of compounds **6-10** we took into account the possibility that two rotational isomers exist with the following disposition of the substituents: **6a** R^1 = OH; **6b** R^5 = OH; **7a** R^1 = OH, R^5 = Br; **7b** R^1 = Br, R^5 = OH; **8a** R^2 = NO$_2$; **8b** R^4 = NO$_2$; **9a** R^1 = OCH$_3$; **9b** R^5 = OCH$_3$; **10a** R^1 = R^3 = OCH$_3$; **10b** R^3 = R^5 = OCH$_3$ (Fig. 1).
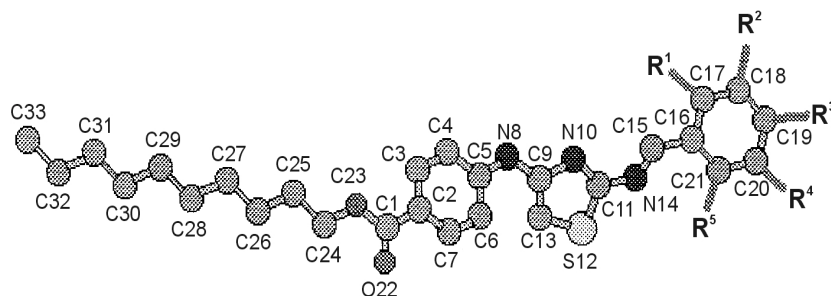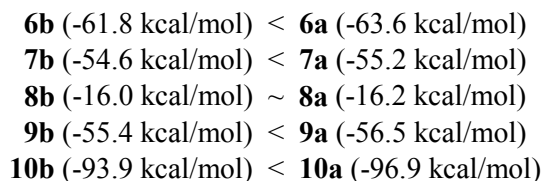
Fig. 1. Numbering of atoms and substituents in molecules of the thiazoles studied.

From the results of the quantum-chemical calculation of the heats of formation (Table 2), the isomers can be placed in the following order of increasing thermodynamic stability relative to the simple substance:

6b (-61.8 kcal/mol) < **6a** (-63.6 kcal/mol)
7b (-54.6 kcal/mol) < **7a** (-55.2 kcal/mol)
8b (-16.0 kcal/mol) ~ **8a** (-16.2 kcal/mol)
9b (-55.4 kcal/mol) < **9a** (-56.5 kcal/mol)
10b (-93.9 kcal/mol) < **10a** (-96.9 kcal/mol)

Thus among the *o*-isomers conformers **6a** and **9a** are somewhat more stable. The same is true for the 1,6-disubstituted compound **7** and the 2,4-disubstituted compound **10**. There is practically no difference in thermodynamic stability in the conformers of the *m*-isomer **8**. Since the differences in thermodynamic stability of the isomers **a** and **b** for compounds **6-10** do not exceed 3 kcal/mol, then, considering the accuracy of the calculation, it is not possible to conclude that one or other of the isomers predominates to any extent in the Schiff base formation reaction.

It may be noted from analysis of the geometric structures of the substituted thiazoles that the bond lengths and valence angles in molecules with different substituents change very little. Nevertheless some regularities can be noticed. Changes in bond lengths with different substituents are observed only in the benzylidene component: the lengths of the bonds $C_{(18)}$–$C_{(19)}$ and $C_{(19)}$–$C_{(20)}$ increase with increasing electron donor properties of the substituents in the *p*-position. For conformer **a**, the presence of an *o*-substituent in the benzylidene component increases the length of the $C_{(16)}$–$C_{(17)}$ and $C_{(17)}$–$C_{(18)}$ bonds, whereas there is no change in conformer **b**. On the other hand, the length of the $N_{(14)}$–$C_{(15)}$ bond is decreased in conformer **b** but is unchanged in conformer **a**. In the presence of a *m*-substituent, the $C_{(18)}$–$C_{(19)}$ and $N_{(14)}$–$C_{(15)}$ bond lengths are decreased and the $C_{(20)}$–$C_{(21)}$ bond length is increased in conformer **b**, while in conformer **a** the $C_{(17)}$–$C_{(18)}$ bond is lengthened and the $C_{(19)}$–$C_{(20)}$ bond is shortened. Among the molecules calculated the angle $N_{(10)}$–$C_{(11)}$–$S_{(12)}$ is decreased only for compounds **9a** and **10a** with a CH_3O substituent at position 2. In comparison with the *p*-substituted, the angle $C_{(15)}$–$C_{(16)}$–$C_{(17)}$ is larger in the *o*-isomers of form **a** and smaller in form **b**, whereas the reverse is true for the *m*-isomers.

The effects of substituents on the torsion and dihedral angles are shown in Fig.2. We note that the size of the torsion angles $O_{(22)}$–$C_{(1)}$–$C_{(2)}$–$C_{(7)}$ ($\varphi 1$), $C_{(4)}$–$C_{(5)}$–$N_{(8)}$–$C_{(9)}$ ($\varphi 2$), and $C_{(13)}$–$C_{(9)}$–$N_{(8)}$–$C_{(5)}$ ($\varphi 3$) are effectively unchanged by the introduction of a substituent into the benzylidene residue, whereas the values of the torsion angles $N_{(10)}$–$C_{(11)}$–$N_{(14)}$–$C_{(15)}$ ($\varphi 4$) and $N_{(14)}$–$C_{(15)}$–$C_{(16)}$–$C_{(21)}$ ($\varphi 5$) change considerably and depend on the nature and position of the substituent. For example for compounds with substituents in the *m*- and *p*- positions the size of the torsion angles $\varphi 4$ and $\varphi 5$ change within the ranges from -13.8° to -8.0° and from -22.8° to -11.8° respectively. For *o*-isomers the values of the torsion angles $\varphi 4$ and $\varphi 5$ for the form **a** lie within the limits from -5.6° to -3.2° and -25.4° to -14.9° respectively; in the form **b** the thiazole and benzene rings are rotated more considerably: $\varphi 4$ and $\varphi 5$ are found within the limits from -2.4° to 10.2° and from -45.3 to -43.0° respectively. Maximum rotation of the rings occurs in the compounds with two *o*-substituents (from 15.1° to 16.8° and from -59.1° to -57.2° for $\varphi 4$ and $\varphi 5$ respectively). Introduction of two *o*-substituents into the molecule leads to rotation of these rings in opposite directions, the amplitude of the rotation being greater for torsion angle $\varphi 5$ than for angle $\varphi 4$.

We have observed a relation between the electronic properties of the substituents in the benzene ring of the benzylidene unit and the values of the torsion angles $\varphi 4$ and $\varphi 5$: the increase in electron acceptor properties of the substituents in the series $N(CH_3)_2 < OCH_3 < OH < Br < NO_2$ leads to an increase in the amplitudes of the deviation of the size of the angles (Fig. 2).

TABLE 2. Calculated Parameters Which Change in Value on Introduction of Substituent into the Molecule

Bond, d, Å	Compound														
	1	2	3	4	5	6		7		8		9		10	
						a	b	a	b	a	b	a	b	a	b
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
N$_{(14)}$–C$_{(15)}$	1.30	1.30	1.30	1.30	1.30	1.30	1.29	1.29	1.30	1.30	1.29	1.30	1.29	1.30	1.29
C$_{(15)}$–C$_{(16)}$	1.47	1.47	1.46	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.46	1.47	1.47	1.46
C$_{(16)}$–C$_{(17)}$	1.40	1.40	1.40	1.40	1.40	1.41	1.40	1.41	1.40	1.40	1.40	1.42	1.40	1.42	1.40
C$_{(17)}$–C$_{(18)}$	1.39	1.39	1.39	1.39	1.39	1.41	1.39	1.41	1.40	1.40	1.39	1.40	1.39	1.40	1.39
C$_{(18)}$–C$_{(19)}$	1.41	1.40	1.42	1.40	1.40	1.39	1.40	1.39	1.39	1.41	1.39	1.40	1.40	1.40	1.40
C$_{(19)}$–C$_{(20)}$	1.41	1.40	1.42	1.41	1.40	1.40	1.39	1.40	1.39	1.39	1.40	1.40	1.39	1.41	1.39
C$_{(20)}$–C$_{(21)}$	1.39	1.39	1.39	1.39	1.39	1.39	1.41	1.40	1.40	1.39	1.40	1.40	1.41	1.40	1.41
C$_{(21)}$–C$_{(16)}$	1.40	1.40	1.40	1.40	1.40	1.40	1.41	1.40	1.41	1.40	1.40	1.41	1.41	1.41	1.41
Valence angle, ω, deg.															
C$_{(1)}$–C$_{(2)}$–C$_{(3)}$	121.7	121.8	121.8	121.7	121.7	121.7	121.7	121.5	121.6	121.9	121.7	121.7	121.6	121.8	121.8
C$_{(2)}$–C$_{(3)}$–C$_{(4)}$	120.6	120.5	120.6	120.5	120.5	120.5	120.5	120.5	120.5	120.5	120.6	120.5	120.5	120.5	120.5
C$_{(3)}$–C$_{(4)}$–C$_{(5)}$	120.5	120.5	120.5	120.5	120.6	120.5	120.6	120.4	120.5	120.5	120.5	120.5	120.5	120.5	120.5
C$_{(4)}$–C$_{(5)}$–C$_{(6)}$	118.4	118.4	118.3	118.3	118.3	118.4	118.3	118.5	118.4	118.4	118.4	118.4	118.3	118.4	118.4
C$_{(7)}$–C$_{(2)}$–C$_{(3)}$	119.5	119.5	119.4	119.5	119.5	119.5	119.4	119.5	119.4	119.5	119.4	119.5	119.4	119.5	119.5
C$_{(4)}$–C$_{(5)}$–N$_{(8)}$	118.0	118.0	118.1	118.0	118.0	118.0	118.0	117.8	118.0	118.0	118.0	118.0	117.9	118.2	118.1
N$_{(8)}$–C$_{(9)}$–N$_{(10)}$	121.0	121.1	121.1	121.0	121.0	121.0	121.0	121.0	120.7	121.2	121.2	121.1	120.8	121.5	121.1
C$_{(9)}$–N$_{(10)}$–C$_{(11)}$	109.0	109.0	109.1	109.0	109.0	109.1	109.0	109.0	109.0	109.0	108.9	109.3	109.1	109.3	109.1

TABLE 2 (continued)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
$N_{(10)}-C_{(11)}-S_{(12)}$	114.3	114.3	114.2	114.3	114.3	114.3	114.3	114.4	114.3	114.4	114.4	113.8	114.3	113.8	114.3
$C_{(11)}-S_{(12)}-C_{(13)}$	91.0	91.1	91.0	91.0	91.0	91.1	91.1	91.1	91.1	91.0	91.1	91.2	91.1	91.1	91.1
$C_{(12)}-C_{(13)}-C_{(9)}$	111.7	111.7	111.6	111.7	111.7	111.7	111.6	111.7	111.6	111.7	111.7	111.6	111.6	111.6	111.6
$C_{(13)}-C_{(9)}-C_{(10)}$	114.0	114.0	114.0	114.0	114.0	113.9	114.0	113.9	113.9	113.9	113.8	114.0	114.0	114.2	114.0
$N_{(10)}-C_{(11)}-N_{(14)}$	129.2	129.2	129.5	129.1	129.0	129.0	129.1	128.5	128.7	128.8	128.9	129.1	129.1	129.6	129.3
$S_{(12)}-C_{(11)}-N_{(14)}$	116.5	116.7	116.3	116.5	116.6	116.7	116.6	117.0	117.0	116.8	116.7	117.1	116.6	116.6	116.5
$C_{(11)}-N_{(14)}-C_{(15)}$	122.2	121.5	122.3	122.2	122.2	122.0	122.2	122.3	122.0	122.3	122.7	121.7	122.1	122.3	121.9
$N_{(14)}-C_{(15)}-C_{(16)}$	122.2	122.6	122.3	122.3	122.0	122.3	122.2	121.3	121.2	121.6	121.4	122.4	122.4	121.9	122.7
$C_{(15)}-C_{(16)}-C_{(17)}$	118.2	118.0	118.6	118.1	118.1	120.4	117.6	118.9	120.3	117.8	118.4	118.8	117.5	119.3	117.5
$C_{(16)}-C_{(17)}-C_{(18)}$	120.8	120.5	121.1	120.6	120.3	120.7	121.0	121.0	120.5	119.2	120.3	121.1	120.9	121.3	121.6
$C_{(17)}-C_{(18)}-C_{(19)}$	119.2	119.1	120.8	119.3	120.0	119.5	120.0	119.1	120.2	121.1	120.6	119.4	119.9	118.8	119.0
$C_{(18)}-C_{(19)}-C_{(20)}$	120.6	121.0	117.6	120.8	119.9	120.4	120.2	120.6	120.4	118.9	118.9	120.1	120.5	121.0	121.1
$C_{(19)}-C_{(20)}-C_{(21)}$	119.4	119.3	120.9	119.2	120.1	120.2	119.8	120.4	119.4	120.7	121.2	120.5	119.8	119.3	119.0
$C_{(20)}-C_{(21)}-C_{(16)}$	120.6	120.4	121.0	120.6	120.2	120.8	120.4	120.2	120.9	120.2	119.0	120.5	120.2	121.5	120.7
Enthalpy of formation, ΔH°_{f}, kcal/mol	-59.2	-15.9	-13.2	-65.5	-15.5	-63.6	-61.8	-55.2	-54.6	-16.2	-16.0	-56.5	-55.4	-96.9	-93.9

TABLE 3. Calculated Parameters Which do not Change on Introduction of the Substituent into the Molecule

Bond	d, Å	Bond	d, Å
$C_{(1)}$–$C_{(2)}$	1.47	$C_{(13)}$–$C_{(9)}$	1.41
$C_{(2)}$–$C_{(3)}$	1.40	$C_{(11)}$–$N_{(14)}$	1.40
$C_{(3)}$–$C_{(4)}$	1.39	$C_{(1)}$–$O_{(22)}$	1.24
$C_{(4)}$–$C_{(5)}$	1.42	$C_{(1)}$–$O_{(23)}$	1.31
$C_{(5)}$–$C_{(6)}$	1.41	$O_{(23)}$–$C_{(24)}$	1.42
$C_{(6)}$–$C_{(7)}$	1.39	$C_{(24)}$–$C_{(25)}$	1.52
$C_{(7)}$–$C_{(2)}$	1.40	$C_{(25)}$–$C_{(26)}$	1.51
$C_{(5)}$–$N_{(8)}$	1.40	$C_{(26)}$–$C_{(27)}$	1.51
$N_{(8)}$–$C_{(9)}$	1.41	$C_{(27)}$–$C_{(28)}$	1.51
$C_{(9)}$–$N_{(10)}$	1.40	$C_{(28)}$–$C_{(29)}$	1.51
$N_{(10)}$–$C_{(11)}$	1.35	$C_{(29)}$–$C_{(30)}$	1.51
$C_{(11)}$–$S_{(12)}$	1.73	$C_{(30)}$–$C_{(31)}$	1.51
$S_{(12)}$–$C_{(13)}$	1.65	$C_{(32)}$–$C_{(33)}$	1.51

Some Valence Angles

Angle	ω, deg.	Angle	ω, deg.
$C_{(5)}$–$C_{(6)}$–$C_{(7)}$	120.5	$C_{(26)}$–$C_{(27)}$–$C_{(28)}$	111.2
$C_{(6)}$–$C_{(7)}$–$C_{(8)}$	120.6	$C_{(27)}$–$C_{(28)}$–$C_{(29)}$	111.2
$O_{(22)}$–$C_{(1)}$–$C_{(23)}$	117.7	$C_{(28)}$–$C_{(29)}$–$C_{(30)}$	111.3
$C_{(1)}$–$O_{(23)}$–$C_{(24)}$	116.3	$C_{(29)}$–$C_{(30)}$–$C_{(31)}$	111.3
$O_{(23)}$–$C_{(24)}$–$C_{(25)}$	106.0	$C_{(30)}$–$C_{(31)}$–$C_{(32)}$	111.3
$C_{(24)}$–$C_{(25)}$–$C_{(26)}$	-110.1	$C_{(31)}$–$C_{(32)}$–$C_{(33)}$	111.5
$C_{(25)}$–$C_{(26)}$–$C_{(27)}$	111.0		

Some Torsion Angles

Angle	τ, deg	Angle	τ, deg
$C_{(1)}$–$C_{(2)}$–$C_{(3)}$–$C_{(4)}$	177.73	$O_{(22)}$–$C_{(1)}$–$C_{(23)}$–$C_{(24)}$	-2.21
$C_{(2)}$–$C_{(3)}$–$C_{(4)}$–$C_{(5)}$	-0.25	$O_{(22)}$–$C_{(1)}$–$C_{(2)}$–$C_{(3)}$	5.58
$C_{(13)}$–$C_{(9)}$–$N_{(10)}$–$C_{(11)}$	1.02	$C_{(1)}$–$O_{(23)}$–$C_{(24)}$–$C_{(25)}$	-177.04
$C_{(13)}$–$S_{(12)}$–$C_{(11)}$–$N_{(10)}$	1.00	$C_{(30)}$–$C_{(31)}$–$C_{(32)}$–$C_{(33)}$	179.33
$C_{(16)}$–$C_{(17)}$–$C_{(18)}$–$C_{(19)}$	0.87		

To investigate the influence of the substituents on the spatial characteristics of the molecules studied the dihedral angles between the thiazole ring and the benzene rings of the benzylidene and aniline components ($\theta 1$ and $\theta 2$ respectively) were calculated from the results of the quantum-chemical calculations. The size of angle $\theta 1$ is practically independent of the substituents in the benzene ring and has a value of 44.2° - 47.0°, whereas the size of the dihedral angle $\theta 2$ lies within the limits 8.2° and 44.3° and does depend on the nature and position of the substituent (Fig. 2).

One of the most important factors which determines the appearance of liquid-crystal properties of azomethines is the geometrical anisotropy of the molecule, the figure of rotation of which around the long axis is a cylinder [3]. An increase in the ratio of the height of the cylinder to its diameter widens the temperature range of the mesophase (ΔT). Because the acoplanar azomethines pack more loosely and have lower melting points, it may be expected that an increase in the acoplanarity of the substituted thiazoles studied (i.e., the angle $\theta 2$) should lead to a decrease in the melting point and ΔT. This relation is followed for the *p*-substituted compounds **1-5**, with the exception of compound **4**, with an OH substituent, for which an increase (not a decrease) in T_{K-1} is observed together with a sharp decrease in the range of existence of a mesophase, ΔT. This is evidently connected with the formation of intramolecular hydrogen bonds, the appearance of which, as a rule,
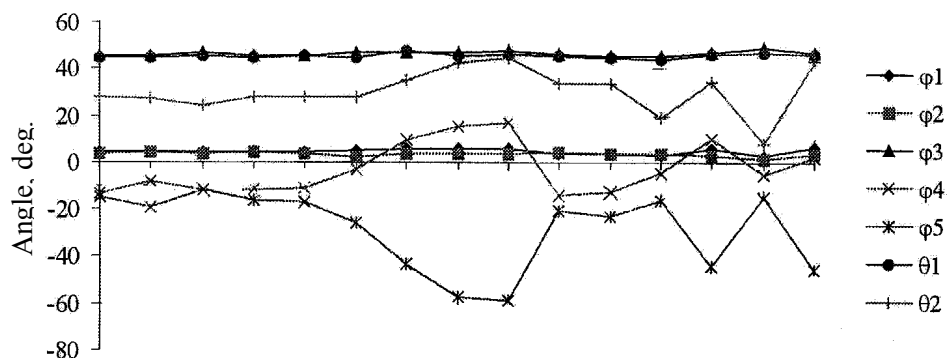
Fig. 2. Relation between the calculated values of the torsion and dihedral angles of the thiazoles investigated on the substituents: torsion angles $O_{(22)}$–$C_{(1)}$–$C_{(2)}$–$C_{(7)}$ $\varphi 1$; $C_{(4)}$–$C_{(5)}$–$N_{(8)}$–$C_{(9)}$ $\varphi 2$; $C_{(13)}$–$C_{(9)}$–$N_{(8)}$–$C_{(5)}$ $\varphi 3$; $N_{(10)}$–$C_{(11)}$–$N_{(14)}$–$C_{(15)}$ $\varphi 4$; $N_{(14)}$–$C_{(15)}$–$C_{(16)}$–$C_{(21)}$ $\varphi 5$; dihedral angles between the planes of the benzene ring of the aniline component and the thiazole ring $\theta 1$ and between the benzylidene component and the thiazole ring $\theta 2$.

leads to increased thermostability of the mesophase, but in some cases to its degeneration. For compounds **6-10** with various substituents in different positions on the benzene ring, no unambiguous correlation was established, because introduction of secondary substituents can considerably decrease the temperature range of the liquid crystal state as a result of decreasing the relative contribution of secondary dipole-dipole interactions and the formation of intermolecular hydrogen bonds.

It is shown, therefore, that geometrical anisotropy is not the determining factor in guaranteeing liquid-crystal properties in the molecules synthesized.

EXPERIMENTAL

^{1}H NMR Spectra of CDCl$_3$ solutions with HMDS as internal standard were recorded on a Bruker WP-200 (200.13 MHz) instrument. Temperatures of the phase transitions were measured on an MIN-10 polarizing microscope with a heating attachment. The purity of all the compounds described were monitored by TLC on alumina (toluene–chloroform 3:7).

The semiempirical AM1 (DFP) method, from the AMPAC package, was used for quantum-chemical calculations. Complete optimization of the molecules was carried out without limiting any parameters.

(4-Decyloxycarbonyl)aniline (11). 92% H$_2$SO$_4$ (11.3 g, 0.115 mol) was added with vigorous stirring to a mixture of 4-aminobenzoic acid (12.3 g, 0.1 mol) and decyl alcohol (94.8 g, 0.6 mol). After refluxing for 6 h the reaction mixture was distilled with steam, the residue was cooled, (4-decyloxycarbonyl)anilinium sulphate was isolated, dissolved in hot water, and treated with conc. NH$_4$OH (16 ml). The precipitate was filtered off and recrystallized from hexane.

N-Chloroacetyl-(4-decyloxycarbonyl)aniline (12). Chloroacetyl chloride (6.3 g, 4.45 ml, 0.055 mol) was added dropwise to a solution of compound **11** (13.9 g, 0.5 mol) in diethyl ether (100 ml). The mixture was kept for 3 h at room temperature, the precipitate was filtered off, washed several times with water, and recrystallized from ethanol.

2-Amino-4-[(4-decyloxycarbonyl)anilino]thiazole (13). A mixture of compound **12** (10.6 g, 0.03 mol) and thiourea (2.28 g, 0.03 mol) was dissolved in absolute ethanol (50 ml) and refluxed for 8 h. At the end of the reaction the solvent was distilled off, the residue was neutralized with 20% sodium carbonate solution, the precipitate was filtered off and recrystallized from ethanol.

2-Arylidenenamino-4-[(4-decyloxycarbonyl)anilino]thiazoles (1-10). A mixture of compound **13** (1.5 g, 0.04 mol) and an aromatic aldehyde (0.04 mol) in absolute THF (40 ml) was refluxed for 4 h in the presence of a catalytic amount of piperidine. The solvent was distilled off and the residue was recrystallized from ethanol.

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