Chemistry of Heterocyclic Compounds, Vol. 40, No. 4, 2004

NEW DERIVATIVES OF THIAZOLE WITH MESOMORPHOUS PROPERTIES

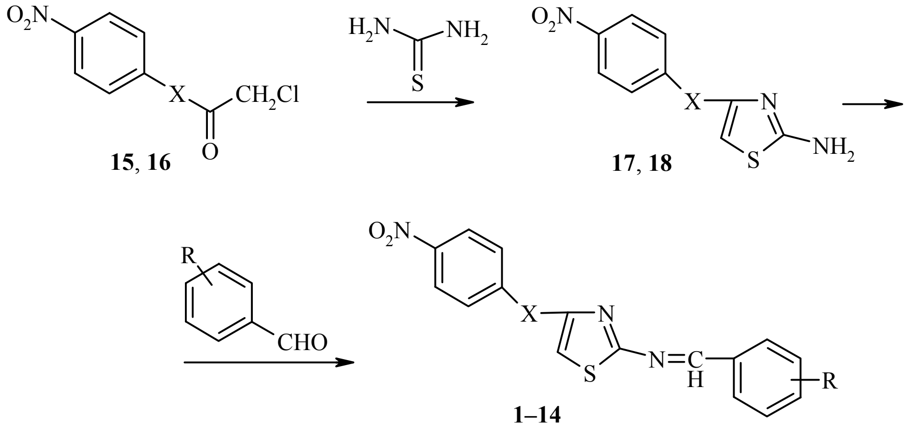
Z. Kh. Kuvatov, M. G. Safarov, and M. M. Murza

Azomethines containing a thiazole ring have been synthesized and their liquid crystal properties have been investigated. The influence of the central group and substituents in the azomethine component on the type and temperature range of the mesomorphous properties of the compounds synthesized has been elucidated.

Keywords: azomethines, thiazole ring, liquid crystal properties.

We have previously investigated the effect of the structure of azomethines with thiazole rings on the type of mesomorphism and its temperature range, with introduction of alkoxy groups with varying length of the aliphatic chain into the benzylidene component [1, 2].

In continuation of the study of the liquid crystal properties of azomethine derivatives of 2-aminothiazole, we have obtained compounds **1-14,** which contain substituents of various types (halogens, nitro, dimethylamino, and methoxy groups) in the benzylidene unit using the following scheme:



1–7, **15**, **17** X = O; **8–14**, **16**, **18** X = NH; **1**, **8** R = 2-F, **2**, **9** R = 3-Br; **3**,**10** R = 4-Cl;
4, **11** R = 2-NO_2; **5**,**12** R = 4-NO_2; **6**, **13** R = 4-NMe_2; **7**, **14** R = 2,4-$(OMe)_2$

Bashkir State University, Ufa 450074, Russia; e-mail: KuvatovZK@ic.bashedu.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, 596-598, April 2004. Original article submitted March 30, 2001.

Sodium *p*-nitrophenoxide, which was quantitatively acylated with chloroacetyl chloride in alkaline medium, was used as the starting material for the preparation of compounds **1**-**7**. Chloroacetyl derivative **15** reacted with thiourea in absolute ethanol to give the corresponding 2-aminothiazole **17**, which condensed with aromatic aldehydes in absolute ethanol in the presence of a catalytic amount of piperidine to give compounds **1-7**.

The Schiff's bases **8-14** were obtained analogously. In this case *p*-nitroaniline was used as the starting material: chloroacetylation was carried out in ether, but condensation with aldehydes – in dry THF.

Investigation of the mesophase properties of azomethines prepared showed that all of the compounds **1-14** possess nematic liquid crystal properties. It should be noted that with X = O the mesophase existed over about twice the range as with X = NH (Table 1), however when nitro group was introduced into the *ortho* position in the benzylidene component (compound **11**) the mesophase interval was 81° for X = NH too, i.e., it was comparable with the temperature ranges for compounds **1-7** (X =O).

Evidently there are intramolecular hydrogen bonds between the proton of the N=CH group and the NO_2 group in the *ortho*-position of the benzylidene component of compounds **4** and **11**, thanks to which the intermolecular interactions in these crystals are not very strong and therefore the temperature range of the mesophase is increased and for the compound with X=O it is maximal (Table 1). Compounds **8-14** are more stable and show enantiotropic mesomorphism (the liquid crystal state is retained on super-cooling the crystalline modification), whereas compounds **1-7** decompose above 200°C and possess monotropic mesomorphism.

TABLE 1. Characteristics of Compounds **1-13**, **17**, and **18**

Compound	Empirical formula	Found, % Calculated, % C	H	N	T, °C* n.m.	i.m.	Yield, %
1	$C_{16}H_{10}FN_3O_3S$	55.82 55.97	2.55 2.92	12.04 12.24	47	116	56
2	$C_{16}H_{10}BrN_3O_3S$	47.12 47.54	2.24 2.49	10.10 10.39	80	112	62
3	$C_{16}H_{10}ClN_3O_3S$	53.06 53.40	2.45 2.80	11.52 11.70	62	152	58
4	$C_{16}H_{10}N_4O_5S$	51.64 51.89	2.36 2.72	14.88 15.13	49	146	55
5	$C_{16}H_{10}N_4O_5S$	51.48 51.89	2.48 2.72	15.04 15.13	70	158	61
6	$C_{18}H_{16}N_4O_3S$	58.30 58.69	4.10 4.35	14.96 15.22	77	148	68
7	$C_{18}H_{16}N_3O_5S$	55.58 55.96	3.92 4.15	10.72 10.88	85	132	65
8	$C_{16}H_{11}FN_4O_2S$	56.02 56.14	3.04 3.22	16.14 16.37	100	133	52
9	$C_{16}H_{11}BrN_4O_2S$	43.88 44.15	2.35 2.53	12.62 12.87	125	152	64
10	$C_{16}H_{11}ClN_4O_2S$	53.22 53.56	2.84 3.07	15.44 15.62	120	150	68
11	$C_{16}H_{11}N_5O_4S$	51.84 52.03	2.70 2.98	18.80 18.97	43	124	56
12	$C_{16}H_{11}N_5O_4S$	51.76 52.03	2.64 2.98	18.64 18.97	64	129	57
13	$C_{18}H_{17}N_5O_2S$	58.50 58.86	4.42 4.63	18.86 19.07	76	137	63
14	$C_{18}H_{16}N_4O_4S$	55.92 56.25	3.96 4.17	14.32 14.58	114	161	57
17	$C_9H_7N_3O_3S$	45.32 45.57	2.64 2.95	17.48 17.72			
18	$C_9H_8N_4O_2S$	45.40 45.76	3.24 3.40	23.45 23.73			

---

* Temperatures at which the nematic (n.m.) and isotropic (i.m.) modifications exist.

EXPERIMENTAL

Phase transition temperatures were measured on MIN-10 polarizing microscope with a thermal adapter in a heating regime. The individuality and purity of all the compounds described were monitored by TLC on aluminum oxide with toluene–chloroform (1:3) as eluent.

o-Chloroaceto-4-nitroaniline (**15**) and N-chloroaceto-4-nitroaniline (**16**) were synthesized by a known method [3].

N-(2-Aminothiazol-4-yl)-4-nitroaniline (18). Solution of compound **16** (14.2 g, 0.06 mol) and thiourea (4.6 g, 0.06 mol) in absolute ethanol (100 ml) was boiled for 8 h. At the end of the reaction the solvent was evaporated and the residue was neutralized with 20% sodium carbonate solution. The precipitate was filtered off and crystallized from water.

Compound 17 was prepared analogously.

4-[Amino-*p*-(4-nitrophenyl)]-2-benzylidenaminothiazoles (8-14). Mixture of compound **18** (1 g, 0.042 mol) and aromatic aldehyde (0.0042 mol) in dry THF (40 ml) was boiled for 4 h in the presence of a catalytic quantity of piperidine. The solvent was evaporated and the residue was crystallized from ethanol.

The Benzylidene Derivatives 1-7 were prepared analogously from compound **17**.

REFERENCES

1. M. M. Murza, A. S Golovanov, and M. G. Safarov, *Khim. Geterotsikl. Soed.,* 546 (1996).
2. M. M. Murza, A. S Golovanov, and M. G. Safarov, *Zh. Org. Khim.,* **31**, 1701 (1995).
3. I. A. Khrizman (Ed.), *Advances in Organic Synthesis in the Chemization of the Agricultural Industry* [in Russian], Ufa, 113 (1970).