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The influence of heteroaromatic rings on mesomorphic properties I. A new series of pyridazine- and pyridine-carboxylates

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PRELIMINARY COMMUNICATIONS

The influence of heteroaromatic rings on mesomorphic properties

I. A new series of pyridazine- and pyridine-carboxylates

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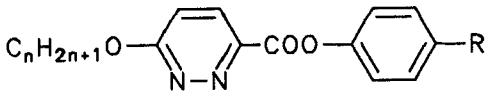
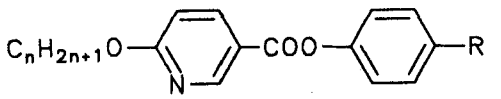
We have prepared new esters of 6-alkyloxypyridazine-3-carboxylic acid and the 6-alkyloxypyridine-3-carboxylic acid. The introduction of the heteroaromatic rings leads to significant changes in mesomorphic behaviour. The compounds exhibit a strong tendency to form smectic C phases.

In recent years the great scientific and practical interest in liquid crystals has generated an increasing requirement for compounds with specific properties. Therefore chemists are still searching for new structural units and structural variations in order to find compounds more capable to meet present requirements. Since heterocyclic compounds can be extremely useful in influencing the dielectric anisotropy, viscosity, birefringence, S_C ranges positively, we have continued our investigations on heteroaromatic carboxylates [1] with the synthesis of various 6-alkyloxypyridazine-3-carboxylates (I) and 6-alkyloxypyridine-3-carboxylates (II). The purpose of this work was to check the influence of heteroaromatic rings with lateral dipole moments on mesomorphic behaviour.

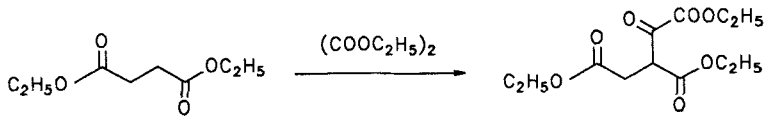


(I)



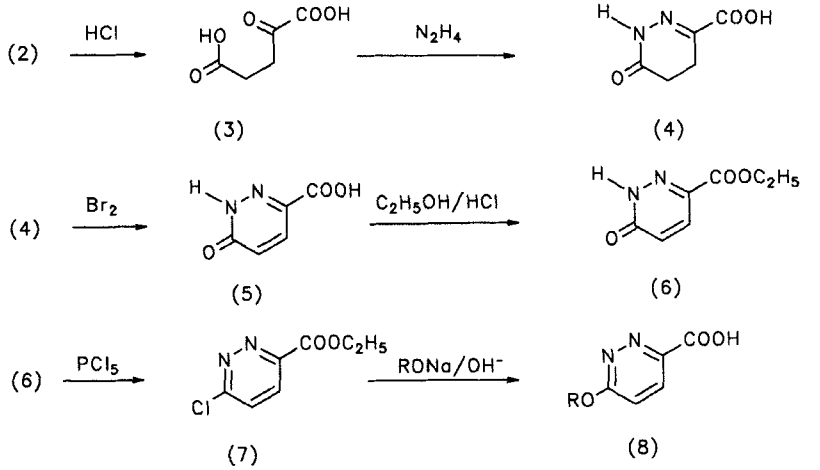
(II)

The synthesis of the pyridazine carboxylic acid was carried out according to the scheme



(1) (2)

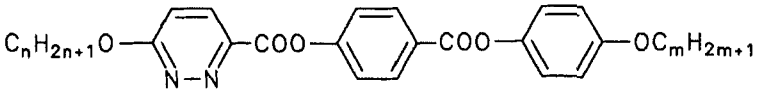
* Author for correspondence.



by improvement of several literature methods [2, 3]. For the synthesis of the 6-alkyloxypyridine-3-carboxylic acid we used the method of Barbera *et al.* [4]. In order to obtain the corresponding pyridine-carboxylates the usual methods (Et_3N, DMAP) were applied [5–7]. The esterification of the 6-alkyloxypyridazine-3-carboxylic acid required water-soluble carbodiimide [8, 9]. The structure of all products was confirmed by ^1H NMR, ^{13}C NMR and elemental analysis. Transition temperatures were measured using a polarizing microscope. The identification of the mesophases was performed by textural observations of similar series. For several members of the homologous series the transition temperatures and enthalpies, ΔH, were obtained by calorimetry (Perkin–Elmer DSC 7).

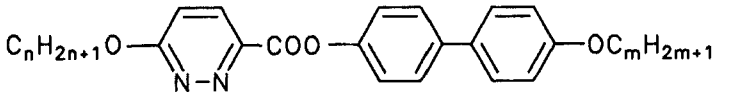
The transition temperatures of the pyridine and pyridazine benzoates and the transition enthalpies of selected examples are given in tables 1–7.

Table 1. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) for the compounds



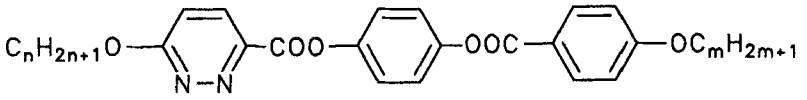
Compound	*n*	*m*	C		S_C		S_A		N		I
1	4	4	●	158		—		—	●	187	●
2	4	5	●	155		—		—	●	194	●
3	4	6	●	143	●	153		—	●	191	●
				(31·3)		(0·61)				(2·3)	
4	4	7	●	136	●	151		—	●	198	●
5	4	8	●	139	●	163		—	●	194	●
6	5	7	●	146	●	173		—	●	188	●
7	6	4	●	151		—		—	●	197	●
8	6	5	●	157		—		—	●	193	●
9	6	6	●	140	●	161		—	●	188	●
				(32·03)		(0·35)				(1·92)	
10	6	7	●	144	●	164	●	168·5	●	185·5	●
				(33·6)		(0·21)		(0·53)		(2·24)	
11	6	8	●	137	●	175	●	180	●	181	●
				(30·1)		(0·6)		(1·6)		(4·9)	
12	6	9	●	128	●	185		—		—	●

Table 2. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) for the compounds



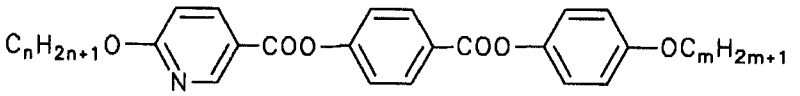
Compound	*n*	*m*	C		S_C		S_A	N		I
13	5	7	•	171 (36·2)	•	182 (0·32)	—	•	194 (2·4)	•
14	6	7	•	176	•	190	—	•	198	•
15	6	8	•	167	•	188	—	•	196	•
16	6	9	•	162	•	189	—	•	193	•

Table 3. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) for the compounds



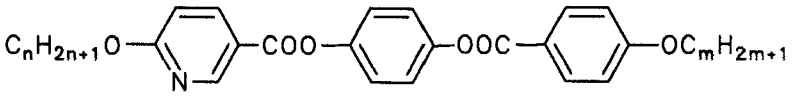
Compound	*n*	*m*	C		S_C	S_A	N		I
17	4	6	•	157	—	—	•	209	•
18	4	7	•	154	—	—	•	193	•
19	4	8	•	157 (41·7)	—	—	•	192 (2·3)	•
20	4	9	•	152 (38·1)	—	—	•	191 (4·1)	•
21	5	7	•	157	—	—	•	197	•
22	5	8	•	159 (32·7)	—	—	•	191 (2·1)	•
23	6	4	•	152	—	—	•	211	•
24	6	8	•	154	—	—	•	187	•
25	6	9	•	143	—	—	•	196	•

Table 4. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) for the compounds



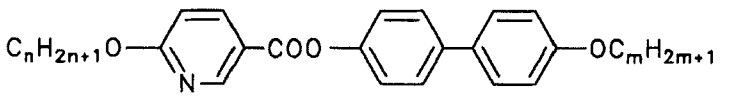
Compound	*n*	*m*	C		S_C		S_A		N		I
26	4	4	●	85 (22·3)	●	137 (0·34)	●	204 (0·15)	●	208 (1·12)	●
27	4	5	●	76 (37·2)	●	109 (0·66)	●	130 (0·31)	●	197 (2·3)	●
28	4	6	●	74 (27·1)	●	120 (0·32)	●	134 (0·19)	●	193 (1·3)	●
29	4	7	●	74	●	99	●	165	●	191	●
30	4	8	●	72	●	100	●	170	●	189	●
31	6	5	●	66	●	106	●	153	●	191	●
32	6	6	●	67	●	129	●	160	●	188	●
33	6	7	●	69 (30·5)	●	134 (0·22)	●	161 (0·26)	●	184 (0·87)	●
34	6	8	●	65	●	138	●	159	●	178	●
35	6	9	●	78	●	140	●	152	●	169	●

Table 5. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) for the compounds



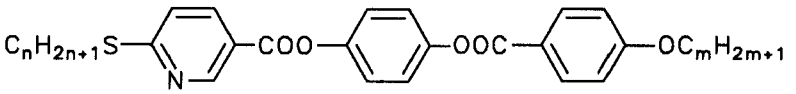
Compound	*n*	*m*	C		S_C		S_A		N		I
36	4	4	●	145		—		—	●	235	●
37	4	6	●	153		—		—	●	245	●
38	4	7	●	151		—		—	●	228	●
39	4	8	●	128 (23·6)	●	131 (0·25)		—	●	211 (1·32)	●
40	6	7	●	154		—		—	●	209	●
41	6	8	●	95	●	129		—	●	203	●

Table 6. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) for the compounds



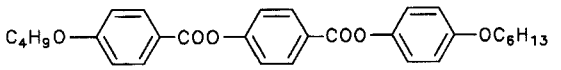
Compound	*n*	*m*	C		S_C		S_A		N		I
42	4	7	●	103	●	205		—	●	209	●
43	4	8	●	107	●	210		—		—	●

Table 7. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) for the compounds

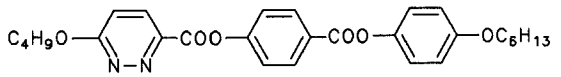


Compound	*n*	*m*	C		S_C		S_A		N		I
44	6	6	•	99	—		•	156	•	167	•
45	6	8	•	97	—		•	149	•	154	•
46	6	9	•	125	—		•	148	•	152	•

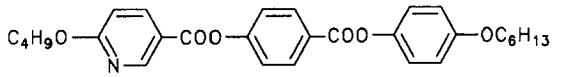
Our results confirm once again that small changes of the structure of mesomorphic systems (substitution of phenyl rings by pyridine and pyridazine) lead to significant changes in the mesomorphic behaviour. For example



C 91 N 215 I

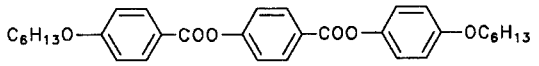


C 143 S_C 153 N 191 I

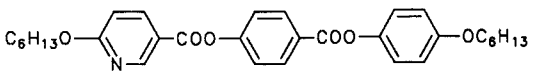


C 74 S_C 120 S_A 134 N 193 I

This demonstrates the changes caused by the introduction of heteroaromatic rings. The alteration of the molecular shape is comparatively small. The observed changes in the melting behaviour and the phase sequence could be attributed to the influence of the lateral dipoles of pyridine with respect to pyridazine. In comparison to the benzoates the melting temperatures of the pyridine compounds are decreased as well as the clearing temperatures:

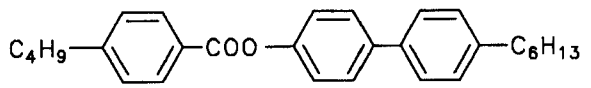


C 93 N 206 I

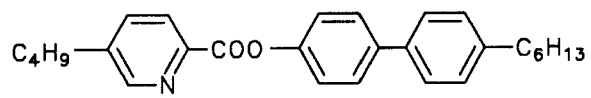


C 67 S_C 129 S_A 160 N 188 I

We had already found similar results with derivatives of fusaric acid [10],



C 78 N 159 I

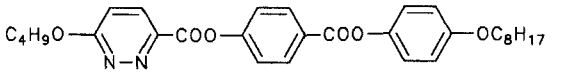


C 57 N 143 I

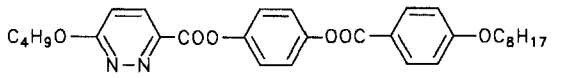
Although the position of the nitrogen within the pyridine is different, a lowering of clearing and melting temperatures could be established. However, a comparison between the pyridine-3-carboxylates and the pyridine-2-carboxylates but also the corresponding benzoates reveals the strong tendency of the 6-substituted pyridine-3-carboxylates to form smectic phases. For the pyridazine-2-carboxylates we found an increase of the melting temperatures and compared to the benzoates a strong tendency to form smectic phases.

The thermal and photochemical stability of the pyridazine esters were as expected lower than the stability of the corresponding pyridine and benzoic esters.

The direction of the ester groups is important for the phase sequence:



C 139 S_C 163 N 194 I



C 157 N 192 I

Contrary directed ester groups lead to the loss of the smectic phases. This is valid for the pyridazine esters as well as for the pyridine esters. A comparison with similar investigations [11–13] on the influence of pyridine and pyridazine rings on the mesomorphic properties confirm many of the observed effects. However it is clear that there is still a lot of synthetic work to do in order to generalize these observations.

References

[1] ZASCHKE, H., 1980, *Advances in Liquid Crystal Research and Applications*, edited by L. Bata (Pergamon Press), p. 1059.
[2] LIEBERMANN, D., and ROUAIX, A., 1959, *Bull. Soc. chim. Fr.*, p. 1793.
[3] BLAISE, E. E., and GAULT, H., 1911, *Bull. Soc. chim. Fr.*, *4*, **9**, 451.
[4] BARBERÁ, J., MELENDEZ, E., ROMERO, P., and SERRANO, J. L., 1985, *Molec. Crystals liq. Crystals*, **126**, 259.
[5] NASH, J. A., and GRAY, G. W., 1974, *Molec. Crystals liq. Crystals*, **25**, 299.
[6] PAVLUCHENKO, A. I., SMIRNOWA, N. I., KOVSHEV, E. I., TITOV, V. V., and PURVANECHAS, G., 1976, *Molec. Crystals liq. Crystals*, **37**, 35.
[7] PAVLUCHENKO, A. I., SMIRNOWA, N. I., KOVSHEV, E. I., and TITOV, V. V., 1979, *J. Phys., Paris*, Coll. C 3, **40**, C 3–1.
[8] SHEEHAN, J. C., and HLAVKA, J. J., 1956, *J. org. Chem.*, **21**, 493.
[9] SHEEHAN, J. C., CRUICKSHANK, P. A., and BOSHART, G. L., 1961, *J. org. Chem.*, **26**, 2525.
[10] PASCHKE, R., and ZASCHKE, H., 1986, *Z. Chem.*, **26**, 64.
[11] BURROW, M. P., GRAY, G. W., LACEY, D., and TOYNE, K., 1986, *Z. Chem.*, **26**, 139.
[12] BURROW, M. P., GRAY, G. W., LACEY, D., and TOYNE, K., 1988, *Liq. Crystals*, **3**, 1643.
[13] KAMOGAWA, H., KAWASHIMA, K., SHIMIZU, M., and SAKAKIBARA, Y., 1991, *Liq. Crystals*, **10**, 101