242. Broad Nematic Phases with High Clearing Points

by **Maged A. Osman**

Brown Boveri Research Center, CH-5400 Baden

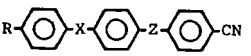
(23.III.82)

Summary

Unbranched 4-(4′-alkylbenzoyloxy)-, 4-(4′-methylaminobenzoyloxy)- and 4-(4′-dimethylaminobenzoyloxy)benzylidene-4″-cyanoanilines were synthesized. They show broad nematic phases with high nematic isotropic transitions. Lateral Cl-substituents decrease the clearing points of these liquid crystals by about 80°. The intermediate 4-(4′-alkylbenzoyloxy)benzaldehydes are monotropic nematic.

Introduction. – Geometrically anisotropic molecules usually show liquid crystalline phases [1]. The thermodynamical stability of their mesophases depends on how dense the molecules can pack together [2]. Molecules with long rigid cores can better pack than flexible molecules which can assume unfavourable configurations and therefore, have higher clearing points. Strong dipole moments along the long molecular axis can lead to association of the molecules [3], thus favouring a dense packing and enhancing the stability of the mesophase. The anisotropic dispersion interactions between conjugated systems can also lead to an improved packing and consequently higher clearing points. The unbranched 4″-alkyl-4-cyano-*p*-terphenyls were reported to have clearing points between 216 and 257° according to the length of the alkyl chain [4].

Results. – Elongating the terphenyl molecule by another ring would enhance the thermodynamic stability of the mesophase, however, this would also appreciably increase the melting point. Another way of enhancing the stability of the mesophase is to introduce relatively rigid bridges between the phenyl groups, whose net dipole moments are in the same direction as those of the terminal substituents (see the general formula **1**).



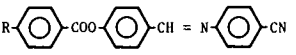
1

Unbranched 4-(4′-alkylbenzoyloxy)-, 4-(4′-methylaminobenzoyloxy)- and 4-(4′-dimethylaminobenzoyloxy)benzylidene-4″-cyanoanilines **2** were synthesized and their mesomorphic properties studied. They all show broad nematic phases with higher nematic to isotropic transitions than their corresponding terphenyl deriva-

0018-019X/82/8/2450-03$01.00/0

tives *(Table 1)*. Compound **3** has a clearing point which is 28° higher than the 4-cyano-4″-propyl-*p*-terphenyl and compound **5** shows even a 43° higher transition than the corresponding pentylterphenyl derivative. The alkylamino compounds **7** and **8** show nematic phases above 300° so that their nematic isotropic transitions could not be measured. The clearing points of compounds **3** and **5** which have an odd number of C-atoms in their alkyl chains show higher clearing points than those with an even number (**4** and **6**). Compounds **2** were synthesized according to the *Scheme*. The intermediate aldehydes **9** were monotropic nematic. Their mesomorphic properties are given in *Table 2*. The effect of lateral substituents on the clearing point is shown in *Table 3*. The replacement of a lateral H-atom by a Cl-atom decreased the clearing points of these liquid crystals by 85° and 86°, respectively [5].

Table 1. *Mesomorphic properties of 4-(4′-substituted-benzoyloxy)benzylidene-4″-cyanoanilines*

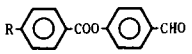


2

Nr.	R	C[a])	N[a])	I[a])	General Formula	C % Calc.	C % Found	H % Calc.	H % Found	N % Calc.	N % Found
3	C_3H_7	138	285		$C_{24}H_{20}N_2O_2$	78.24	78.19	5.47	5.49	7.60	7.54
4	C_4H_9	127	275		$C_{25}H_{22}N_2O_2$	78.51	78.47	5.80	5.87	7.33	7.37
5	C_5H_{11}	107	282		$C_{26}H_{24}N_2O_2$	78.76	78.71	6.10	6.08	7.07	6.94
6	C_6H_{13}	94	256		$C_{27}H_{26}N_2O_2$	79.00	79.05	6.38	6.33	6.83	6.75
7	$NHCH_3$	224	> 300		$C_{22}H_{17}N_3O_2$	74.35	74.20	4.82	4.88	11.84	11.72
8	$N(CH_3)_2$	241	> 300		$C_{23}H_{19}N_3O_2$	74.78	74.60	5.18	5.12	11.38	11.24

[a]) C = crystalline, N = nematic, I = isotropic.

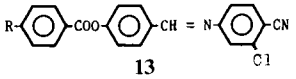
Table 2. *Mesomorphic properties of unbranched 4-(4′-alkylbenzoyloxy)benzaldehydes*



9

Nr.	R	C	N	I	General Formula	C % Calc.	C % Found	H % Calc.	H % Found
10	C_3H_7	45	(11)		$C_{17}H_{16}O_3$	76.10	76.30	6.01	6.01
11	C_4H_9	48	(7)		$C_{18}H_{18}O_3$	76.57	76.59	6.43	6.48
12	C_5H_{11}	34	(24)		$C_{19}H_{20}O_3$	77.00	77.10	6.80	6.76

Table 3. *Mesomorphic properties of 4-(4′-substituted-benzoyloxy)benzylidene-3″-chloro-4″-cyanoanilines*



13

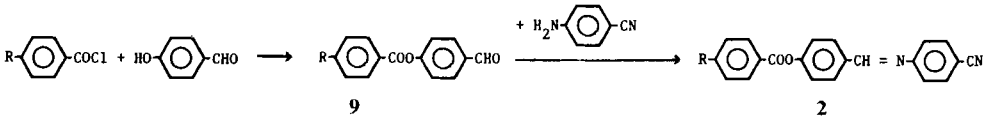
Nr.	R	C	N	I	General Formula	C % Calc.	C % Found	H % Calc.	H % Found	N % Calc.	N % Found
14	OC_4H_9	135	214		$C_{25}H_{21}ClN_2O_3$	69.30	69.30	4.89	4.83	6.47	6.36
15	C_6H_{13}	110	170		$C_{27}H_{25}ClN_2O_3$	72.88	72.71	5.66	5.58	6.30	6.23

Experimental Part

Preparation of 4-(4'-substituted-benzoyloxy)benzaldehydes. 4-Hydroxybenzaldehyde was esterified in pyridin with the corresponding benzoylchloride [6] [7] in the usual way; addition of an antioxidant is needed. The products were purified either by crystallization from ethanol or by destillation under reduced pressure.

Condensation of the aldehydes with the anilines. Equimolar amounts of the aldehyde and 4-cyano-aniline or 3-chloro-4-cyanoaniline [8] were heated under reduced N_2-pressure (40 Torr) at 150° for 4 h. The raw products were crystallized from benzene or CCl_4.

Scheme



9 2

REFERENCES

[1] *D. Demus, H. Demus & H. Zaschke*, «Flüssige Kristalle in Tabellen», VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1974.
[2] *M.A. Osman & L. Revesz*, Mol. Cryst. Liq. Cryst. *82*, 41 (1982).
[3] *Hp. Schad & M.A. Osman*, J. Chem. Phys. *75* (2), 880 (1981).
[4] *G. W. Gray*, J. Phys. (Paris) C-1 *36*, 337 (1975).
[5] *W. Weissflog, G. Pelzl & D. Demus*, Mol. Cryst. Liq. Cryst. *76*, 261 (1981).
[6] *M.A. Osman*, Helv. Chim. Acta *65*, 2448 (1982).
[7] *R. Graf & W. Langer*, J. Prakt. Chemie *148*, 11 (1937).
[8] *M. Grivsky & G.H. Hitchings*, Ind. Chim. Belg. *39*, 490 (1974).