Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Maged A. Osman [a] & Laszlo Revesz [a]

[a] Brown Boveri Research Center, CH-5405, Baden-Dättwil, Switzerland

To cite this article: Maged A. Osman & Laszlo Revesz (1980): Mesomorphic Properties of Some Alkyl-Amino Substituted Phenylcyclohexanes, Molecular Crystals and Liquid Crystals, 56:5, 133-138

To link to this article: http://dx.doi.org/10.1080/01406568008070900

Mol. Cryst. Liq. Cryst. Vol. 56 (Letters), pp. 133-138
0140-6566/80/5605-0133$04.50/0

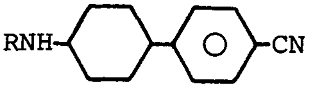
MESOMORPHIC PROPERTIES OF SOME ALKYLAMINO SUBSTITUTED PHENYLCYCLOHEXANES

MAGED A. OSMAN AND LASZLO REVESZ
Brown Boveri Research Center,
CH-5405 Baden-Dättwil, Switzerland

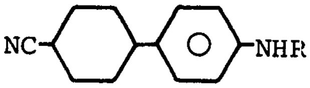
(Submitted for publication 14 November 1979)

The most widely used nematic phases in twisted nematic (TN) displays today are the alkyl cyano biphenyls[1] and the alkyl cyano phenylcyclohexanes[2] (PCH). The biphenyls possess higher dielectric anisotropy $\Delta\varepsilon$, optical anisotropy Δn and viscosity η than the PCHs[3]. Alkylamino cyano biphenyls[4] have still higher $\Delta\varepsilon$, Δn and η values than the alkyl biphenyl derivatives. For a TN-display the product of $\Delta n \cdot d$ (d=thickness) must be larger than a certain constant, the value of which depends on the tilt bias angle used. Since the response time of a TN-display is proportional to d^2, it is quite advantageous to use a nematic phase with a high Δn for such a display type. The response time also depends on the viscosity of the nematic phase. A high $\Delta\varepsilon$ leads to a lower operating voltage or a faster rise time if the same voltage is used. The ideal nematic phase for a parallel driven TN-display should then have a high $\Delta\varepsilon$ and Δn in addition to a low viscosity.

One way of achieving these properties is to combine the high Δε and Δn of the alkylamino cyano biphenyls with the low viscosity of the PCHs. We therefore, prepared representatives of the 4-(trans-4-alkylaminocyclohexyl)-benzonitriles I and the N-alkyl-4-(trans-4-cyanocyclohexyl)-anilines II to study their mesomorphic properties.



I

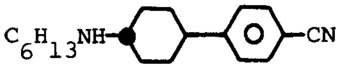
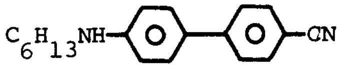
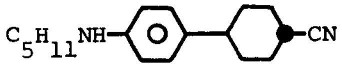
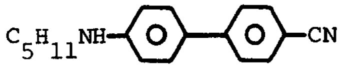


II

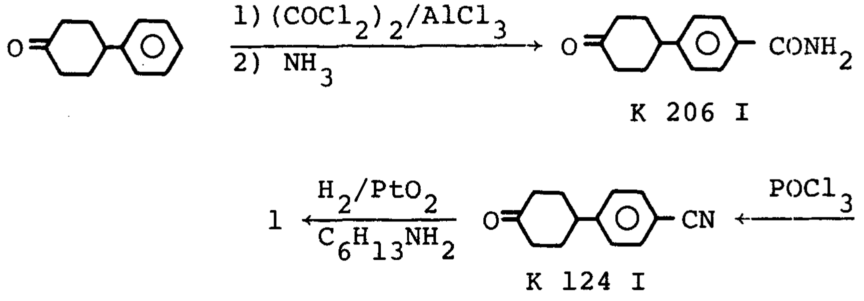
Table 1 shows a comparison between the alkylamino cyano substituted phenylcyclohexanes and their corresponding biphenyl derivatives. The hexylaminocyclohexyl derivative 1 as well as the pentylaminophenyl compound 3 showed monotropic nematic phases. No smectic phases could be observed in these compounds.

Replacement of a phenyl group by a cyclohexyl ring in compounds 2 and 4 lowered the clearing points by about 70°C. The clearing point of compound 1 is even lower than the corresponding alkyl cyclohexane derivative (PCH7). It is evident from other investigations[2,5-8] that the substitution of a phenyl group by a cyclohexane ring can either thermodynamically stabilize or destabilize the mesophase. The stability of a mesophase depends to a great extent on the geometrical anisotropy of the molecules and their ability to pack together. The stabilizing effect of the cyclohexane ring in compounds like PCH and CCH can be explained by the

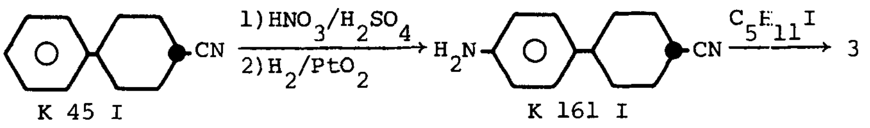
TABLE 1 Transition temperatures (°C) of alkylamino cyano substituted phenylcyclohexanes.

Nr.	Compound	K		N		I
1		•	67.5	•	(27.6)	•
2		•	105.3	•	(93.8)	•
3		•	80.7	•	(16.9)	•
4		•	86.3	•	(90.7)	•

better packing and consequently stronger interaction between the molecules. Recently, Gray[8] tried to explain the destabilizing effect of this ring in other compounds by pointing out its conformational isomerism. It is well known that the chair form of a trans-1,4-disubstituted cyclohexane ring has two conformational isomers (a,a and e,e) which are always in equilibrium above the coalescence temperature[9]. The predominant anisotropic conformer (e,e) is inverted through the envelope, twist and boat forms to the isotropic (a,a) isomer, since the potential-energy barrier between the rigid and flexible forms is high enough to ensure the entities of these conformations but not high enough to prevent their rapid interconversion at room temperature. The conformational free energy difference $-\Delta G_x^o$, which shows an appreciable temperature dependence, determines the inversion rate and consequently the amount of the (a,a) isomer[10] which is responsible for lowering the clearing point. The most common substituents in liquid crystals can be ordered according to their $-\Delta G^o$ as follows[11]: $C_6H_5 > C_6H_{11} \approx N(CH_3)_2 > CH_3 \approx C_2H_5 > COOH > NH_2 \approx COOCH_3 \approx COOC_2H_5 > NHCH_3 > OH \approx OCH_3 \approx OCOCH_3 > CN$. It is to be noted that many liquid crystals with high clearing points begin to decompose near this transition temperature and the depression of the clearing point is then not only due to the enhanced cyclohexane ring inversion but also to the impurities formed on long and strong heating. The low conformational energy of the cyano group explains the depression in the clearing point of compound 3 as compared to 1. It is also clear that 1 must have a lower N-I transition than PCH7. Compound 1 was synthesized according to the following scheme:

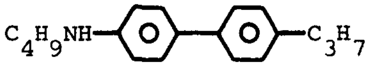
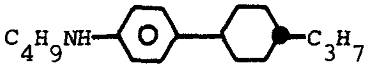
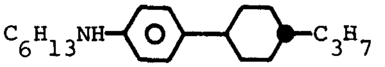
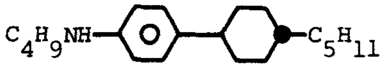


Compound 3 was obtained as follows:

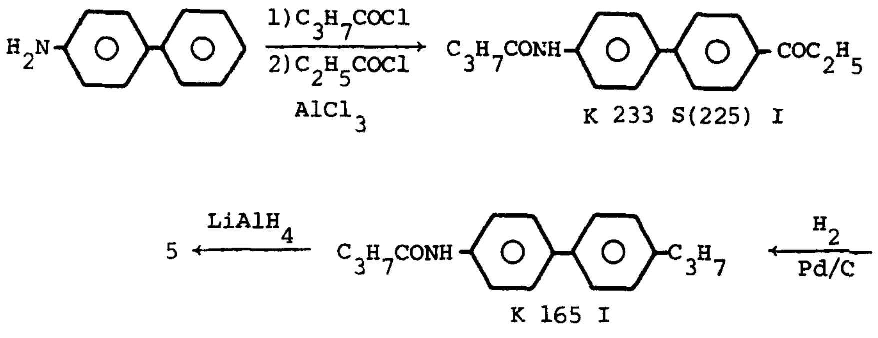


The melting points of the alkylamino cyano phenylcyclohexanes are much higher than their clearing points. In an attempt to lower the melting points, the cyano group was replaced by an alkyl group, although it was to be expected that Δn and Δε would be smaller. Table 2 shows the transition temperatures of the alkylamino phenylcyclohexanes.

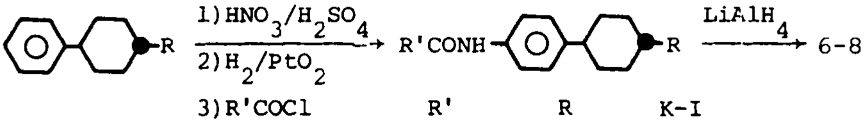
TABLE 2 Transition temperatures (°C) of alkyl alkylamino substituted phenylcyclohexanes.

Nr.	Compound	K		S		N		I
5		•	75.0	•	(74.1)			•
6		•	32.3	•		•	(28.4)	•
7		•	28.7	•		•	31.6	•
8		•	35.1	•		•	40.4	•

The cyclohexyl derivatives 6-8 showed nematic phases, in contrast to the biphenyl 5 which was only smectic. They also melted at much lower temperatures than the cyano derivative 3. Compound 5 was synthesized as follows:



Compounds 6-8 were synthesized according to the following scheme:



R'	R	K-I
C_3H_7	C_3H_7	155
C_5H_{11}	C_3H_7	151
C_3H_7	C_5H_{11}	140

While this work was in progress[12] McMillan[13] reported lower transition temperatures for compound 8.

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