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A New Liquid Crystal Family: 5-Alkyl-2-(4′-Cyanophenyl)-1, 3-Dioxanes

Howard Sorkin [a] [b]

[a] Timex Corporation Waterbury, Connecticut, 06702

[b] School of Chemistry, Rutgers, The State University of New Jersey, Piscataway, N.J., 08854

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A NEW LIQUID CRYSTAL FAMILY: 5-ALKYL-2-(4'-CYANOPHENYL)-1,3-DIOXANES

HOWARD SORKIN[+]
Timex Corporation
Waterbury, Connecticut 06702
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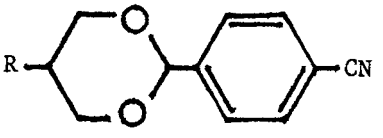
5-Alkyl-2-(4'-cyanophenyl)-1,3-dioxanes have been synthesized and are found to be liquid crystalline. A very low threshold voltage (0.76 V) and saturation voltage (1.25 V) characterizes a mixture of several of these compounds.

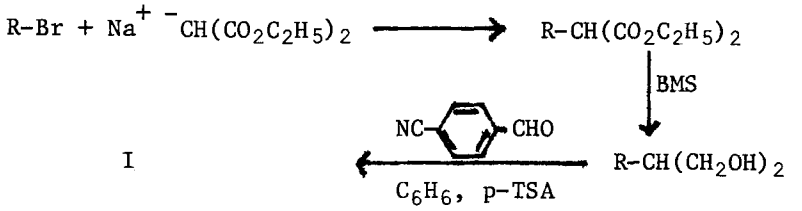
A new family of namatic liquid crystals, derivatives of 1,3-dioxanes, have been discovered. The compounds are 5-alkyl-2-(4'-cyanophenyl)-1,3-dioxanes (I).



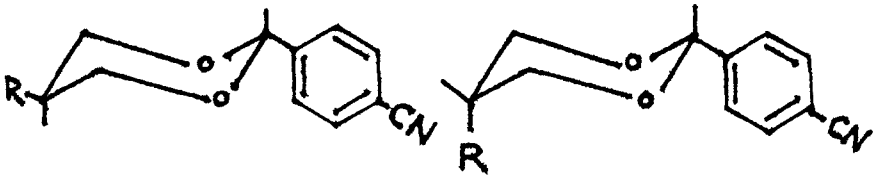
I (R = alkyl)

The dioxanes are conveniently synthesized in three steps from readily available materials. Diethyl sodiomalonate is reacted with an alkyl bromide to yield diethyl alkylmalonates. Reduction to 2-alkyl-1,3-propanediols is accomplished with borane-methyl sulfide (BMS). The diols are condensed with 4-cyanobenzaldehyde in benzene with p-toluenesulfonic acid to yield the desired products.

[+]Present Address: School of Chemistry, Rutgers, The State University of New Jersey, Piscataway, N.J. 08854



Gas chromatography and IR spectroscopy of the product reveals the presence of a mixture consisting of two isomers in the ratio of 3:1. Trapping the GC fractions and examination between crossed polarizers on a Mettler FP52 Hot Stage demonstrated that the major component was nematic. Attempts to increase the ratio of the desired component by varying reaction conditions were not successful. By analogy with the reported[1] phenylcyclohexanes the trans configuration is assigned to the nematic isomer. The less elongated structure of the cis isomer would not be expected to give rise to a mesophase.



I (trans) I (cis)

The isomers may be conveniently separated by one or two recrystallizations from isopropanol. Transition temperatures are given in the Table.

TABLE 1. Transition temperatures ($0^{o}C$) for compounds (I)

R	Crystal-nematic (crystal-isotropic)	Nematic-isotropic (isotropic-nematic)
C_2H_5	(66.2)	(14.8)
C_3H_7	(52.9)	(39.3)
C_4H_9	32.2	34.6
C_5H_{11}	46.0	47.5
C_6H_{13}	(51.0)	(43.8)
C_7H_{15}	(54.1)	(49.8)
C_8H_{17}	(59.0)	(47.3)

Electro-optic properties of the materials were determined on PVA-coated In_2O_3 which had been unidirectionally rubbed to produce a twisted structure. A mixture of the pentyl, hexyl, heptyl, and octyl compounds (CN = 22^{o}, NL = 45^{o}) containing 0.1% cholesteryl nonanoate was used. At $25^{o}C$ the displays show V_{10} = 0.76 V, V_{50} = 0.84 V, V_{SAT} = 1.25 V.

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References

1. R. Eidenschink, D. Erdmann, J. Krause, and L. Pohl, Angew. Chem. Int. Ed. Engl. 16 (1977) No. 2, 100.