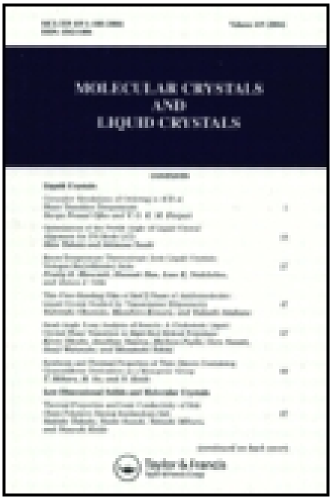


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Mesomorphic Properties of 4-(4-Pyridyl)-Benzoic Acid Esters

Ona Adomėnienė [a] , Povilas Adomėnas [a] , Antanas Gleiznys [a] , Lidija Poloudina [a] & Yasuyuki Gotoh [b]

[a] Laboratory of Liquid Crystals , Vilnius University , Naugarduko 24, Vilnius, 2006, LITHUANIA

[b] Chisso Corporation 7-3 , Marunouchi 2-Chome, Chiyoda-ku, Tokyo, 100-8333, JAPAN

To cite this article: Ona Adomėnienė , Povilas Adomėnas , Antanas Gleiznys , Lidija Poloudina & Yasuyuki Gotoh (2001) Mesomorphic Properties of 4-(4-Pyridyl)-Benzoic Acid Esters, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 75-79, DOI: 10.1080/10587250108025283

To link to this article: http://dx.doi.org/10.1080/10587250108025283

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 75-79
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint,
a member of the Taylor & Francis Group,
Printed in the USA

Mesomorphic Properties of 4-(4-Pyridyl)-Benzoic Acid Esters

ONA ADOMĖNIENĖ[a], POVILAS ADOMĖNAS[a],
ANTANAS GLEIZNYS[a], LIDIJA POLOUDINA[a] and
YASUYUKI GOTOH[b]

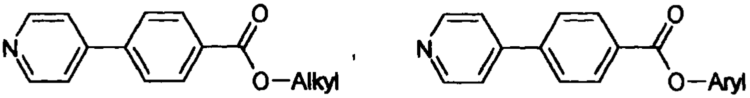
[a]*Laboratory of Liquid Crystals, Vilnius University Naugarduko 24, Vilnius 2006, LITHUANIA and* [b]*Chisso Corporation 7–3, Marunouchi 2-Chome, Chiyoda-ku, Tokyo 100–8333, JAPAN*

Formerly unknown 4-(4-pyridyl)benzoic acid was synthesized and some of its esters were prepared, their mesomorphic properties were examined. Alkyl-esters of the said acid are non-mesomorphic, while three-ring aryl esters form monotropic smectic A state. Esters aren't stable, they hydrolize easily.

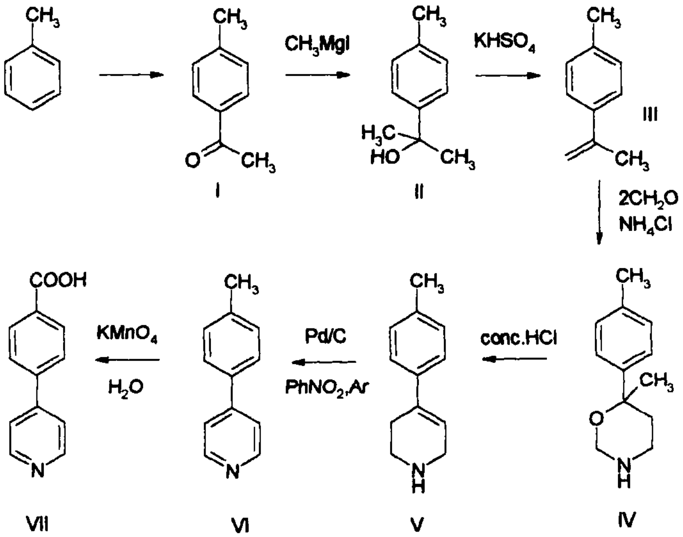
Keywords: 4-(4-pyridyl)benzoic acid; mesomorphic

That's well known, that almost all possible simple structure units were examined during last decades for their suitability as building blocks in creating of mesogenic compounds. So it was a surprise for us when we noticed that 4-(4-pyridyl)benzoic acid wasn't ever used for synthesis of possible mesogenic compounds, though evidently an introduction of terminally oriented nitrogen electron pair might lead to compounds possesing interesting material properties. Even more, we couldn't detect any report about synthesis of the a.m. 4-(4-pyridyl)benzoic acid in literature.

In this work, we have prepared some esters of the a.m. acid. Their common structural formulas

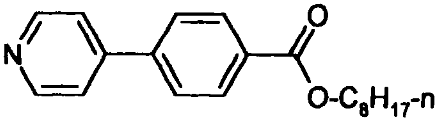


The key intermediate, 4-(4-pyridyl)benzoic acid, was prepared by an oxidation of 4-(4-methylphenyl)pyridine by potassium permanganate. The latter was prepared by the next sequence of transformations:

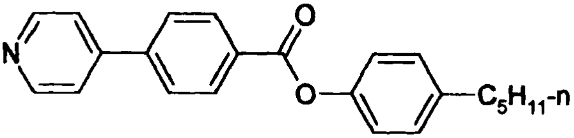


First steps of these transformations are commonly known. A transition from 4,α-dimethylstyrene (III) to 4-(4-methylphenyl)-pyridine (VI) was worked out by M.D. Hartough, C. J. Schmidle and their co-workers in 1952-54 [1-4]. To our experience, that's the simplest and the most reliable route of synthesis of aryl-substituted 4-arylpyridines. An oxidation of (VI) to target 4-(4-pyridyl)-benzoic acid (VII) was smoothly performed by potassium permanganate in water, both pyridine and benzene rings remain uneffected. 4-(4-Pyridyl)-benzoic acid (VII) is a colorless crystalline compound, its m.p.310^{0}C (decomp.) – much higher that that of structurally similar biphenylcarboxylic acid (226^{0}C). It may be crystallized from diluted nitric acid.

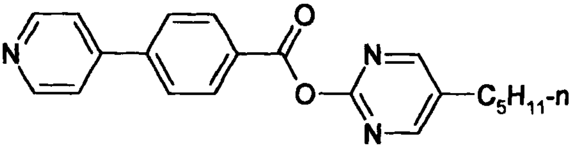
Esters of 4-(4-pyridyl)-benzoic acid were obtained by a standard reaction of 4-(4-pyridyl)-benzoyl chloride with alcohol either phenol in pyridine solution. It should be noted, that long-chain alkanols (decanol or higher) failed to react at these conditions. Other esterification conditions, such as acid-catalyzed either PEP -induced condensation reaction between free acid and alkanol either phenol, didn't led to formation of target esters. DCC induced esterification of 4-(4-pyridyl)-benzoic acid by alkanols, but not by phenols. In this case (acid VII, phenol and DCC in chloroform solution) 4-(4-pyridyl)-benzoic anhydride was obtained instead of target esters. Alkyl 4-(4-pyridyl)benzoates (I) are nonmesomorphic compounds possesing rather low melting points, while three-ring compounds (II) form monotropic smectic mesophases:



Cr 49^0 Is

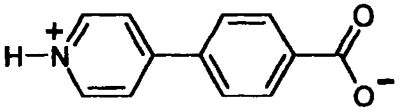


Cr 96^0 (S 82^0) Is



Cr 99^0 (S 67^0) Is

Esters of 4-(4-pyridyl)-benzoic acid aren't stable, much less than corresponding esters of carbocyclic aromatic acids. This may be caused by energetic reasons – free 4-(4-pyridyl)-benzoic acid evidently exists in the form of inner salt, which is energetically more favorable, than that in the case of uncharged esters:



References

[1] M.D. Hartough, J.J. Dickert and S.L. Meisel. U.S. 2, 647, 117 (C.A. 1954, v. 48, 8265).
[2] C. J. Schmidle and Richard C. Mansfield.. J. Am. Chem. Soc. 1956, v. 78, p. 425.
[3] C. J. Schmidle and Richard C. Mansfield. J. Am. Chem. Soc. 1956, v. 78, p. 1702.
[4] C. J. Schmidle, John E. Locke and Richard C. Mansfield. J. Org. Chem. 1954, v. 21, p. 1194.