Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Green Chemistry Approach to the Synthesis of Liquid Crystalline Materials

Sandeep Kumar [a], Hari Krishna Bisoyi [a] & Santanu Kumar Pal [a]

[a] Raman Research Institute, Bangalore, India

Version of record first published: 22 Sep 2010

To cite this article: Sandeep Kumar, Hari Krishna Bisoyi & Santanu Kumar Pal (2008): Green Chemistry Approach to the Synthesis of Liquid Crystalline Materials, Molecular Crystals and Liquid Crystals, 480:1, 287-294

To link to this article: http://dx.doi.org/10.1080/15421400701826795

Mol. Cryst. Liq. Cryst., Vol. 480, pp. 287–294, 2008

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701826795

Taylor & Francis
Taylor & Francis Group

Green Chemistry Approach to the Synthesis of Liquid Crystalline Materials

Sandeep Kumar, Hari Krishna Bisoyi, Santanu Kumar Pal
Raman Research Institute, Bangalore, India

This article presents a simple, rapid, economic and environmentally acceptable microwave promoted "green chemistry" approach to the synthesis of some conventional and non-conventional liquid crystalline materials. Alkylation of 4′-hydroxy-4-biphenylcarbonitrile with various alkyl halides under microwave irradiation furnished alkoxycynobiphenyl-based calamitic liquid crystals in very high yield within one minute. Similarly, terminally-functionalized alkoxycyanobiphenyls and alkoxycyanobiphenyl dimers can also be prepared. Microwave irradiation of hexaalkoxytriphenylene in the presence of ionic liquids gives monohydroxy-pentaalkoxytriphenylene in about 30% yield. Novel imidazolium-based ionic liquid crystalline dimers can be easily prepared via quaternization reaction using microwaves. Classical reaction conditions failed to produce these dimers.

INTRODUCTION

Developing green methodologies is one of the main themes of modern synthetic chemistry. In this context, use of microwaves and ionic liquids are powerful tools. The high-speed chemical synthesis using microwaves has attracted a considerable attention in the past decade. After the discovery of microwave dielectric heating to facilitate organic reactions in 1986 [1,2], almost all types of organic reactions have been performed using the efficiency of microwave flash heating [3]. This is not only due to the fact that all organic reactions proceed significantly faster and more selective than under thermal conditions, but also because of the operational simplicity, high yields of products and cleaner reactions with easier work-up. Enormous accelerations in reaction time can be achieved using microwave irradiation. In

Address correspondence to Sandeep Kumar, Raman Research Institute, C. V. Raman Avenue, Sadashivanagar, Bangalore 560 080, India. E-mail: skumar@rri.res.in

majority of reactions, only thermal effect has been found, however, non-thermal effects do play a role in some reactions.

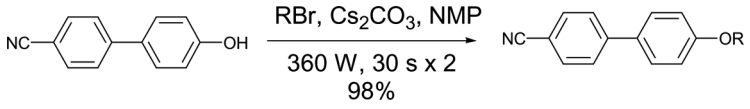
On the other hand ionic liquids, a class of organic salts with usually low melting points, have attracted considerable attention. Due to their unique characteristics such as non-volatility, thermal stability, non-flammability, extremely high ionic conductivity, very low vapour pressure, reusability and diverse solvating ability they can be used as environmentally benign solvent media to replace conventional volatile organic solvents in many chemical processes. Ionic liquids serve the dual purpose of solvent as well as reagent and allow easy isolation of the product. Surprisingly these green methodologies have not been applied for the synthesis of liquid crystalline materials.

Alkoxycyanobiphenyls are indispensable ingredients of the liquid crystal layer used in liquid crystal display devices. Because of their commercial importance, a number of cyanobiphenyl derivatives have been extensively studied for various physical properties [4]. Their dimers, i.e., α,ω-bis (4′-cyanobiphenyl-4-yloxy) alkanes, have served the purpose as model compounds to understand the more complex polymeric systems [4]. In the family of discotic liquid crystals, triphenylene derivatives are the most widely synthesized and well studied materials [5]. However, the potential utility of their dimers, oligomers and polymers has been back held because of the synthetic problems in obtaining mono-functionalized triphenylenes. Imidazolium-based ionic liquid crystals have attracted considerable attention recently because of their anisotropic ionic conductivity [6].

Here we present an efficient, simple, rapid, economic and environmentally acceptable microwave assisted and/or ionic liquid mediated green chemistry approach to the synthesis of (i) alkoxycyanobiphenyls (ii) α,ω-bis(4′-cyanobiphinyl-4-yloxy)alkanes (alkoxycyanobiphenyl dimers) (iii) ω-bromoalkoxycyanobiphenyls (iv) monohydroxy-pentaalkoxy-triphenylenes and (v) novel imidazolium-based alkoxycyanobiphenyl dimers.

MICROWAVE-ASSISTED SYNTHESIS OF ALKOXYCYANOBIPHENYLS

The traditional synthesis of alkoxycyanobiphenyls involves alkylation of 4′-hydroxy-4-biphenylcarbonitriles with an appropriate alkyl halide [4]. The reaction is usually carried out in moderate yield by heating 4′-hydroxy-4-biphenylcarbonitriles with an appropriate alkyl halide in the presence of a base and in polar solvents for 24 hours. We have observed that this reaction (Scheme 1) could be finished in about one minute in very high yield by using microwave heating [7].

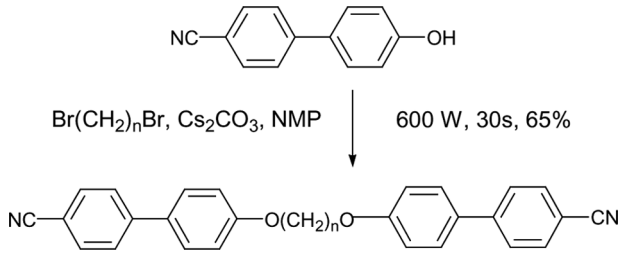


SCHEME 1 Synthesis of alkoxycyanobiphenyls using microwaves.

Thus, when a mixture of 4′-hydroxy-4-biphenylcarbonitrile (1 equivalent), octyl bromide and sodium carbonate (2 equivalent of each) in 1-methylpyrrolidinone was irradiated with 360 W microwave power for 1 minute (30 s X 2), about 80%of pure 4-octyloxycyanobiphenyl was isolated. The use of potassium carbonate under similar reaction conditions afforded about 90% of the product. The best yield of 4′-(octyloxy)[1,1′-biphenyl]-4-carbonitrile (98%) was obtained using cesium carbonate as a base. Other solvents such as, DMSO, DMF, PEG furnished slightly lower yield. By using 600 W microwave power, the same reaction can be accomplished in 30 seconds in 94% yield.

MICROWAVE-ASSISTED SYNTHESIS OF ALKOXYCYANOBIPHENYL DIMERS

Physical properties of liquid crystalline dimers are significantly different to that of conventional low molar mass liquid crystals. Dimers represent ideal model compounds for polymers or networks, due to their ease of purification and characterization and the possibility of freezing, in their mesophase, to a glassy state. Dimers containing two calamitic units show interesting mesomorphic behaviour depending on the length of the spacer and structure of the linking group. A variety of liquid crystalline dimers are known in the literature [8,9]. The most extensively studied series of liquid crystalline dimers is the α,ω-bis(4′-cyanobiphenyl-4-yloxy)alkanes [9]. The symmetrical dimers have been generally prepared by a single-step alkylation of 4′-hydroxy-4-biphenylcarbonitrile with 0.5 equivalent of the appropriate α,ω-dibromoalkanes. Using the reaction conditions mentioned for the preparation of alkoxycyanobiphenyls, their dimers can be easily prepared in about 65% yield within one minute (Scheme 2). Thus, when a mixture of 1,6-dibromohexane (1 equivalent) and 4′-hydroxy-4-biphenylcarbonitrile (2 equivalent) in the presence of cesium carbonate in 1-methylpyrrolidinone was irradiated with 360 W microwave power for 1 minute (30 s X 2), about 65% of pure α,ω-bis(4′-cyanobiphenyl-4-hexyloxy)alkane can be isolated. The use of 600 W microwave power furnished the reaction in 30 s only.



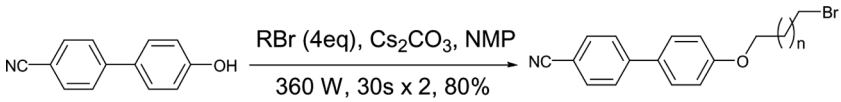
SCHEME 2 Synthesis of alkoxycyanobiphenyl dimers using microwaves.

MICROWAVE-ASSISTED SYNTHESIS OF ω-BROMOALKOXYCYANOBIPHENYLS

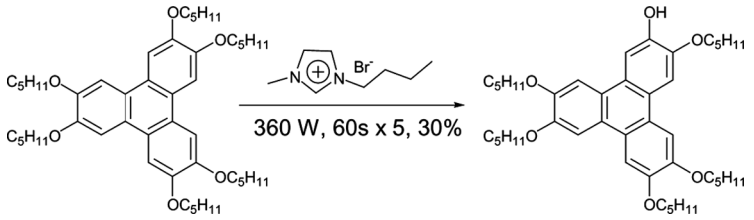
While the symmetrical dimers can be easily prepared by a single-step alkylation of 4′-hydroxy-4-biphenylcarbonitrile with 0.5 equivalent of an appropriate α,ω-dibromoalkanes, a two-step process is required to prepare unsymmetrical dimers. In a two-step procedure, the hydroxyl-functionalized core is first reacted with an excess of appropriate α,ω-dibromoalkane to obtain the ω-brominated product (Scheme 3) that can be further reacted with the same or different hydroxyl-functionalized core to get the symmetrical or unsymmetrical dimer. When 4′-hydroxy-4-biphenylcarbonitrile was irradiated with excess of 1,6-dibromohexane as mentioned above, ω-bromohexyloxycyanobiphenyl was formed exclusively in 80% yield. The ω-bromoalkoxycyanobiphenyl is a key intermediate in the synthesis of various other liquid crystalline materials, such as, trimers [10], tetramers [11] and terminally functionalized alkoxycyanobiphenyls [12].

MICROWAVE-ASSISTED SYNTHESIS OF MONOHYDROXY-PENTAALKOXYTRIPHENYLENES

Monohydroxy-pentaalkoxytriphenylenes are valuable precursors for the preparation of a variety of discotic liquid crystals. A number of methods have been developed to prepare monohydroxy-functionalized



SCHEME 3 Synthesis of ω-bromoalkoxycyanobiphenyls using microwaves.

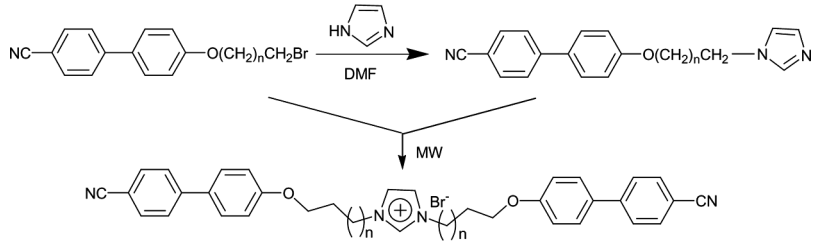


SCHEME 4 Synthesis of monohydroxy-pentaalkoxytriphenylenes using microwaves.

triphenylene derivatives [13]. Recently ionic liquids and particularly imidazolium-based ionic liquids have attracted considerable attention as environmentally benign solvents for various chemical reactions due to their interesting properties, such as thermal stability, non-flammability, very low vapour pressure and reusability [14]. The anion, Br^- or I^-, of these ionic liquids may be used to cleave the aryl-ether bond(s) of hexaalkoxytriphenylene and, thus, hydroxyl-functionalized triphenylenes can be prepared (Scheme 4). With this idea, we mixed hexapentyloxytriphenylene with 1-n-butyl-3-methyl imidazolium bromide (3 equivalents) and the mixture was subjected to microwave irradiation for five minutes (1 minute X 5). The reaction product on column chromatography yielded about 30% of monohydroxy-pentapentyloxytriphenylene. It is noteworthy that no other side product forms in the reaction and about 60% of the starting material was recovered which can be recirculated.

SYNTHESIS OF NOVEL IMIDAZOLIUM-BASED IONIC LIQUID CRYSTALLINE DIMERS

It is well known that ionic molecules form amphotropic liquid crystals [15]. They have great potential as ordered reaction media that can impart selectivity in reactions by ordering reactants [16]. Alkali metal soaps were the first salts identified as displaying liquid crystalline properties, followed by alkylammonium, pyridinium, vinamidinium, phosphonium salts [17]. A number of calamitic liquid crystalline imidazolium salts have recently been prepared and the formation of lamellar phases in these materials has been recognized [18]. Self-assembly of a non-liquid crystalline imidazolium ionic liquid and a hydroxyl-terminated liquid crystal leads to the formation of phase-segregated layered structures on the nano scale. These materials have been found to exhibit two-dimensional ionic conductivities with high anisotropy [19]. Recently, Yoshio *et al*. reported one-dimensional ion



SCHEME 5 Microwave promoted synthesis of ionic liquid crystalline dimers.

transport in self-organized columnar ionic liquids [6]. We have recently reported a number of pyridinium and imidazolium-based discotic ionic liquid crystals [20]. However, ionic liquid crystalline dimers based on imidazolium moiety containing two mesogenic groups have not yet been explored. To realize these dimers, we prepared imidazole-substituted alkoxycyanobiphenyl by reacting imidazole with ω-bromoalkoxycyanobiphenyl (Scheme 5). The liquid crystalline imidazolium dimer was obtained by microwave-assisted quaternization of the above product with another molecule of ω-brominated cyanobiphenyl. It is interesting to note that the quaternization under classical reaction conditions does not yield the desired product. The ionic dimmer (n = 7) shows a monotropic SmC phase. The crystalline compound melts at 133°C to the isotropic phase on heating. The smectic C phase appears at 102°C on cooling the isotropic liquid and remains stable down to room temperature.

CONCLUSION

An efficient, simple, rapid, economic and environmentally acceptable "green chemistry" approach to the synthesis of various liquid crystalline materials has been described. The present facile and clean protocol can be employed for the synthesis of many other liquid crystalline materials.

REFERENCES

[1] Gedye, R., Smith, F., Westaway, K., Ali, H., Baldisers, L., Laberge, L., & Rousell, J. (1986). *Tet. Lett.*, *27*, 279.
[2] Giguere, R. J., Bray, T. L., Duncan, S. M., & Majetich, G. (1986). *Tet. Lett.*, *27*, 4945.
[3] Due to the large number of publications in the field of MW-assisted synthesis (more than 3000 papers), it is almost impossible to cover all the literature and, therefore, only a few recent references are given here. de la Hoz, A., Diaz-Ortiz, A., & Moreno, A. (2005). *Chem. Soc. Rev.*, *34*, 164; Molteni, V. & Ellis, D. A. (2005). *Curr. Org. Synth.*,

2, 333; Bogdal, D. (2005). *Microwave-Assisted Organic Synthesis-One Hundred Reaction Procedures*, Elsevier: Amsterdam; Kappe, O. C. & Stadler, A. (2005). *Microwaves in Organic and Medicinal Chemistry*, Wiley-VCH: Weinheim; Van der Eycken, E. & Kappe, C. O. (Eds.), (2006). Microwave-Assisted Synthesis of Heterocycles. Springer: Heidelberg.

[4] Gray, G. W., Harrison, K. J., Nash, J. A., Constant, J., Hulme, J. S., Kirton, J., & Raynes, E. P. (1973). in *Liquid Crystals and Ordered Fluids*, Vol. 2, Porter, R. S. &Johnson, J. F. (Eds.), Plenum: New York, 617; Dunmur, D. A., Fukuda, A., & Luckhurst, G. R. (Ed.), (2001). *Physical Properties of Liquid Crystals: Nematics*, INSPEC: London.

[5] Kumar, S. (2004). *Liq. Cryst.*, *31*, 1037.

[6] Yoshio, M., Mukai, T., Ohno, H., & Kato, T. (2004). *J. Am. Chem. Soc.*, *126*, 994.

[7] Bisoyi, H. K. & Kumar, S. (2006). *Phase Trans.*, *79*, 285.

[8] For example see, Walba, D. M., Dyer, D. J., Sierra, T., Cobben, P. L., Shao, R., & Clark, N. A. (1996). *J. Am. Chem. Soc.*, *118*, 1211; Kumar, S. & Varshney, S. K. (2002). *Org. Lett.*, *4*, 157; Kumar, S. (2005). *Liq. Cryst.*, *31*, 1089; Kumar, S. (2006). *Chem. Soc. Rev.*, *35*, 83 and references therein.

[9] Imrie, C. T. & Henderson, P. A. (2002). *Current Opinion in Colloid & Interface Sci.*, *7*, 298; Imrie, C. T. (2001). *Structure and Bonding*, Mingos, D. M. P.(Ed.), Springer-Verlag: Berlin, 149; Imrie, C. T. & Luckhurst, G. R. (1998). *Handbook of Liquid Crystals*, Vol. 2B, Demus, D., Goodby, J., Gray, G. W., Spices, & Vill, V. (Eds.), Chap. X, Wiley-VCH: Weinheim; Emsley, J. W., Luckhurst, G. R., Shilestone, G. N. & Sage, I. (1984). *Mol. Cryst. Liq. Cryst.*, *102*(Letters), 223; Griffin, A. C., Vaidya, S. R., Hung, R. S. L., & Gorman, S. (1985). *Mol. Cryst. Liq. Cryst. Letters*, *1*, 131; Emsley, J. W., Luckhurst, G. R., & Shilestone, G. N. (1984). *Mol. Phys.*, *53*, 1023; Abe, A. & Furuya, H. (1988). *Polymer Bulletin*, *19*, 403; Tsvetkov, N. V., Zuev, V. V., Ksenofontov, I. V., & Tsvetkov, V. N., (1998). *Liq. Cryst.*, *25*, 727; Ionescu, D., Luckhurst, G. R., & de Silva, D. S. (1997). *Liq. Cryst.*, *23*, 833; Tsvetkov, N. V., Zuev, V. V., Ksenofontov, I. V., & Tsvetkov, V. N. (1999). *Mol. Cryst. Liq. Cryst.*, 331, 41; Tsvetkov, V. N., Tsvetkov, N. V., Didenko, S. A., & Zuev, V. V. (1995). *Mol. Cryst. Liq. Cryst.*, *265*, 341; Barnes, P. J., Douglass, A. G., Heeks, S. K., & Luckhurst, G. R. (1993). *Liq. Cryst.*, *13*, 603; Ferrarini, A., Luckhurst, G. R., Nordio, P. L., & Roskilly, S. J. (1993). *Chem. Phys. Lett.*, *214*, 409.

[10] Imrie, C. T. & Luckhurst, G. R. (1998). *J. Mater. Chem.*, *8*, 1339.

[11] Imrie, C. T., Stewart, D., Remy, C., Christie, D. W., Hamley, I. W., & Harding, R. (1999). *J. Mater. Chem.*, *9*, 2321.

[12] Kumar, S. & Pal, S. K. (2005). *Liq. Cryst.*, *32*, 659.

[13] Closs, F., Häussling, L., Henderson, P., Ringsdorf, H., & Schuhmacher, P. (1995). *J. Chem. Soc., Perkin Tran. I*, 829; Boden, N., Bushby, R. J., & Cammidge, A. N. (1995). *J. Am. Chem. Soc.*, *117*, 924; Henderson, P., Ringsdorf, H., & Schuhmacher, P. (1995). *Liq. Cryst.*, *18*, 191; Kumar, S. & Manickam, M. (1998). *Synthesis*, 1119; Bushby, R. J. & Lu, Z.(2001). *Synthesis.*, 763; Kumar, S. & Lakshmi, B. (2005). *Tet. Lett.*, *46*, 2603 and references therein.

[14] For reviews, see: (a) Seddon, K. R. (1997). *J. Chem. Technol. Biotechnol.*, *68*, 351; (b) Welton, T. (1999). *Chem. Rev.*, *99*, 2071; (c) Wasserscheid, P. & Keim, W. (2000). *Angew. Chem. Int. Ed.*, *39*, 3772; (d) Sheldon, R. (2001). *Chem. Commun.*, 2399; (e) Dupont, J., de Souza, R. F., Suarez, P. A., & Suarez, Z. (2002). *Chem. Rev.*, *102*, 3667; (f) Corma, A. & Garcia, H. (2003). *Chem. Rev.*, *103*, 4307; (g) Song, C. E. (2004). *Chem. Commun.*, 1033.

[15] Tschierske, C. (2002). *Curr. Opin. Colloid Interface Sci.*, *7*, 355.

[16] (a) Weiss, R. G. (1998). *Tetrahedron*, *44*, 3413; (b) Kansui, H., Hiraoka, S., & Kunieda, T. (1996). *J. Am. Chem. Soc.*, *118*, 5346.

[17] A large number of papers have appeared on thermotropic ionic liquid crystals. It is difficult to cover all these and, therefore, only a few selected references are given here. (a) Bruce, D. W., Dunmur, D. A., Lalinde, E., Maitlis, P. M., & Styring, P. (1986). *Nature*, *323*, 791; (b) Marcos, M., Ros, M. B., Serrano, J. L., Esteruelas, M. A., Sola, E., Oro, L. A., & Barbera, J. (1990). *Chem. Mater.*, *2*, 748; (c) Bravo-Grimaldo, E., Navarro-Rodriguez, D., Skoulios, A., & Guillon, D. (1996). *Liq. Cryst.*, *20*, 393; (d) Bernhardt, H., Weissflog, W., & Kresse, H. (1998). *Liq. Cryst.*, *24*, 895; (e) Cui, L., Sapagovas, V., & Lattermann, G. (2002). *Liq. Cryst.*, *29*, 1121; (f) De Roche, J., Gordon, C. M., Imrie, C. T., Ingram, M. D., Kennedy, A. R., Celso, F. L., & Triolo, A. (2003). *Chem. Mater.*, *15*, 3089; (g) Bhowmik, P. K., Han, H., Nedeltchev, I. K., & Cebe, J. J. (2004). *Mol. Cryst. Liq. Cryst.*, *419*, 27; (h) Haristoy, D. & Tsiourvas, D. (2004). *Liq. Cryst.*, *31*, 697.

[18] Lee, K. M., Lee, C. K., & Lin, I. J. B. (1997). *Chem. Commun.*, 899; Gordon, C. M., Holbrey, J. D., Kennedy, A. R., & Seddon, K. R. (1998). *J. Mater. Chem.*, *8*, 2627; Holbrey, J. D. & Seddon, K. R. (1999). *J. Chem. Soc., Dalton Trans.* 2133; Lee, K. M., Lee, Y. T., & Lin, I. J. B. (2003). *J. Mater. Chem.*, *13*, 1079.

[19] Yoshio, M., Kato, T., Mukai, T., Yoshizawa, M., & Ohno, H. (2004). *Mol. Cryst. Liq. Cryst.*, *413*, 99.

[20] Kumar, S. & Pal, S. K. (2005). *Tet. Lett.*, *46*, 4127; Kumar, S. & Pal, S. K. (2005). *Tet. Lett.*, *46*, 2607.