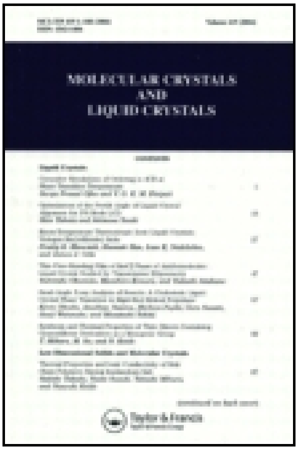


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Synthesis of Liquid Crystals based on Bicyclo[1.1.1]Pentane

Piotr Kaszynski [a], Andrienne C. Friedli [a], Neil D. McMurdie [a] & Josef Michl [a]

[a] Center for Structure and Reactivity, Department of Chemistry, The University of Texas at Austin, Austin, Texas, 78712-1167, USA

Version of record first published: 22 Sep 2006.

To cite this article: Piotr Kaszynski, Andrienne C. Friedli, Neil D. McMurdie & Josef Michl (1990): Synthesis of Liquid Crystals based on Bicyclo[1.1.1]Pentane, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 191:1, 193-197

To link to this article: http://dx.doi.org/10.1080/00268949008038593

Mol. Cryst. Liq. Cryst. 1990, Vol. 191, pp. 193–197
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

SYNTHESIS OF LIQUID CRYSTALS BASED ON BICYCLO[1.1.1]PENTANE

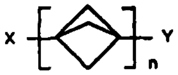
PIOTR KASZYNSKI, ANDRIENNE C. FRIEDLI, NEIL D. McMURDIE, and JOSEF MICHL
Center for Structure and Reactivity, Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712-1167, USA

ABSTRACT An overview of the chemistry of bicyclo[1.1.1]pentane leading to a variety of mesogenic building blocks and liquid crystals is presented.

INTRODUCTION

During the last three years a variety of substituted bicyclo[1.1.1]pentanes 1 have become readily available. This relatively compact structure with collinear bridgehead 1,3-substituents may be attractive for the synthesis of new mesogenic materials. Recently we reported[1] the first mesogenic compounds containing the bicyclo[1.1.1]pentane 1 or polybicyclo[1.1.1]pentane ([n]staffane) [n]2 moiety. We now present a brief overview of the chemistry leading to these new mesogenic building blocks and of their general properties. We also provide several new examples of liquid crystals based on 1.

1

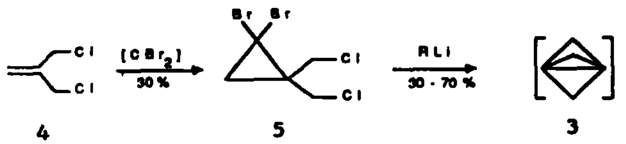


[n]2

RESULTS AND DISCUSSION

Synthesis

The synthesis of bicyclo[1.1.1]pentanes (1) or [n]staffanes ([n]2) is based on radical addition[2,3] to the central bond in [1.1.1]propellane[4] (3), easily prepared[2] from methallyl dichloride (4) via the tetrahalo compound 5. In our work,[5] the propellane 3 is typically used as a 3% ethereal solution, although in some cases an ether-free pentane solution is necessary, and the addition is induced by irradiation through a Pyrex filter.



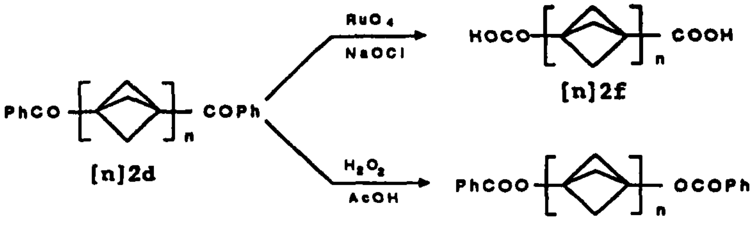
(i) ***Radical oligomerization reactions leading to [n]staffanes [n]2.*** Disulfides[1,5-7], benzil[5] and iodobenzene produce the doubly end-functionalized oligomers [n]2a-c, [n]2d, and [n]2e respectively, with n = 1-5.

[n]2

	a	b	c	d	e
X:	MeCOS	BuS	MeS	PhCO	Ph
Y:	MeCOS	BuS	MeS	PhCO	I

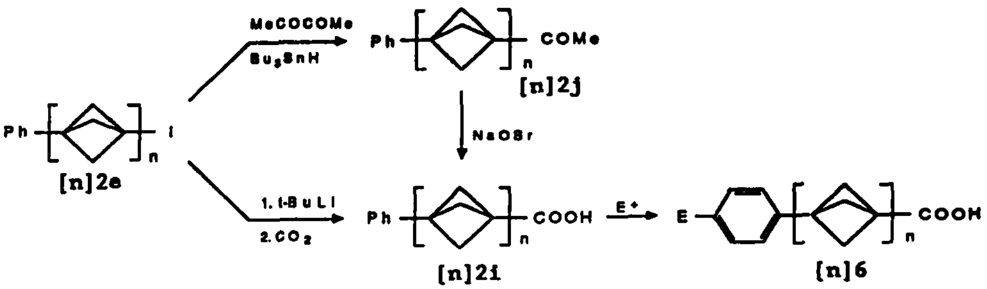
[3]2a and [3]2b as well as their higher homologues are liquid crystals.[1] [n]2a also is a very convenient starting material for further substitution on sulfur. In fact, [n]2b were also obtained by the hydrolysis of [n]2a followed by S-butylation[5,6].

Oxidation of the dibenzoyl compounds [n]2d with RuO_4 or peracetic acid offers convenient access to a series of diacids[5] [n]2f and to $3,3^{(n-1)}$-[n]staffanediols ([n]2g, X = Y = OH) via their dibenzoates[5] [n]2h.

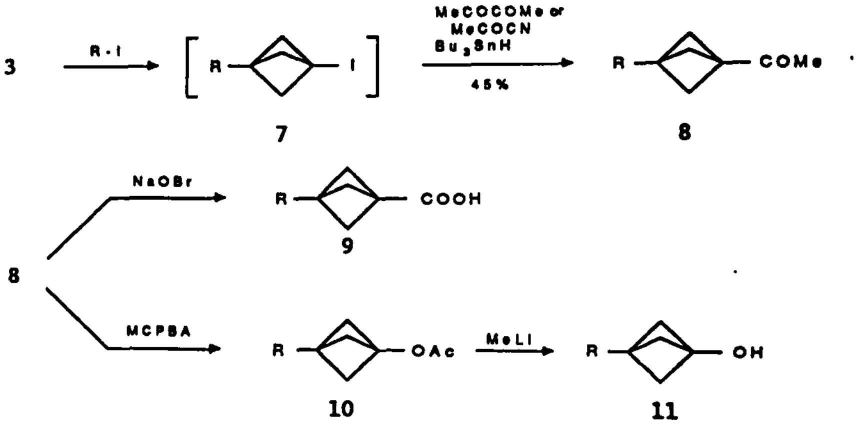


[n]2h

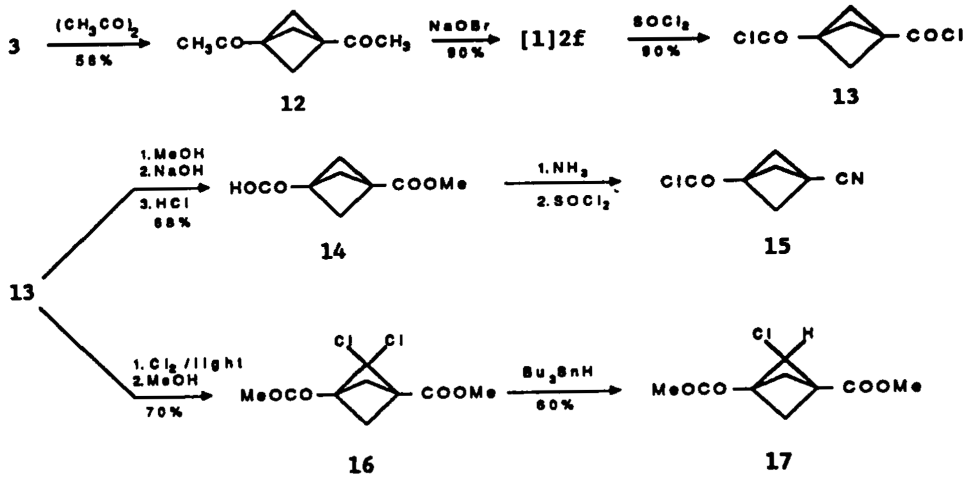
The iodobenzene adducts [n]2e were transformed into the corresponding acids [n]2i via the ketones [n]2j or directly by lithiation followed by carboxylation. The phenyl ring can be substituted at the *para* position by Br or NO_2, providing the doubly end-functionalized rods [n]6. Also, the phenyl moiety is an equivalent of a carbonyl group, to which it can be oxidized with RuO_4. This process may serve to differentiate the carbonyl groups.



(ii) *Synthesis of 1,3-disubstituted bicyclo[1.1.1]pentanes via alkyl iodides*.[8,9] Alkyl iodides react photochemically with [1.1.1]propellane (3) to give the bridgehead iodides 7. Subsequent reaction of the iodide 7 with biacetyl or puryvonitrile in the presence of tri-*n*-butyltin hydride gives the methyl ketone 8. The ketone has been oxidized either with hypohalite to the bridgehead acid 9 or with peracid to the corresponding bridgehead alcohol acetate 10. The acetate 10 has been cleaved by reaction with MeLi or by acid catalyzed hydrolysis to the alcohol 11.



(iii) *Synthesis of bicyclo[1.1.1]pentane-1,3-dicarboxylic acid and its derivatives*. The diacid [1]2f is best obtained via the diacetyl compound 12 in three steps from 5 in an overall yield of 52%.[10] This very convenient precursor can be further efficiently converted into a variety of promising mesogenic building blocks, 13-15. The diacid [1]2f has been chlorinated at the bridge,[11] providing access to the building blocks 16 and 17 with polar lateral substituents on carbon; the latter may also be chiral.



Structure and Properties

X-ray structure analysis[12] shows that the interbridgehead intracage distance is about 1.85-1.90 Å and the intrabridgehead intercage distance a remarkably short 1.47 Å, adding to an ~3-1/3 Å length increment per cage. The van der Waals diameter of the cylinder of rotation is about 5.3 Å.

It is noteworthy that the bicyclo[1.1.1]pentane ring structure is quite stable[5] in air up to 290 °C, despite its large strain energy content.

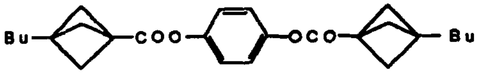
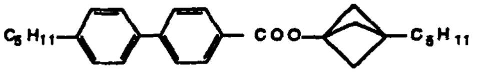
Liquid crystals based on bicyclo[1.1.1]pentane

Several new compounds have been synthesised from the precursors discussed above by standard esterification methods. Selected results are given in TABLE I. Comparison of these preliminary results with literature data for closely related compounds containing other rings in place of bicyclo[1.1.1]pentane allows us to propose the following order of mesophase stabilizing ability:

CONCLUSIONS

In this paper we presented some relatively simple chemistry leading to a

TABLE I **Mesogenic properies of bicyclo[1.1.1]pentane derivatives**

compound	K	S	N	I
	129	-	144	
	110	-	-	
	53	64	105	

variety of new mesogenic building blocks. The choice of substituents, including carboxyl, hydroxyl, thiol, halogen, alkyl, and phenyl groups, is wide. However, preliminary results show that the mesogens based on bicyclo[1.1.1]pentane have a relatively low T_{N-I} and are poorer in this regard than those based on bicyclo[2.2.2]octane, cyclohexane or benzene rings.

Acknowledgment

This work was supported by the NSF, TARP and the Welch Foundation.

REFERENCES

1. P. Kaszynski, A. C. Friedli, and J. Michl, Mol. Cryst. Liq. Cryst. Lett., 6, 27 (1988).
2. K. Semmler, G. Szeimies, and J. Belzner, J. Am. Chem. Soc., 107, 6410 (1985).
3. K. B. Wiberg, S. T. Waddell, and K. Laidig, Tetrahedron Lett., 27, 1553 (1986).
4. K. B. Wiberg and F. H. Walker, J. Am. Chem. Soc., 104, 5239 (1982).
5. P. Kaszynski, A. C. Friedli, and J. Michl, submitted for publication.
6. A. C. Friedli, P. Kaszynski, and J. Michl, Tetrahedron Lett., 30, 455 (1989).
7. U. Bunz, K. Polborn, H.-U. Wagner, and G. Szeimies, Chem. Ber., 121, 1785 (1988).
8. P. Kaszynski, N. D. McMurdie, and J. Michl, submitted for publication.
9. K. Hassenrück, G. S. Murthy, V. M. Lynch, and J. Michl, submitted for publication.
10. P. Kaszynski and J. Michl, J. Org. Chem., 53, 4593 (1988).
11. R. E. Robinson and J. Michl, J. Org. Chem., 54, 2051 (1989).
12. A. C. Friedli, V. M. Lynch, P. Kaszynski, and J. Michl, submitted for publication.