



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>

New Nematics Incorporating a 2,6- Difluorophenyl Acetylene Group

Richard Buchecker^a, Guy Marck^a & Martin Schadt^a

^a F. Hoffmann-La Roche Ltd., Dept. RLCR, CH-4002, Basle,
Switzerland

Version of record first published: 23 Sep 2006.

To cite this article: Richard Buchecker, Guy Marck & Martin Schadt (1995): New Nematics Incorporating a 2,6-Difluorophenyl Acetylene Group, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 260:1, 93-105

To link to this article: <http://dx.doi.org/10.1080/10587259508038685>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

NEW NEMATICS INCORPORATING A 2,6-DIFLUOROPHENYL ACETYLENE GROUP

RICHARD BUCHECKER, GUY MARCK and MARTIN SCHADT
F. Hoffmann-La Roche Ltd., Dept. RLCR, CH-4002 Basle, Switzerland

Abstract A large series of thin film transistor compatible nematic liquid crystals incorporating a 2,6-difluorophenyl acetylene group have been synthesised. Most of them exhibit high clearing points and an increased dielectric anisotropy.

INTRODUCTION

Liquid crystalline materials with large positive dielectric anisotropies ($\Delta\epsilon \gg 0$) are essential to achieve low threshold voltages in nematic mixtures. Such molecules usually possess at least one group with a large dipole moment (e.g. nitriles). This leads to a strong increase of the polarity of the whole molecule. As a consequence such polar structures considerably increase the conductivity of less polar compounds when combined, a disadvantage which is of crucial importance for the design of thin film transistor (TFT) compatible mixtures.

In order to overcome this problem it is an advantage to design molecules which incorporate a whole series of substituents with comparatively small dipole moments distributed over the rigid core. The substitution pattern must be chosen such that each single group dipole moment contributes positively to the dipole moment of the molecule. A disadvantage of this approach however is that such molecules are provided with a number of lateral substituents which usually decrease the mesophase stability considerably¹⁻⁴. Sporadic exceptions however have previously been reported^{4,5}. The intention of this work was to find and investigate in a systematic way components which combine the

advantages of distributed dipole moments with a minimal depression of mesophase stability.

RESULTS AND DISCUSSION

Due to its small size and its relatively large electronegativity fluorine was exclusively used for lateral substituents. As a first series a number of structures incorporating different linking units were synthesised. Their mesomorphic properties are plotted in Fig. 1. While the melting points remain roughly constant throughout the whole series, large differences of the clearing points, reaching more than 120 °C, were observed. Only in combination with an acetylenic linking unit high enantiotropic clearing points could be achieved.

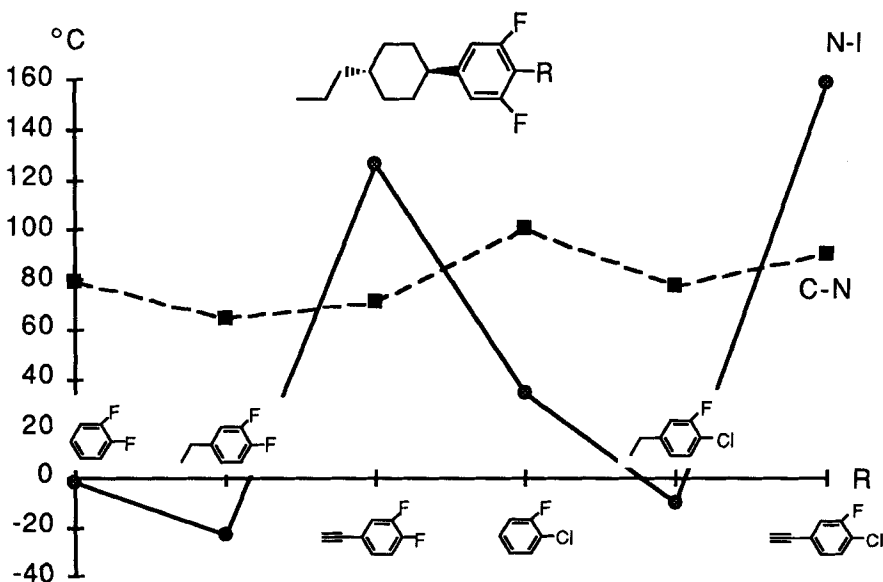


FIGURE 1 Influence of different linking units between a phenyl ring and the 2,6-difluorophenyl residue on the mesomorphic properties

In the next series the influence of lateral difluoro substitution on the mesomorphic properties was studied. As can be seen from Fig. 2, the depression of the mesophase of the fluorinated compared with the unsubstituted tolane is distinct but still relatively small (29 °C and 46 °C) if the fluorine substituents are

positioned ortho to the acetylenic linking unit (central or terminal positions within the three membered core). This finding is in contrast to the compound where the fluorine substituents are in the meta position (head position). Here the clearing point is decreased by 85 °C compared with the unsubstituted tolane. Interestingly the opposite effect is observed for the melting points. Here the ortho fluorinated tolanes exhibit much stronger depressions (45 °C and 52 °C respectively) than the tolane fluorinated at the head position (6 °C). Consequently the range of the mesophase is even enlarged for the former two compounds while it becomes extremely narrow for the latter. From this follows that the incorporation of a 2,6-difluorophenyl acetylene subunit into the rigid core decreases the clearing point much less than generally expected for similar laterally fluorinated liquid crystals. This and the results described in the previous paragraph made us to keep the 2,6-difluorophenyl acetylene substructure unchanged during the investigations below.

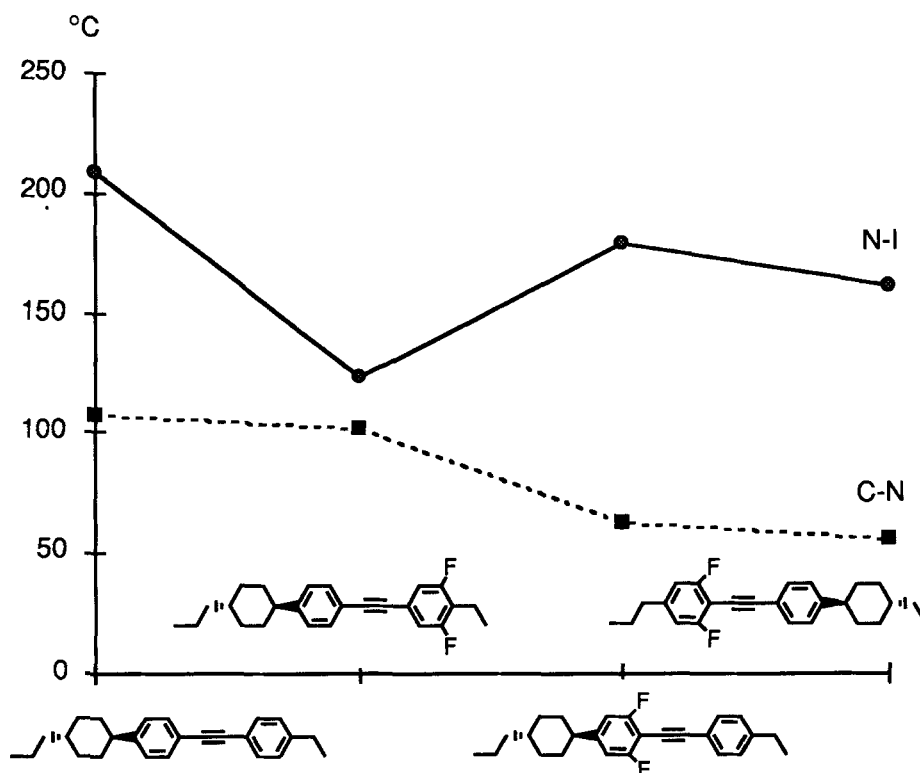


FIGURE 2 Mesomorphic properties of cyclohexyltolanes unfluorinated and difluorinated at changing positions

During the previous experiments the terminal, non fluorinated ring was always a cyclohexyl unit. The next step therefore was to replace the cyclohexane ring by a 1,3-dioxane, phenyl, pyridine or pyrimidine ring. Comparison of the clearing points (Fig. 3) reveals that 1,3-dioxanes and pyrimidines lead to the highest clearing temperatures followed by cyclohexane and pyridine. The lowest clearing points, which are 42 °C and 62 °C lower than the highest transition, are achieved if a phenyl ring is incorporated. If the melting points are also taken into consideration then the saturated rings (cyclohexane and dioxane) lead to improved components regarding the broadness of mesophase. This preference

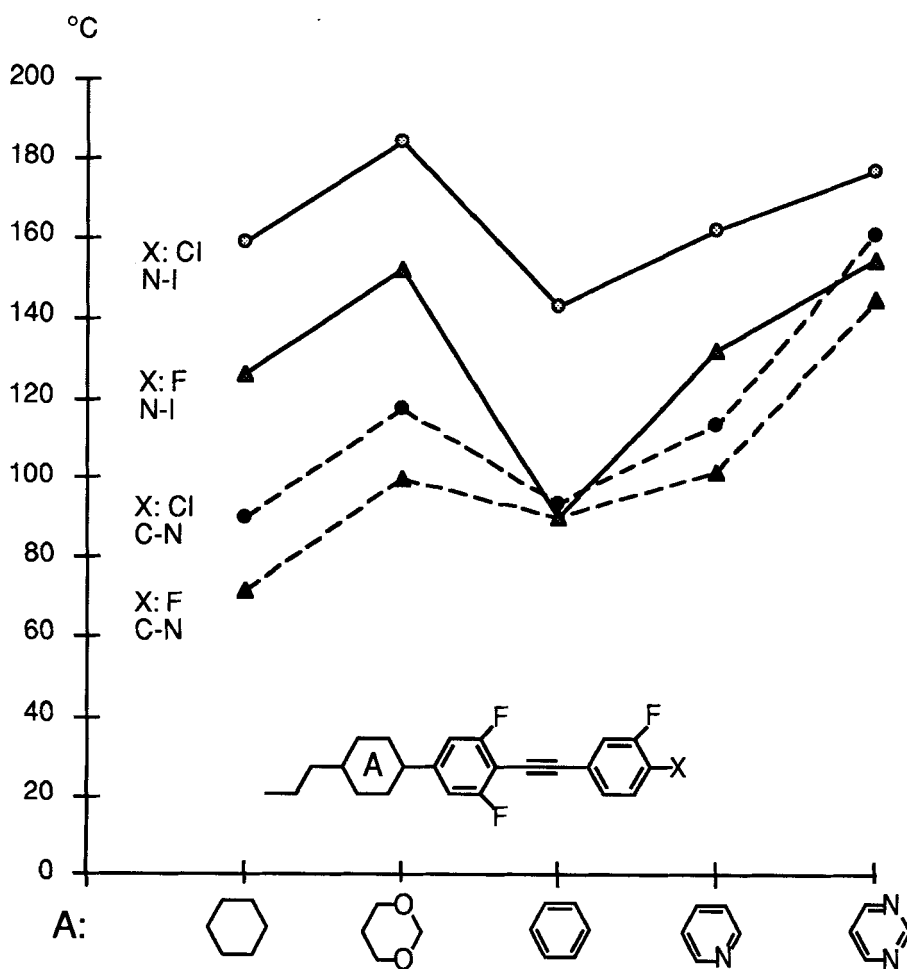


FIGURE 3 Mesomorphic properties of 2,6-difluorotolanes incorporating different third rings

is further supported by the rather low solubility observed for the pyrimidine compounds.

In Fig. 4 a variety of different compounds based on the difluoro cyclohexyltolane structure are compared. They all possess one to three partially different substituents at the remaining phenyl ring (head position). Regarding the stabilities of the mesophases, the following general trends are observed for the substituent in 4-position (X): $\text{CN} > \text{Cl} > \text{OCHF}_2 > \text{OCF}_3 > \text{F} > \text{H}$. For the

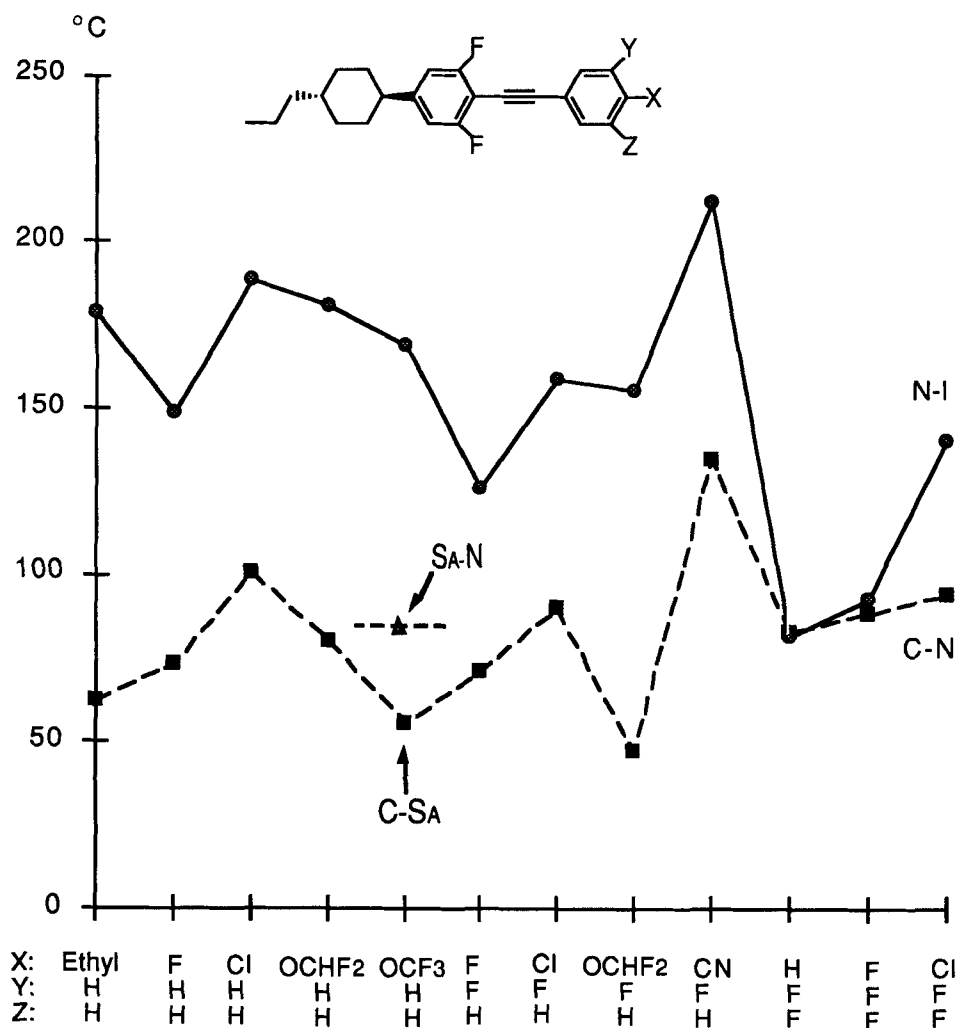


FIGURE 4 Mesomorphic properties of cyclohexyl 2,6-difluorotolanes with different substituents

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:15 18 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:15 18 February 2013



Downloaded by [Tomsk State University of Control Systems and Radio] at 12:15 18 February 2013

112 °C), however was not unexpected.

Broad mesophases are also obtained with compounds where the difluorophenyl acetylene moiety is linked to a bicyclohexane unit (Fig. 5, right side). The clearing points of the different derivatives move within a relatively narrow range from 163 °C (ethyl side chain) to 192 °C (difluorovinyl side chain). On the other hand, the melting points are all similarly low: from 32 °C (4-pentenyl side chain) to 51.5 °C (difluorovinyl side chain). All mesophases are purely nematic.

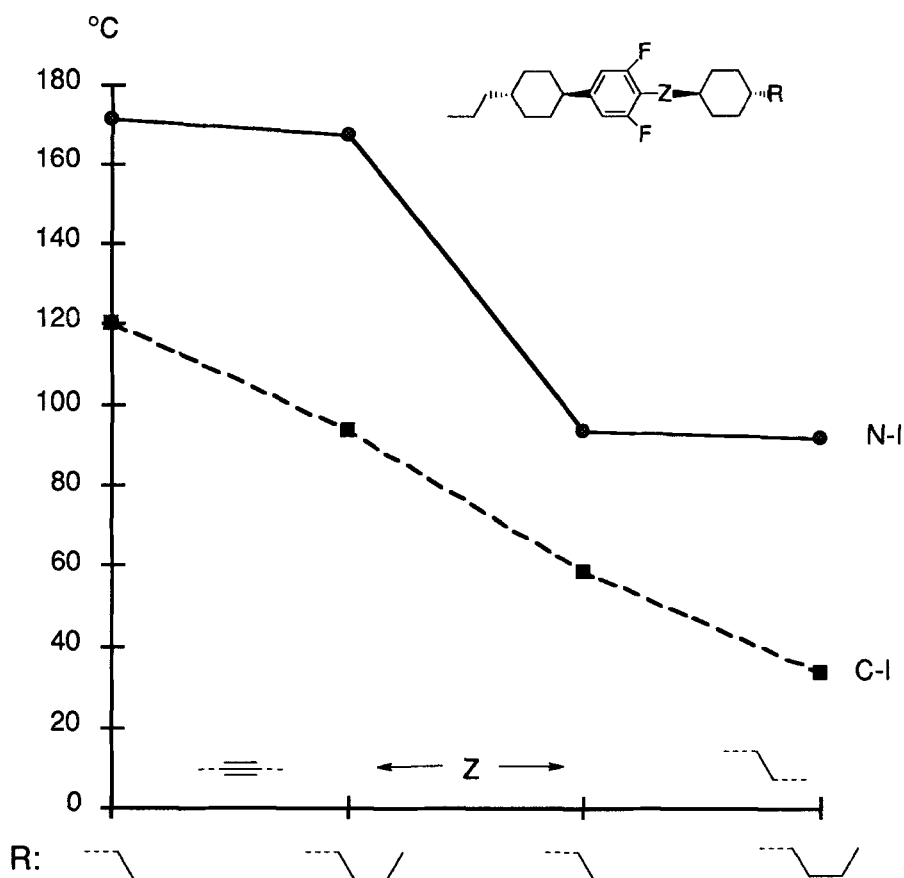


FIGURE 6 Mesomorphic properties of 2,6-difluorophenyl ethanes incorporating two cyclohexane rings in comparison to 1,6-difluorophenyl acetylenes

If the acetylenic bridging group in cyclohexyl 2,6-difluorophenyl cyclohexyl acetylenes is replaced by a saturated ethane bridge the mesomorphic properties collated in Fig. 6 are obtained. From Fig 6 follows a sharp drop of the clearing points of the ethane series (-77°C of the propyl and -75°C of the butyl derivative). The melting points of the ethane bridged derivatives are also lower. Moreover T_m decreases with increasing length of the side chain.

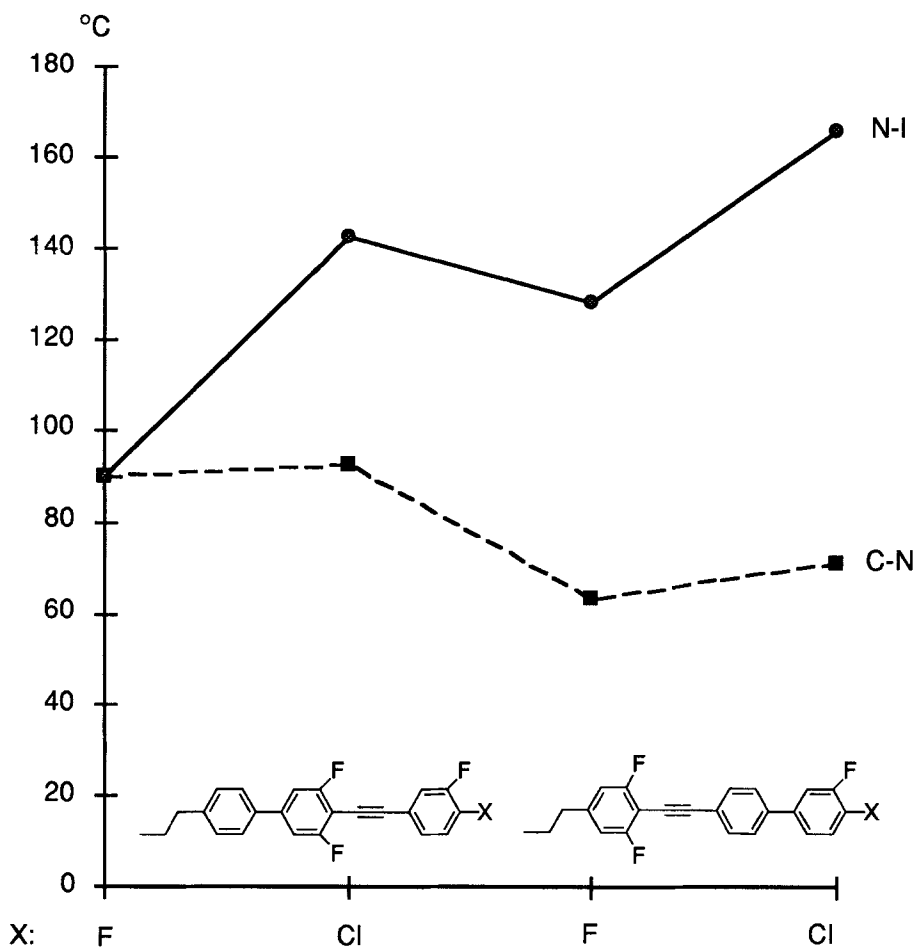
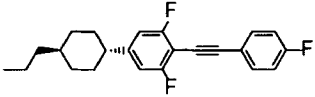
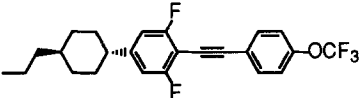
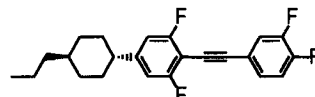
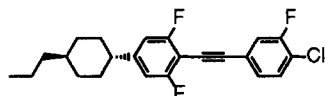
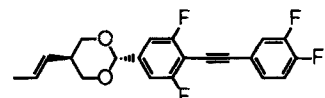
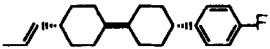
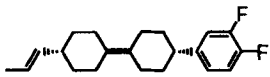
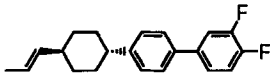


FIGURE 7 Mesomorphic properties of phenyl 2,6-difluorotolanes with central or terminal position of the difluorophenyl ring

Because of their large optical anisotropy, phenyl tolans are of special interest for narrow cell gap LCDs. As mentioned at the beginning, phenyl as a third ring leads to rather low clearing points. If however the 2,6-difluorophenyl acetylene unit is shifted to the outer position of the rigid core (see Fig. 7), the

clearing points increase by 38 °C (X = F) and 23 °C (X = Cl) respectively. At the same time the melting points are lowered by 27 °C and 21 °C respectively. Therefore this concept leads to much broader mesophases in the terphenyl series.

TABLE 1 Dielectric Anisotropies $\Delta\epsilon = (\epsilon_{\parallel} - \epsilon_{\perp})$ of selected compounds measured at reduced temperature ($T = T_c - 10$ °C).

| Structure | T_c [°C] | ϵ_{\parallel} | ϵ_{\perp} | $\Delta\epsilon$ | Ref. |
|---|------------|------------------------|--------------------|------------------|------|
|  | 150 | 6.8 | 3.2 | 3.6 | |
|  | 170 | 8.1 | 3.6 | 4.5 | |
|  | 123 | 11.6 | 5.0 | 6.6 | |
|  | 162 | 10.4 | 4.6 | 5.8 | |
|  | 157 | 28.5 | 7.7 | 20.8 | |
|  | 194 | | | 1.8 | 7 |
|  | 159 | | | 3.2 | 7 |
|  | 134 | | | 4.0 | 5 |

In Table 1 the dielectric anisotropies of some selected difluorophenyl tolanes are collated. For comparison the data of two fluorinated bicyclohexyl phenyl and of a cyclohexyl biphenyl derivative are included. The measurements clearly show that the $\Delta\epsilon$ -values of the difluorophenyl acetylenes are considerably higher than those of the reference compounds at the bottom of the

table. An extremely high dielectric anisotropy ($\Delta\epsilon = 20.8$) was achieved with the 2,6-difluorotolane unit attached to a dioxane ring.

In Table 2 all the mesomorphic data, which are used in the Figures are listed with reference to the number of the Figure where they occur.

TABLE 2 Summary of melting- and clearing points of all components. Nomenclature: C = cyclohexyl, P = phenyl, D = 1,3-dioxanyl, Py = pyridinyl, P₁ = pyrimidinyl, T = triple bond, A = ethyl, d_x = in chain double bond at position x, lower case atomic symbols = lateral substituents, number = number of C atoms in sat. chain. [] means a virtual clearing point measured in pentyl cyclohexylphenyl nitrile.

| Compound | T _{C/N} °C | T _{N/I} °C | Fig. | Compound | T _{C/N} °C | T _{N/I} °C | Fig. |
|---|------------------------|------------------------|---------|--|------------------------|------------------------|------|
| 3CP _{F,F} P _F F | 79.6 | [-2] | 1 | 3CP _{F,F} TPOCF ₃ | 56.0* | 169.4 | 4 |
| 3CP _{F,F} AP _F F | 64.7 | [-23] | 1 | 3CP _{F,F} TP _F OCHF ₂ | 47.5 | 155.6 | 4 |
| 3CP _{F,F} TP _F F | 71.3 | 126.0 | 1, 3, 4 | 3CP _{F,F} TP _F CN | 134.8 | 211.8 | 4 |
| 3CP _{F,F} P _F Cl | 100.7 | [34] | 1 | 3CP _{F,F} TP _{F,F} H | 83.4 | 81.9 | 4 |
| 3CP _{F,F} AP _F Cl | 77.6 | ---- | 1 | 3CP _{F,F} TP _{F,F} F | 88.8 | 92.9 | 4 |
| 3CP _{F,F} TP _F Cl | 90 | 158.9 | 1,3,4 | 3CP _{F,F} TP _{F,F} Cl | 94.5 | 140.6 | 4 |
| 3CPTP ₂ | 107.3 | 208.1 | 2 | 3CP _{F,F} TC ₂ | 86.3 | 152.2 | 5 |
| 3CPTP _{F,F} 2 | 101.2 | 122.9 | 2 | 3CP _{F,F} TC ₃ | 120.2 | 171.4 | 5, 6 |
| 3CP _{F,F} TP ₂ | 62.6 | 178.6 | 2, 4 | 3CP _{F,F} TC ₄ | 93.6 | 167.0 | 5,6 |
| 3P _{F,F} TPC ₂ | 55.6 | 161.8 | 2 | 3CP _{F,F} TC ₀ d ₁ F ₂ | 53.1 | 169.9 | 5 |
| 3DP _{F,F} TP _F F | 99.4 | 151.9 | 3 | 3CP _{F,F} TCO ₂ | 93.3 | 112.1 | 5 |
| 3PP _{F,F} TP _F F | 90.0 | ---- | 3, 7 | 3P _{F,F} TCC ₂ | 41.6 | 163.1 | 5 |
| 3PyP _{F,F} TP _F F | 101.1 | 131.7 | 3 | 3P _{F,F} TCC ₀ d ₁ | 48.8 | 181.1 | 5 |
| 3P ₁ P _{F,F} TP _F F | 144.6 | 154.0 | 3 | 3P _{F,F} TCC ₀ d ₁ F ₂ | 51.5 | 192.6 | 5 |
| 3DP _{F,F} TP _F Cl | 117.2 | 184.4 | 3 | 3P _{F,F} TCC ₃ 0 | 48.0 | 189.8 | 5 |
| 3PP _{F,F} TP _F Cl | 92.3 | 142.7 | 3, 7 | 3P _{F,F} TCC ₄ 0 | 31.7 | 182.0 | 5 |
| 3PyP _{F,F} TP _F Cl | 113.4 | 161.7 | 3 | 3CP _{F,F} AC ₃ | 58.6 | 93.7 | 6 |
| 3P ₁ P _{F,F} TP _F Cl | 160.3 | 176.5 | 3 | 3CP _{F,F} AC ₄ | 33.5 | 92.2 | 6 |
| 3CP _{F,F} TPF | 73.6 | 148.6 | 4 | 3P _{F,F} TPP _F F | 63.5 | 128.3 | 7 |
| 3CP _{F,F} TPCl | 100.4 | 188.9 | 4 | 3P _{F,F} TPP _F Cl | 70.7 | 165.9 | 7 |
| 3CP _{F,F} TPOCHF ₂ | 80.5 | 181.2 | 4 | | | | |

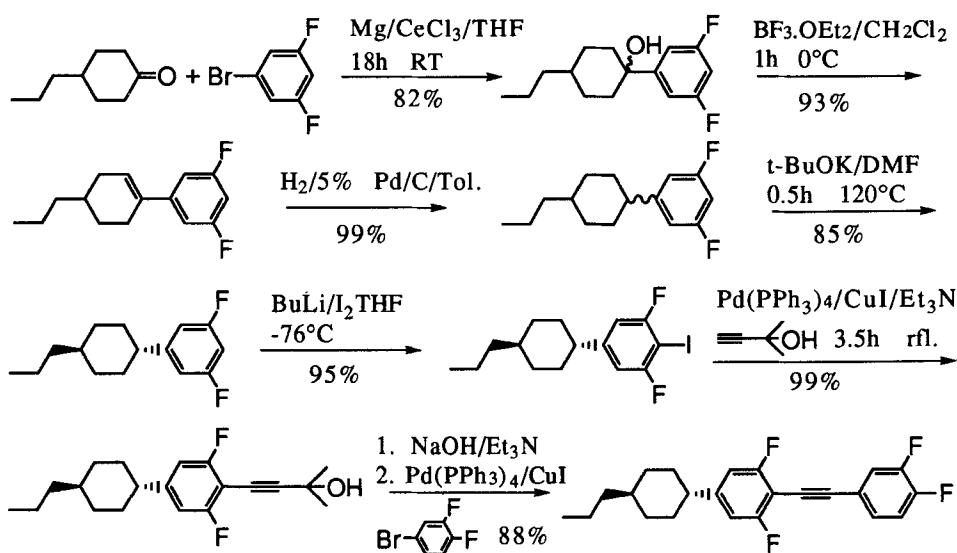
* smectic/nematic transition at 84.5 °C

In conclusion, liquid crystals incorporating a 2,6-difluorophenyl acetylene substructure proved to be valuable components with almost exclusively nematic mesophases, high clearing points, and large dielectric anisotropies. The structural concept employed allows to realise a large number of laterally fluorinated molecules without considerable loss of mesophase stability.

SYNTHESIS

The synthesis of the cyclohexyltolanes was generally realised according to scheme 1. Thus the reagent of bromo-3,5-difluorobenzene and 4-propylcyclohexanone were brought to reaction in the presence of cerium chloride⁸, then dehydrated with boron trifluoride⁹ and subsequently hydrogenated. The cis/trans mixture of the resulting cyclohexylphenyl

SCHEME 1 Synthesis of 2,6-difluorotolane derivatives

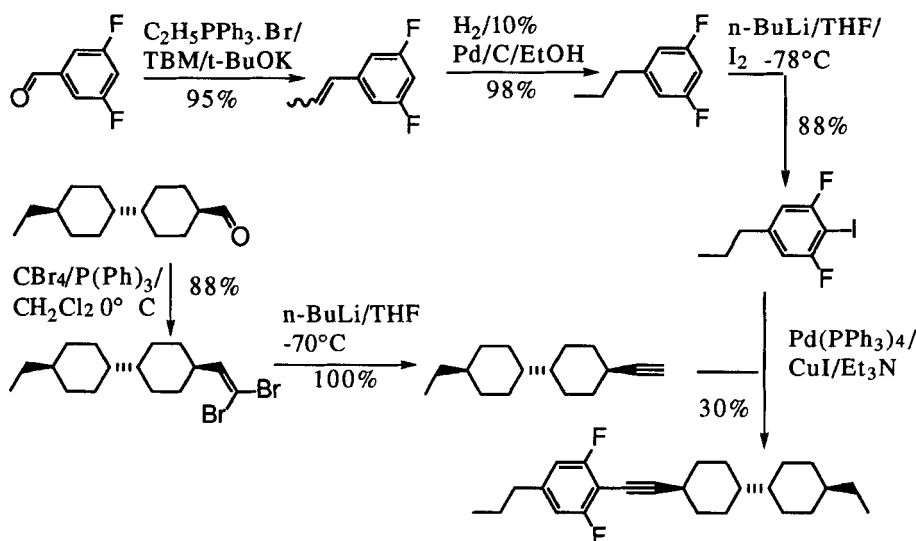


derivative was isomerised by using potassium t-butyrate at elevated temperature. The purified trans product was then transformed into the corresponding iodinated derivative with butyl lithium and iodine¹⁰. The formation of the tolane subsequently was accomplished by a copper catalysed

coupling with 2-methyl-3-buten-2-ol followed by an alkaline cleavage of acetone¹¹ and a second analogous coupling with bromo-3,4-difluorobenzene.

The bicyclohexyl-2,6-difluorophenyl acetylene derivatives were synthesised according to scheme 2. Thus the 4' substituted trans/trans bicyclohexyl carboxaldehyd was transferred according to a well known procedure¹² via the dibromovinyl derivative to the corresponding acetylene. On the other side commercial 3,5-difluorobenzaldehyde was transferred to the corresponding propyl derivative via Wittig reaction and subsequent hydrogena-

SCHEME 2 Synthesis of 1,6-difluorophenyl acetylene bicyclohexyl derivatives



tion. The iodination and the final coupling with the acetylene derivative were accomplished analogous to the above description.

The authors express their gratitude to M. B. Blöchliger, Mr. G. Daub, Mr. A. Germann, Mr. T. Lukàc, Mr. J. Reichardt and Mr. H. Sommer for technical assistance in the preparation and evaluation of the compounds. Dr. W. Arnold (NMR), Mr. W. Meister (MS), Dr. M. Grosjan (IR), Mr. F. Wild and Mr. B. Halm (DTA) are thanked for the measurements and interpretation of the required spectra

REFERENCES

1. P. Balkwill, D. Bishop, A. Pearson and I. Sage, Mol. Cryst. Liq. Cryst., **123**, 1, (1985).
2. L.K.M. Chan, G.W. Gray and D. Lacey, Mol. Cryst. Liq. Cryst., **123**, 185 (1985).
3. S.M. Kelly and H. Schad, Helv. Chim Acta, **68**, 813 (1985).
4. E. Bartmann, U. Finkenzeller, E. Poetsch, V. Reiffenrath and K. Tarumi, Proc.22th Freiburger Arbeitstagung Flüssigkristalle, (March 31 - April 2, 1993).
5. M. Schadt, 14th int. Liquid Crystal Conference, Pisa (June 21-26, 1992); Liquid Crystals, **14**, 73 (1993).
6. V. Vill, Landolt-Börnstein, IV/7, Subvol. a-d, Ed. by J. Thiem (Springer Verlag, Berlin,1992/94).
7. M. Schadt, R. Buchecker and A. Villiger, Liquid Crystals, **7**, 519 (1990).
8. T. Imamoto, N. Takiyama, K. Nakamura, T. Hatajima and Y. Kamiya, J. Am. Chem. Soc., **111**, 4392 (1989).
9. G. H. Posner, E. M. Shulman-Roskes, Ch. Ho Oh, J.-Ch. Carry, J. V. Green, A. B. Clark H. Dai and T. E. N. Anjeh, Tetrahedron Lett., **32**, 6489 (1991).
10. G. L. Grunewald, A.J. Kolar, M. S. S. Palanki, V. M. Paradkar, T. J. Reitz, D. J. Sall, Org. Prep. Proced. Int. **22**, 747 (1990)
11. D.E. Ames, D. Bull and C. Takundwa, Synthesis Comm., **1981**, 364; A. Carpita, A. Lessi and R. Rossi, ibid., **1984**, 571.
12. E. J. Corey and P. L. Fuchs, Tetrahedron Lett., **1972**, 3769.