(10 mL) containing sorbitol (200 – 1000 mM). Lipid bilayers were labeled with *N*-(6-tetramethylrhodaminethiocarbamoyl)-1,2-dihexadecanoyl-*sn*-glycero-3-phosphoethanolamine (TRITC-DHPE, 0.07 %). The vesicles in solution and fused to surfaces were observed with a laser scanning microscope (Zeiss, LSM 510, Zeiss 60x/1.25 apochromat water immersion objective, pinhole size 100 μm) on either poly-L-lysine or 4-aminobutyldimethylmethoxysilane-modified glass coverslips coated with a 50 nm PECVD-SiO_2 layer.

Standard experiments were performed in 85 mM KCl, 2 mM *N*-(2-hydroxyethyl)piperazine-*N*′-(2-ethanesulfonic acid) (HEPES), at pH 7.4 using vesicles filled with 200 mM of sorbitol.

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[1] O. P. Hamill, A. Marty, E. Neher, B. Sakmann, F. J. Sigworth, *Pflügers Arch.* **1981**, *391*, 85.

[2] W. R. Schlue, W. Hanke, *Planar Lipid Bilayers*, Academic Press, London, **1993**.

[3] a) G. Jung, *Combinatorial Chemistry. Synthesis*, *Analysis*, *Screening*, Wiley-VCH, Weinheim, **1999**; b) J. Rademann, G. Jung, *Science* **2000**, *287*, 1947.

[4] a) M. Eigen, R. Rigler, *Proc. Natl. Acad. Sci. USA* **1994**, *91*, 5740; b) J. Hanes, L. Jermutus, S. Weber-Bornhauser, H. R. Bosshard, A. Plückthun, *Proc. Natl. Acad. Sci. USA* **1998**, *95*, 14130.

[5] J. Denyer, J. Worley, B. Cox, G. Allenby, M. Banks, *Drug Discovery Today* **1998**, *3*, 323.

[6] B. Sackmann, E. Neher, *Single-Channel Recording*, Plenum, New York, **1983**.

[7] H. Schindler, *Methods Enzymol.* **1989**, *171*, 225.

[8] R. B. Gennis, *Biomembranes*, Springer, New York, **1989**.

[9] A. Balasubramanian, S. McLaughlin, *Biochim. Biophys. Acta* **1982**, *685*, 1.

[10] P. Mueller, T. F. Chien, B. Rudy, *Biophys. J.* **1983**, *44*, 375.

[11] E. Sackmann, *Science* **1996**, *271*, 43.

[12] B. S. Jacobson, D. Branton, *Science* **1977**, *195*, 302.

[13] B. Hille, *Ionic Channels of Excitable Membranes 2nd ed.*, Sinauer, Sunderland, **1992**.

[14] G. Boheim, W. Hanke, G. Jung, *Biophys. Struct. Mech.* **1983**, *9*, 181.

[15] W. Hanke, G. Boheim, *Biochim. Biophys. Acta* **1980**, *596*, 456.

[16] I. Vodyanoy, J. E. Hall, T. M. Balasubramanian, *Biophys. J.* **1983**, *42*, 71.

[17] a) B. A. Cornell, V. L. Braach-Maksvytis, L. G. King, P. D. Osman, B. Raguse, L. Wieczorek, R. J. Pace, *Nature* **1997**, *387*, 580; b) P. Fromherz, V. Kiessling, K. Kottig, G. Zeck, *Appl. Phys. A* **1999**, *69*, 571; c) S. M. Bezrukov, I. Vodyanoy, V. A. Parsegian, *Nature* **1994**, *370*, 279.

[18] a) L. Q. Gu, O. Braha, S. Conlan, S. Cheley, H. Bayley, *Nature* **1999**, *398*, 686; b) M. Pawlak, U. Meseth, B. Dhanapal, M. Mutter, H. Vogel, *Protein Sci.* **1994**, *3*, 1788.

[19] T. Stora, J. H. Lakey, H. Vogel, *Angew. Chem.* **1999**, *111*, 402; *Angew. Chem. Int. Ed.* **1999**, *38*, 389.

[20] a) D. W. Deamer, M. Akeson, *Trends Biotechnol.* **2000**, *18*, 147; b) A. Meller, L. Nivon, E. Brandin, J. Golovchenko, D. Branton, *Proc. Natl. Acad. Sci. USA* **2000**, *97*, 1079; c) J. J. Kasianowicz, E. Brandin, D. Branton, D. W. Deamer, *Proc. Natl. Acad. Sci. USA* **1996**, *93*, 13770; d) D. Branton, J. Golovchenko, *Nature* **1999**, *398*, 660.

[21] a) B. U. Keller, R. Hedrich, W. L. Vaz, M. Criado, *Pfluegers Arch.* **1988**, *411*, 94; b) A. Moscho, O. Orwar, D. T. Chiu, B. P. Modi, R. N. Zare, *Proc. Natl. Acad. Sci. USA* **1996**, *93*, 11443; c) G. Riquelme, E. Lopez, L. M. Garcia-Segura, J. A. Ferragut, J. M. Gonzalez-Ros, *Biochemistry* **1990**, *29*, 11215; d) M. Criado, B. U. Keller, *FEBS Lett.* **1987**, *224*, 172; e) H. Kawai, L. Cao, S. M. Dunn, W. F. Dryden, M. A. Raftery, *Biochemistry* **2000**, *39*, 3867.

[22] a) G. Boheim, W. Hanke, F. J. Barrantes, H. Eibl, B. Sakmann, G. Fels, A. Maelicke, *Proc. Natl. Acad. Sci. USA* **1981**, *78*, 3586; b) C. Miller, *Physiol. Rev.* **1983**, *63*, 1209.

[23] a) S. J. Edelstein, O. Schaad, J. P. Changeux, *Biochemistry* **1997**, *36*, 13755; b) S. Weiss, *Science* **1999**, *283*, 1676; c) A. Cha, G. E. Snyder, P. R. Selvin, F. Bezanilla, *Nature* **1999**, *402*, 809; d) L. M. Mannuzzu, M. M. Moronne, E. Y. Isacoff, *Science* **1996**, *271*, 213.

[24] J. D. Jackson, *Klassische Elektrodynamik*, 2nd ed., de Gruyter, Berlin, **1982**.

A Room-Temperature Discotic Nematic Liquid Crystal**

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Liquid crystal displays (LCDs) have played a vital role in information technology. The twisted nematic and supertwisted nematic display devices have dominated commercial displays since their invention. The liquid crystal layer in these devices is made up exclusively of calamitic liquid crystals (composed of rod-shaped molecules). A number of calamitic nematic liquid crystals having room-temperature mesophases—such as, cyanobiphenyls, phenylpyrimidines, phenylcyclohexanes, and Schiff bases—have been synthesized and used in practical displays.[1, 2]

The major disadvantage with these types of devices is the narrow and nonuniform viewing cone, which is considered to be an unacceptable aspect of their performance. Several methods have been put forward to improve the viewing angle characteristics, for example the multidomain technique,[3] the introduction of an optical compensator to reduce the amount of light leakage in the dark state,[4] the application of an electric field parallel to the plane of the substrates,[5] and the "amorphous" twisted nematic liquid crystal displays (TNLCD).[6] We recently disclosed a novel approach to overcome this problem by utilizing discotic nematic liquid crystals instead of calamitic nematic liquid crystals.[7] Compared to the large number of calamitic molecules showing a nematic phase, there are only few disk-shaped molecules showing a discotic nematic phase N_D. Several derivatives of triphenylene,[8, 9] truxene,[10] thiotruxene,[11] and naphthalene[12] show stable discotic nematic phases, but these phases are high-temperature and narrow. For any application as a liquid crystal device, stability of the mesophase well below and above room temperature is one of the most important criteria.

Hitherto, no room-temperature discotic nematic liquid crystal was known. The common procedure for extending the mesophase range of calamitic liquid crystals is by mixing different components and preparing an eutectic mixture, but such a procedure has not been applied to discotic nematic till now. Therefore, it is of great practical interest to prepare room-temperature discotic nematic liquid crystals. Here we report on the synthesis of the first example of a room-temperature discotic nematic liquid crystal.

Hexa- and pentaalkynylbenzene derivatives having N_D phases have recently received a great deal of attention as their clearing temperatures are not very high and they show a chiral nematic-discotic phase on doping with suitable chiral molecules. Several hexa- and pentaalkynylbenzenes and their dimers were prepared and studied extensively.[9, 13]

When the peripheral alkyl chains are attached to the phenyl ring in the hexaalkynylbenzene derivatives through a hetero-

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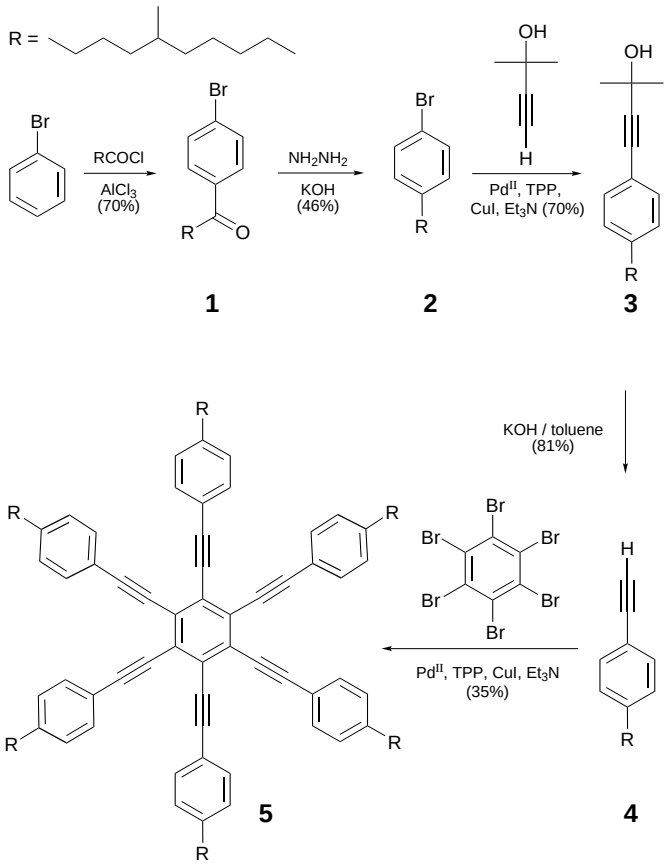
atom such as oxygen, the melting and clearing temperatures are higher than when the alkyl chains are directly attached to the ring.[14] Furthermore when the peripheral aliphatic side chains of various cores are branched, the mesophase is widened, but the type of the mesophase formed is not affected by the introduction of branching in many cases.[15] We anticipated that by replacing the normal alkyl chains by branched alkyl chains connected directly to the phenyl ring, the melting points of the alkynylbenzene derivatives would reduce and thus stabilize the mesophase. The synthesis of the new branched chain hexalkynylbenzene is outlined in Scheme 1.



Scheme 1. Synthesis of **5**. TPP = triphenylphosphane.

4-Methylnonanoic acid was converted into the acid chloride with oxalyl chloride at room temperature. Friedel–Crafts acylation of bromobenzene with this acid chloride gave 1-bromo-4-(4-methylnonanoyl)benzene (**1**). Wolff–Kishner reduction of this ketone furnished 1-bromo-4-(4-methylnonanyl)benzene (**2**). Palladium-catalyzed alkynylation of **2** with 2-methyl-3-butyn-2-ol afforded the protected phenylacetylene **3**, which was deprotected with KOH in refluxing toluene to yield phenylacetylene **4**. Palladium-catalyzed coupling[16] of this branched, alkyl-chain-substituted species with hexabromobenzene provided the desired hexakis[4-(4-methylnonanyl)phenylethynyl]benzene (**5**). The product, purified by repeated column chromatography, was homogenous according to thin-layer chromatography (TLC), and the HPLC purity was found to be 99.8% (silica, hexane; flow 1.2 mL min^{-1}, retention time 39.25 min.). The spectral data were in accordance with the structure.[17] Both the starting material (4-methylnonanoic acid) and the product **5** were optically inactive.

The thermal behavior of **5** was checked by polarizing microscopy and by differential scanning calorimetry (DSC). The compound exhibits textural features of a nematic phase at room temperature (Figure 1). On heating it transforms to the isotropic phase at about 70 °C. The nematic phase reappears with very limited supercooling and crystallizes at −12 °C. These crystals melt at about 6 °C on subsequent heating. The DSC traces obtained on the heating and cooling runs are shown in Figure 2.

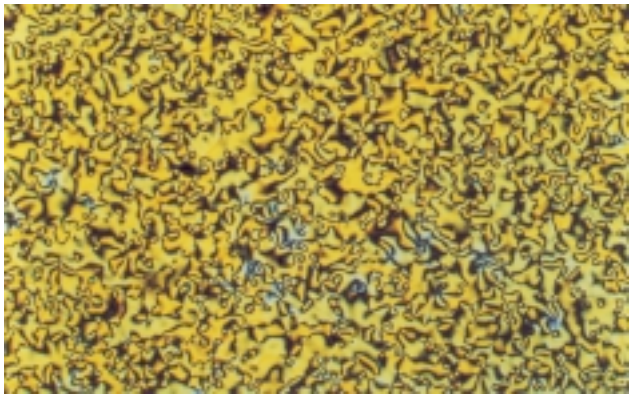


Figure 1. Optical textures of **5**. Photomicroscopic images of the mesophase were obtained with a polarizing microscope (Leitz DMRXP equipped with a Mettler FP82HT hot stage) on cooling from the isotropic liquid at 25 °C (crossed polarizer, magnification × 100)

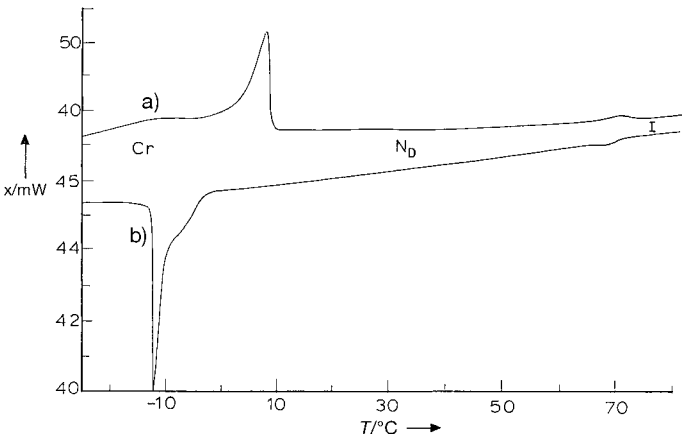


Figure 2. DSC traces for compound **5** on a) heating and b) cooling (scan rate 5 °C min^{-1}). x = heat flow, Cr = crystal phase, N_D = nematic phase, I = isotropic phase.

Compound **5** shows a broad melting transition at 6.1 °C (peak temperature, enthalpy 18.1 kJ mol^{-1}) and a transition from nematic discotic to isotropic at 69.3 °C (enthalpy 0.3 kJ mol^{-1}). The cooling run shows the isotropic to nematic transition at 68.1 °C (enthalpy 0.2 kJ mol^{-1}) and a broad transition from the nematic phase to the crystal phase at −12.2 °C (enthalpy 18.2 kJ mol^{-1}). However, we realized that the thermal behavior of **5** obtained in different batches is not

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consistent, though the spectral data are identical. This could be due to the stereoheterogeneity of the product (with one chiral center in each of the six side chains, the product derived from racemic starting material consists of a mixture of stereoisomers). A mixture of stereoisomers could be the cause of the varying melting (0–10 °C) and clearing points (40–80 °C) in different batches.

Efforts to crystallize the material in various solvents at low temperature met with failure, but **5** can be fractionalized by triturating with acetone at about −10 °C. Two such treatments give a product with higher melting and clearing points. Fractionation of **5** is also possible by column chromatography over alumina and elution with hexane/dichloromethane in small fractions (1 mL). The first few collections have a relatively lower clearing point (40–50 °C) than the latter fractions (70–80 °C). This indicates that the product **5** is a statistical mixture of stereoisomers. The different solubilities of the isomers account for the variations in the composition of the different batches. The preparation of pure stereoisomers of 4-methylnonanoic acid and other derivatives is currently under investigation.

The nematic phase shown by **5** is stable well below and above ambient temperature. Previously, experimental studies have been presented to demonstrate the wide and symmetrical viewing angle of devices having similar but high-temperature nematic discotic material.[7] Similar studies with the present room-temperature nematic discotic material will be presented in due course.

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[1] G. W. Gray, S. M. Kelly, *J. Mater. Chem.* **1999**, *9*, 2037.
[2] *Hand Book of Liquid Crystals, Vol. 2a* (Eds.: D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, V. Vill), Wiley-VCH, Weinheim, **1998**.
[3] T. Sugiyama, T. Hashimoto, K. Katoh, Y. Iimura, S. Kobayashi, *Jpn. J. Appl. Phys.* **1995**, *34*, 2071.
[4] H. Mori, *Jpn. J. Appl. Phys.* **1997**, *36*, 1068.
[5] M. Oh-e, M. Yoneya, K. Kondo, *J. Appl. Phys.* **1997**, *82*, 528.
[6] Y. Toko, T. Sugiyama, K. Katoh, Y. Iimura, S. Kobayashi, *J. Appl. Phys.* **1993**, *74*, 2071.
[7] S. Chandrasekhar, S. Krishna Prasad, G. G. Nair, D. S. Shankar Rao, S. Kumar, M. Manickam in *EuroDisplay '99, The 19th International Display Research Conference Late-news papers*, Berlin, **1999**, p. 9.
[8] a) C. Destrade, M. C. Mondon-Bernaud, N. H. Tinh, *Mol. Cryst. Liq. Cryst.* **1981**, *71*, 111; b) T. J. Phillips, J. C. Jones, D. G. McDonnell, *Liq. Cryst.* **1993**, *15*, 203; c) P. Hindmarsh, M. J. Watson, M. Hird, J. W. Goodby, *J. Mater. Chem.* **1995**, *5*, 2111.
[9] K. Praefcke, B. Kohne, D. Singer, *Angew. Chem.* **1990**, *102*, 200; *Angew. Chem. Int. Ed. Engl*. **1990**, *29*, 177.
[10] a) C. Destrade, H. Gasparoux, A. Babeau, N. H. Tinh, *Mol. Cryst. Liq. Cryst.* **1981**, *67*, 37; b) W. K. Lee, B. A. Wintner, E. Fontes, P. A. Heiney, M. Ohba, J. N. Haseltine, A. B. Smith, *Liq. Cryst.* **1989**, *4*, 87.
[11] R. Cayuela, H. T. Nguyen, C. Destrade, A. M. Levelut, *Mol. Cryst. Liq. Cryst.* **1989**, *177*, 81.
[12] K. Praefcke, B. Kohne, K. Gutbier, N. Johnen, D. Singer, *Liq. Cryst.* **1989**, *5*, 233.
[13] a) B. Kohne, K. Praefcke, *Chimia* **1987**, *41*, 196; b) K. Praefcke, B. Kohne, D. Singer, D. Demus, G. Pelzi, S. Diele, *Liq. Cryst.* **1990**, *7*, 589; c) C. J. Booth, D. Kruerke, G. Heppke, *J. Mater. Chem.* **1996**, *6*, 927.
[14] A. N. Cammidge, R. J. Bushby in *Hand Book of Liquid Crystals, Vol. 2B* (Eds.: D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, V. Vill), Wiley-VCH, Weinheim, **1998**, pp. 693–748.
[15] a) D. M. Collard, C. P. Lillya, *J. Am. Chem. Soc.* **1991**, *113*, 8577; b) S. Kumar, D. S. Shankar Rao, S. Krishna Prasad, *J. Mater. Chem.* **1999**, *9*, 2751.
[16] R. Diercks, J. C. Armstrong, R. Boese, K. P. C. Vollhardt, *Angew. Chem.* **1986**, *98*, 270; *Angew. Chem. Int. Ed. Engl*. **1986**, *25*, 268.
[17] Selected data for **5**: MS (FAB); *m/z*: 1520.2 [M^+]; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.58$ (d, 12H), 7.20 (d, 12H), 2.64 (t, 12H), 1.63–1.1 (m, 78H), 0.90 (m, 36H); ^{13}C NMR ($CDCl_3$): $\delta = 144.03$, 131.79, 128.52, 127.3, 120.53, 99.41, 87.06, 36.95, 36.72, 36.36, 32.66, 32.21, 28.78, 26.72, 22.70, 19.65, 14.10.

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