Synthesis of Rodlike Dispiro Hydrocarbon Skeletons for New Liquid Crystal Compounds

Nina Feuerbacher,[a] Fritz Vögtle,*[a] Jens Windscheidt,[a] Eike Poetsch,[b] Martin Nieger[c]

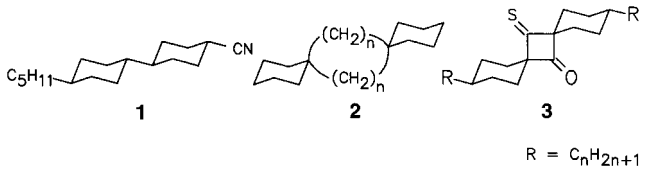
[a] Kekulé-Institut für Organische Chemie und Biochemie der Universität Bonn, Gerhard-Domagk-Straße 1, D-53121 Bonn, Germany
Tel +49(228)7334956, Fax +49(228)735662; E-mail: voegtle@uni-bonn.de
[b] Merck KG, Liquid Crystal Research, Frankfurter Str. 250, D-64271 Darmstadt, Germany
[c] Institut für Anorganische Chemie der Universität Bonn, Gerhard-Domagk-Straße 1, D-53121 Bonn, Germany

Received 2 June 1998

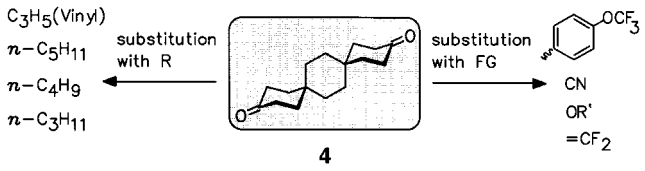
Abstract: A simple synthesis of the dispiro[5.2.5.2]hexadecane skeleton was developed. Starting from the cyclohexanedicarbaldehyde **6** the dispirane was prepared in one step. The synthesised dispirodiketone **4** is a key compound for the preparation of a number of new liquid crystalline compounds, as its linear molecular shape is proved by an x-ray structural analysis of the corresponding diketal **10**. Additionally the synthesis of the first dispirane **4** with a [5.2.3.2]-linkage is described.

Keywords: Cyclobutane, Cyclohexane, Ketals, Liquid crystals, Spiro compounds

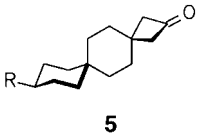
Carbocyclic spiro compounds[1] are not only part of natural products such as sesquiterpenes, but can also be used as building blocks in thermotropic liquid crystals.[2] The required and characteristic molecular shape[3] of a calamitic liquid crystal[4] is a linear elongated structure as it is achieved by the bicyclohexyl compounds **1** synthesised by Eidenschinck et al[5] which show remarkable mesophases. The interest in new rodlike liquid crystals is due to their broad applicability in optical displays and screens. In search of novel nematogenic compounds we synthesised several dispiranes and spiranes and investigated the influence of their molecular shape on the liquid crystalline behaviour.[6] We showed that the spiro linkage of cyclohexyl units only retain their required linearity if an even number of carbon atoms in the middle ring is given (cf. **2**). In this contribution we have reported the synthesis of terminally substituted dispiro[5.1.5.1]tetradecanes **3**, which show enantiotopic mesophases over a large temperature range of more than 100°C.[6b,c]



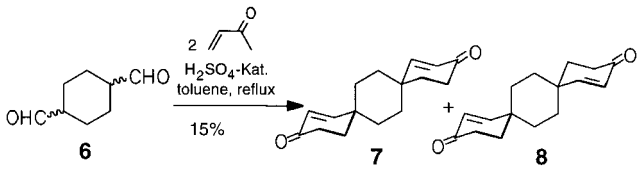
Now we report the facile synthesis of a dispiro-[5.2.5.2]hexadecane **2** (n = 2) as an excellent precursor for new liquid crystal compounds. The dispirodiketone **4** is a key intermediate which provides the possibility to investigate the consequences of different terminal substitution patterns on its physical properties.



Additionally the synthesis of an alkyl substituted dispirotetradecane **5** which would be the first dispirane with a [5.2.3.2]-linkage allows further examinations of the influence of the molecule geometry on liquid crystal behaviour.



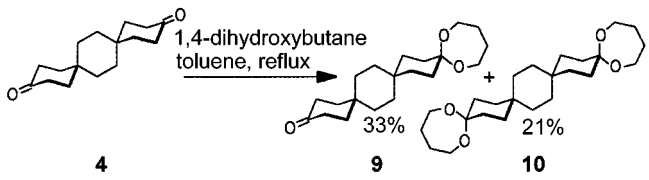
Various methods of preparing polyspiro compounds consisting of cyclohexane rings are described in the literature.[7] However, to our knowledge, no preparation of a dispirohexadecane which can be twice terminally substituted has been discovered and the known syntheses of dispiro[5.2.5.2]hexadecanes are still very complex.[8] For this reason a simple and efficient synthesis is desirable. Following the acid-catalysed annelation of α-alkyl aldehydes and α,β-unsaturated ketones found by Flaugh et al.[9] we succeeded in performing a one-pot synthesis of cyclohexanedicarbaldehyde **7**.[10] Treatment of **6** with methyl vinyl ketone yields the desired dispirodiketenones **7** and **8** respectively. The synthesis was carried out by treating a mixture of the dialdehyde and methyl vinyl ketone in toluene with a catalytic amount of sulfuric acid and direct azeotropic removal of water.



Scheme 1

The dialdehyde **6** was prepared by a convenient TEMPO-catalysed oxidation of cyclohexanedimethanol with sodium hypochlorite.[11] Subsequent hydrogenation of the dienones **7** and **8** afforded the dispirodiketone **4** in an overall

yield of 13%. In order to achieve further successive substitution with typical end groups the protection of one ketone group was necessary. We have experienced that protection of diketones with butanediol facilitates the column chromatographic separation of the mono- and diketals.[12] As expected the R_f-values differed sufficiently so that the separation of the formed mono- and diketals could be achieved easily.



Scheme 2

The tetraspiro[6.2.2.2.6.2.2.2]-1,6,17,22-tetraoxaoctacosane **10** crystallised in the form of colourless prisms from a mixture of dichloromethane and methanol. The x-ray structure[13] shows a molecule with nearly linear shape obeying the necessary form anisotropy. The synthesised diketone **4** therefore is a promising key precursor for new liquid crystal compounds with a dispiro[5.2.5.2]hexadecane building block.

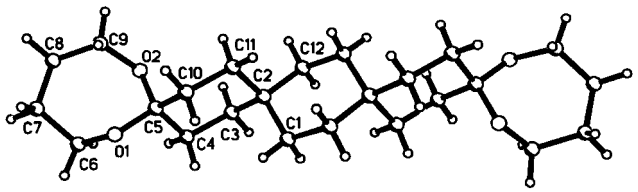
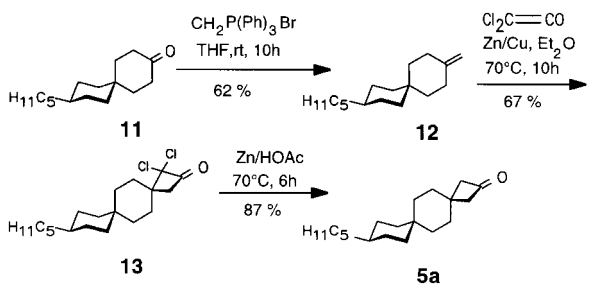


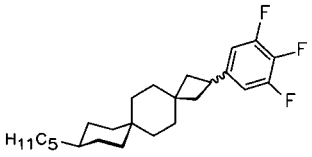
Figure. First x-ray structure analysis of the dispiro[5.2.5.2]hexadecane skeleton

With regard to our investigations on the dispiro[5.1.5.1]tetradecanes we set out to synthesize the first dispiro[5.2.3.2]tetradecane **5a** which is already substituted in position 10. Starting with a Wittig-alkenation[14] of the pentane substituted spiro[5.5]undecanone **11**[6e] the dispiro[5.2.3.2]tetradecanone **13** could be obtained by in situ cycloaddition of dichloroketene with the alkene **12**.[15] The reductive removal of the chlorine was carried out by treating the dihalogenide **13** with zinc, affording the desired dispiroketone **5a** in an overall yield of 54%.



Scheme 3

Terminal substitution of the dispirotetradecanone oxygen in **5** leads to two diastereomers in the same way as they would occur when substituting the two ketone groups of the dispirohexadecandione **4**. In the case of a *trans*-substitution the linear shape of the system is preserved. The dispirane **14** provided with suitable groups typical for an application in liquid crystal displays are currently under further investigation.[16]



Solvents were purified by standard methods and dried with appropriate drying agents prior to use. Mps are uncorrected. Microscope heating unit (Reichert, Vienna). ^{1}H and ^{13}C NMR spectra: Bruker AM 250 (250 and 62,9 MHz, respectively), ^{13}C NMR data were verified by DEPT 135 experiments. MS (EI): A.E.I. MS-50 spectrometer, Manchester, GB. GC-MS: Hewlett Packard HP 5980, Series 2 with mass spectrometer HP 5989. Microanalyses: Mikroanalytische Abteilung der Universität Bonn. Thin-layer chromatography (TLC): Silica gel 60 F_{254} (Merck), detection of the aliphatic compounds was achieved by treatment with a solution of rhodamine 6G in ethanol. Column chromatography (CC) on silica gel 60, mesh size 63-100 μm (Merck, Darmstadt, Germany). FTIR: Spectrometer 1600, Perkin-Elmer, on KBr [Abbreviations: (w): weak, (m): medium, (s): strong, (vs): very strong, EE: ethyl acetate].

***cis,trans*-Cyclohexane-1,4-dicarbaldehyde (6)**

cis,trans-1,4-Bis(hydroxymethyl)cyclohexanes (28.4 g, 0.2 mol) were dissolved in CH_2Cl_2 (300 mL). 2,2,6,6-Tetramethylpiperidine 1-oxide (1.2 g, 7.6 mmol) and KBr (1.2 g, 7.6 mmol) dissolved in H_2O (40 mL) were added. A solution of sodium hypochlorite (396 mL, 13% chlorine-active), $NaHCO_3$ (15.0 g) and H_2O (490 mL) was added dropwise in such a way that slight reflux could be observed. The mixture was stirred for 1 h. Subsequently the phases were separated. The aqueous phase was extracted twice with dichloromethane (50 mL). The combined organic phases were treated with a solution of KI (2.65 g) dissolved in 10% HCl (150 mL). The excess iodine was destroyed by sat. aq $Na_2S_2O_3$. The organic phase was washed with H_2O and dried (Na_2SO_4). After removal of the solvent the residue was purified by column chromatography and gave 14.0 g (50%) of a colorless oil. R_f = 0.51 [cyclohexane/EE 3:1].

GC-MS (EI, 70 eV, 200 °C): *m/z* (%): 140 (10) [M^+], 112 (23) [M^+–CO], 94 (98), 79 (90), 55 (100).

^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.31–1.37 (m, 4 H, 2 CH_2), 1.74–1.80 (m, 2 H, CH_2), 2.10–2.20 (m, 4 H, 2 CH_2), 9.60 (d, ^3J = 1 Hz, CHO), 9.63 (d, ^3J = 1 Hz, CHO).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 23.31 (2 CH_2), 24.90 (2 CH_2), 47.98 (CH), 49.65 (CH), 204.04 (CHO), 204.51 (CHO).

IR (KBr, cm^{-1}): ν = 1722 (vs), 2714 (m), 2858 (s), 2933 (s).

Dispiro[5.2.5.2]hexadecane-1,10-diene-3,12-dione (7) and Dispiro-[5.2.5.2]hexadecane-1,13-diene-3,12-dione (8)

To a stirred suspension of *cis,trans*-cyclohexane-1,4-dicarbaldehyde (12.5 g, 89 mmol, **6**) and methyl vinyl ketone (15 mL, 178 mmol) in toluene (75 mL) was added slowly conc. H_2SO_4 (0.1 mL) and the mixture was stirred for 0.5 h at r.t. The solution was cautiously heated to reflux and stirred at this temperature for 6 h with constant removal of the H_2O. After cooling to r.t. the mixture

was treated with 1 M aq $NaHCO_3$ (50 mL). The phases were separated and the aqueous phase was extracted with toluene (2 × 50 mL). The combined organic phases were washed subsequently with brine and H_2O. After drying (Na_2SO_4) and removal of the solvent the residue was purified by column chromatography to yield 5.1 g (15%) of a colourless solid (mixture of the two isomers), mp 192–196 °C. R_f = 0.51 [CH_2Cl_2/EE 15:1].

GC-MS (EI, 70 eV, 200 °C): *m/z* (%): 244 (100) [M^+], 202 (72) [M^+–C_2H_2O], 160 (24) [M^+–2C_2H_2O], 79 (78).

^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.42–1.51 (m, 16 H, CH_2), 1.82–2.00 (m, 8 H, CH_2), 2.40 (t, ^3J = 6.3 Hz, 8 H, CH_2), 5.85 (d, ^3J = 10.2 Hz, 2 H, CH), 5.90 (d, ^3J = 10.2 Hz, 2 H, CH), 6.75 (d, ^3J = 10.2 Hz, 2 H, CH), 6.88 (d, ^3J = 10.2 Hz, 2 H, CH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 30.8 (4 CH_2), 31.18 (8 CH_2), 33.60 (4 CH_2), 34.87 (4 C_q), 127.10 (2 CH), 128.06 (2 CH), 157.17 (2 CH), 158.00 (2 CH), 199.48 (2 CO), 199.56 (2 CO).

IR (KBr, cm^{-1}): ν = 1663 (vs), 2848 (m), 2899 (m), 2943 (m).

HRMS: [M^+] ($C_{16}H_{20}O_2$), calcd. 244.1463, found 244.1459.

Dispiro[5.2.5.2]hexadecane-3,12-dione (4)

Dispiro[5.2.5.2]hexadecanedienedione (3.40 g, 14 mmol, **7**, **8**: a mixture of the two isomers) were dissolved in 500 mL toluene. After addition of Pd/C (700 mg) the solution is stirred at r.t. under H_2 (pressure: 3.0 bar). Subsequently the catalyst is filtered off and the solvent is removed to afford the crude product which can be crystallized from MeOH to yield 3.0 g (86%) of colourless crystals, mp 208 °C.

GC-MS (EI, 70 eV, 200 °C): *m/z* (%): 248 (100) [M^+], 192 (23) [M^+–2CO], 175 (69).

^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.47 (s, 8 H, CH_2), 1.70 (t, ^3J = 6.9 Hz, 8 H, CH_2), 2.28 (t, ^3J = 6.9 Hz, 8 H, CH_2).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 31.16 (8 CH_2), 32.28 (2 C_q), 37.25 (4 CH_2), 212.5 (2 C_q, CO).

IR (KBr, cm^{-1}): ν = 1718 (vs), 2852 (m), 2917 (m).

HRMS: [M^+] $C_{16}H_{24}O_2$: calcd. 248.1776, found 248.1774 (MS). – (248.36) C 77.38, H 9.74, found C 76.97 H 9.69.

Trispiro[6.2.2.5.2.2]-1,6-dioxadocosane-16-one (9)

To a solution of dispiro[5.2.5.2]hexadecane-3,12-dione (700 mg, 2.8 mmol, **4**) and butan-1,4-diol (260 mg, 2.8 mmol)[17] in toluene (200 mL) was added *p*-toluenesulfonic acid (40 mg). The solution was refluxed with direct azeotropic removal of the H_2O. When the H_2O removal ceased, the mixture was cooled to r.t. and 1 M $NaHCO_3$ (100 mL) was added. The phases were separated and the aqueous phase was extracted with toluene (2 × 100 mL). The combined organic phases were washed with H_2O and dried (Na_2SO_4). The solvent was evaporated and the crude residue subjected to column chromotography to yield 300 mg (33%) monoketal **9** as a colourless solid which can be recrystallised from MeOH, mp 161 °C. R_f = 0.46 (cyclohexane/acetone 4:1).

GC-MS (EI, 70 eV, 200 °C): *m/z* (%): 320 (10) [M^+], 248 (2) [M^+–C_4H_8O], 127 (100).

^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.22–1.42 (m, 8 H, CH_2), 1.45–1.60 (m, 8 H, CH_2), 1.65–1.80 (m, 8 H, CH_2), 2.28 (t, ^3J = 6.9 Hz, 4 H, CH_2), 3.62 (br, 4 H, OCH_2).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 29.06 (4 CH_2), 30.21 (6 CH_2), 31.45 (2 CH_2), 32.37 (2 C_q), 37.42 (2 CH_2), 61.85 (2 OCH_2), 101.63 (CO_2), 213.10 (CO).

IR (KBr, cm^{-1}): ν = 1716 (vs), 2851 (m), 2916 (m).

$C_{20}H_{32}O_3$ (320.47): calcd. C 73.17, H 10.18 for $C_{20}H_{32}O_3 \cdot 1/2\ CH_3OH$; found C 73.33, H 10.14.

Tetraspiro[6.2.2.6.2.2]-1,6,17,22-tetraoxooctacosane (10)

The above experimental procedure also yielded 230 mg (21%) of the diketal **10** as a colourless solid, mp 224 °C.

R_f = 0.75 (cyclohexane/acetone 4:1).

GC-MS (EI, 70 eV, 200 °C): *m/z* (%): 392 (10) [M^+], 320 (2) [M^+–C_4H_8O], 248 (2) [M^+–2 C_4H_8O], 127 (100).

^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.25 (br, 8 H, CH_2), 1.30–1.45 (m, 8 H, CH_2), 1.50–1.65 (m, 16 H, CH_2), 3.66 (m, 8 H, OCH_2).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 29.74 (6 CH_2), 30.10 (6 CH_2), 32.53 (2 C_q), 37.66 (4 CH_2) 61.85 (4 OCH_2), 101.86 (2 CO_2).

3-Methylene-9-pentylspiro[5.5]undecane (12)

To a suspension of methylenetriphenylphosphonium bromide (4.50 g, 12.6 mmol) and anhyd THF (120 mL) was added BuLi (9.75 mL, 1.5 molar solution in hexane) dropwise at r.t. The mixture was stirred for 0.5 h. Subsequently 9-pentylspiro[5.5]undecan-3-one[6e] (1.0 g, 4.2 mmol, **11**) dissolved in anhyd THF (50 mL) was added and the mixture stirred for 10 h. The excess of BuLi was hydrolised with H_2O (10 mL). The solvent was removed under reduced pressure. The aqeuous phase was extracted with Et_2O (2 × 50 mL) and the combined organic layers were washed with diluted HCl and H_2O. Subsequently the solution was dried (with Na_2SO_4) and the Et_2O removed. The crude product was purified by column chromatography: 612 mg (62%) of a colourless oil were obtained.

R_f = 0.84 (hexane).

MS (EI, 70 eV, 200 °C): *m/z* (%): 234 (48) [M^+], 206 (100) [M^+–C_2H_4], 163 (84).

^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 0.87 (t, ^3J = 6.9 Hz, 3 H, CH_3), 0.92–1.38 (m, 15 H, CH_2, CH), 1.40–1.52 (m, 4 H, CH_2), 1.60–1.70 (m, 2 H, CH_2), 2.08 (t, ^3J = 7 Hz, 2 H, CH_2), 2.13 (t, ^3J = 6.8 Hz, 2 H, CH_2), 4.55 (s, 2 H, =CH_2).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.30 (CH_3), 22.91 (CH_2), 26.9 (CH_2), 28.57 (2 CH_2), 30.59 (CH_2), 30.82 (CH_2), 32.33 (CH_2), 32.45 (C_q), 33.51 (CH_2), 36.28 (2 CH_2), 37.36 (CH_2), 38.30 (CH), 42.90 (CH_2), 106.28 (=CH_2), 150.79 (C_q).

$C_{17}H_{30}$: (234.43) calcd. C 87.09 H 12.91 found C 87.06 H 12.94.

1,1-Dichloro-10-pentyldispiro[3.2.5.2]tetradecan-2-one (13)

To a solution of alkene (600 mg, 2.6 mmol, **11**) in anhyd Et_2O (50 mL) was added Zn (280 mg) and cupric acetate (16 mg). Subsequently trichloroacetyl chloride (0.45 mL, 4 mmol) was added dropwise. The mixture was heated to 70 °C and stirred at that temperature overnight. After cooling to r.t. the inorganic residues were filtered off and the crude product was purified by column chromatography to yield 605 mg (67%) of a colourless liquid.

R_f = 0.68 (hexane/toluene 1:1).

GC-MS (EI, 70 eV, 200 °C): *m/z* (%): 302 (100) [M^+–CH_2CO], 267 (26) [302–Cl], 232 (38) [302–2Cl], 137 (23).

^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 0.86 (t, ^3J = 6.7 Hz, 3 H, CH_3), 0.96 (d, ^3J = 9.3 Hz, 2 H, CH_2), 1.10–1.46 (m, 14 H, CH_2), 1.47–1.65 (m, 5 H, CH_2, CH), 1.72–2.10 (m, 4 H, CH_2), 3.0 (s, 2 H, CH_2–cyclobutane).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.27 (CH_3), 22.85 (CH_2), 26.80 (2 CH_2), 28.34 (CH_2), 28.44 (CH_2), 29.12 (2 CH_2), 31.64 (C_q), 31.99 (CH_2), 32.35 (CH_2), 37.19 (CH_2), 38.13 (CH), 38.19 (CH_2), 40.20 (CH_2), 46.67 (C_q), 52.22 (CH_2), 93.17 (C_q), 193.74 (C_q).

HRMS: [M^+–CH_2CO] $C_{17}H_{28}Cl_2$ calcd. 302.1568 found 302.1567.

10-Pentyldispiro[3.2.5.2]tetradecan-2-one (5a)

1,1-Dichloro-10-pentyldispiro[3.2.5.2]tetradecan-2-one (600 mg, 1.8 mmol, **13**) were dissolved in HOAc (5 mL). Zn powder (0.45 g,

6.5 mmol) was added and the mixture was stirred for 6 h at 70°C. After cooling to r.t. the inorganic residues were filtered off. The crude residue was purified by colomn chromatography and afforded 410 mg (85%) of a colourless solid, mp 46–47°C.

R_f = 0.75 (CH_2Cl_2).

GC-MS (EI, 70 eV, 200°C): *m/z* (%): 276 (20) [M^+], 232 (72) [M^+–C_2H_4O], 206 (100).

^{1}H NMR (250 MHz, $CDCl_3$, 25°C): δ = 0.85 (t, ^3J = 6.7 Hz, 3 H, CH_3), 1.20 (d, ^3J = 9.1 Hz, 4 H, CH_2), 1.10–1.40 (m, 15 H, CH_2, CH), 1.47–1.64 (m, 6 H, CH_2), 2.68 (s, 4 H, 2 CH_2 cyclobutane).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.26 (CH_3), 22.84 (CH_2), 26.60 (2 CH_2), 28.38 (2 CH_2), 29.57 (CH_2), 30.86 (C_q), 31.79 (C_q), 32.07 (2 CH_2), 32.34 (CH_2), 32.82 (CH_2), 32.91 (CH_2), 36.27 (CH_2), 38.17 (CH), 57.08 (2 CH_2), 209.00 (C_q).

$C_{19}H_{32}O$ (276.46): calcd. C 82.55 H 11.67, found C 82.43 H 11.98.

Acknowledgement

We thank Merck KG, Darmstadt for support of this work.

References

(1) Detailed review on spiro compounds: Krapcho, A. *Synthesis* **1974**, 383.
Krapcho, A. *Synthesis* **1976**, 425.
Krapcho, A. *Synthesis* **1977**, 77.

(2) Karamyshewa, L. A.; Geivandova, T. A.; Roitman, K. V.; Ljukmanov, N. F. Kovshev, E. I. *Mol. Cryst. Liq. Cryst.* **1983**, *99*, 169.
Chan, K. M.; Gemmell, P. A.; Gray, G. W.; Lacey, D.; Toyne, K. J. *Mol. Cryst. Liq. Cryst.* **1987**, *147*, 113.

(3) Vorländer, D. *Z. Phys. Chem.* **1923**, *105*, 211.

(4) Overviews on liquid crystals:
Kelker, H.; Hatz, R. *Handbook of Liquid Crystals*, Verlag Chemie, Weinheim, Deerfield Beach, Florida, Basel **1980**.
Brown, G. H.; Crooker, P. P. *Chem. Eng. News* **1983**, 24.
Stegemeyer, H (Ed.) *Top. Phys. Chem.* **1994**, *Vol. 3*.
Internet: http://abalone.cwru.edu; http://scorpio.kent.edu.

(5) Eidenschinck, R.; Erdmann, D.; Krause, J.; Pohl, L. *Angew. Chem.* **1977**, *89*, 103; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 100.
Eidenschinck, R. *Kontakte* **1979**, *1*, 15.

(6) (a) Redloff, H.; Vögtle, F.; Puff, H.; Reuter, H.; Woller, P. *J. Chem. Res. (S)* **1984**, 314.
Redloff, H.; Vögtle, F.; Puff, H.; Reuter, H.; Woller, P. *J. Chem. Res. (M)* **1984**, 2910.
(b) Calaminus, W.; Vögtle, F.; Eidenschink, R. *Z. Naturforsch.* **1986**, *41b*, 1011.
(c) Calaminus, W.; Vögtle, F.; Eidenschink, R. *German Patent P 3543997.1* **1985, CAS 107**: 96503t
(d) Boettcher, J.; Hartmann, R.; Vögtle, F. *Chem. Ber.* **1992**, *125*, 1865.
(e) Schmidt, W.; Vögtle, F.; Poetsch, E. *Liebigs Ann.* **1995**, 1319.

(7) Dreiding, A. S. *Helv. Chim. Acta* **1957**, *40*, 1812.
Dreiding, A. S. *Helv. Chim. Acta* **1967**, *50*, 23.
de Jongh, H. A. P.; Wynberg, H. *Recl. Trav. Chim. Pay-Bas* **1963**, *82*, 202.
de Jongh, H. A. P.; Wynberg, H. *Tetrahedron*, **1964**,*20*, 2553.
Rice, L. M.; Geschickter, C. F.; Grogan, C. H. *J. Med. Chem.* **1963**, *6*, 388.

(8) Rice, L. M.; Scott, K. R. *J. Med. Soc.* **1968**, 378.

(9) Flaugh, M. E.; Crowell, T. A.; Farlow, D. S. *J. Org. Chem.* **1980**, *45*, 5399.
Hamata, M. personal communication, **1996**.

(10) Herwig, W.; Soomer, S.; Erbes, K. Ger. Patent 1,173,449 (cl. C 07c), 4.7 **1964 CAS 61**: 9414d

(11) Anelli, P. L.; Montanari, F.; Qiunci, S. *Org. Synth.* **1990**, *45*, 5399.

(12) Herold, D. *Ph. D. Thesis* University of Bonn, **1996**.

(13) Crystal data: $C_{24}H_{40}O_4$, colourless crystals, dimension 0.90 * 0.50 * 0.40 mm, triclinic, space group: P-1 (No. 2), α = 6.632(1), *b* = 7.854(1), *c* = 10.580(2) Å, α = 80.73(1), β = 78.93(1)°, γ = 84.78(1), V = 532.7(2) Å^3, F(000) = 216, Z = 1, wR(F^2) = 0.217 [R_1 = 0.079 for I>2σ(I)] μ(Cu-K_α) = 0.638 mm^{-1}. A total of 2101 reflections were recorded on an MACH3-Diffractometer at K = 293K [graphite monochromator, λ(Cu-K_α = 1,54178 Å)]. Of these 1930 independent reflexions were used for structure solution (SHELXTL-Plus) and refinement (128 parameters, SHELXL-93). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102294. Copies of the data can be obtained free of charge on application to: CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

(14) Wittig, G.; Schoellkopf, U. *Org. Synth.* **1973**, *Vol. V*, 751.

(15) Bak, D. A.; Brady, W. T. *J. Org. Chem.* **1979**, *44*, 107.

(16) Feuerbacher, N.; Schmidt, W.; Vögtle, F.; Poetsch, E. *Patent application: Spiroverbindungen*, *No. 97129*, German Patent Office **1997.**

(17) Higher yields of the product **10** may be achieved by the use of 5.6 mmol (2 eq.) butane-1,4-diol.