Synthesis and Mesomorphic Properties of 4,4′-Di-n-alkyl-bibicyclo[2.2.2]octanes

V. Reiffenrath and F. Schneider
Physikalische Chemie, Universität Siegen

Z. Naturforsch. **36a**, 1006–1008 (1981); received July 27, 1981

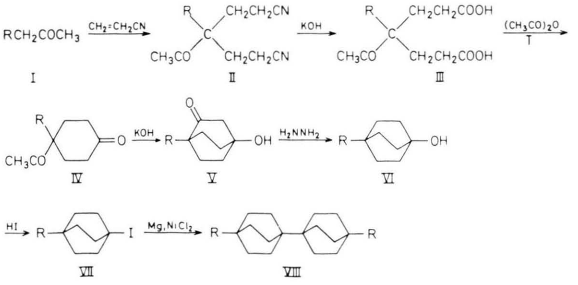
The homologous series of di-alkyl-bibicyclo[2.2.2]octanes (methyl to octyl) was prepared. All homologues with the exception of the methyl compound show broad smectic phase ranges. For the pentyl homologue the smectic phase exists between 46 °C and 247 °C. X-ray investigations show a novel type of diffraction pattern.

Introduction

Recently Gray and Kelly [1–3] have shown that the incorporation of bicyclo[2.2.2]octane in mesogenic systems leads to liquid crystals with higher clearing points and in some cases lower melting points than the corresponding benzene or cyclohexane compounds. For technical applications the bicyclooctane system has the further advantages of light transmission in the near UV, of well defined stereochemistry and of chemical stability. Analogous to the biphenyl [4] and bicyclohexane system [5], it could be expected that a liquid crystal with a core of two directly coupled bicyclooctane systems should exhibit strong mesomorphic properties. Therefore we have synthesized the 4,4′-di-n-alkyl-bicyclo[2.2.2]-octanes and have investigated their mesomorphic properties.

Results and Discussion

The compounds were synthesized according to the following scheme:



The mesomorphic properties of bibicyclooctanes VIII are shown in Table 1.

Table 1. Properties of 4,4′-di-n-alkyl-bibicyclo[2.2.2]-octanes.

R	t_{mp}/° C	t_{cl}/° C	Found		Calculated	
			%C	%H	%C	%H
CH_3	196	—	87.76	12.22	87.73	12.27
C_2H_5	119	209	87.70	12.45	87.52	12.48
C_3H_7	155	222	87.38	12.51	87.34	12.66
C_4H_9	92	246	87.25	12.69	87.20	12.80
C_5H_{11}	46	247	87.18	12.79	87.07	12.93
C_6H_{13}	60	240	87.04	13.00	86.97	13.03
C_7H_{15}	47	226	86.90	13.00	86.88	13.12
C_8H_{17}	68	212	86.74	13.10	86.80	13.20

With the exception of the methyl homologue (1,1-BBCO), the compounds show smectic phases with a broad stability range covering up to 200 K for 5,5-BBCO. The type of the smectic phase could not be determined unambiguously till now. Observations with a polarizing microscope yielded a strong tendency to form homeotropic textures. Only small areas showed lancet textures or gray coloured regions with small birefringence. Therefore the smectic phase should be of the uniaxial type S_A, S_B or S_E. Because of the formation of homeotropic textures the determination of miscibility of the smectic phases was difficult. At least, the smectic phases of the BBCOs seem to belong to the same phase type because of a complete miscibility of the smectic phases of 5,5-BBCO and 8,8-BBCO with a monotonous decrease of the clearing point and because of a complete miscibility in the system 5,5-BBCO/2,2-BBCO which shows a minimum at 165 °C in the clearing point curve. The determination of miscibility with liquid crystals with known phase sequences was not possible till now due to the same difficulties.

The structure of the smectic phases was further investigated by means of X-ray measurements. All

---

Reprint requests to Dr. F. Schneider, Institut für Physikalische Chemie, Universität Siegen, D-5900 Siegen 21.

0340-4811 / 81 / 0900-1006 $ 01.00/0. — Please order a reprint rather than making your own copy.

Table 2. X-ray data.

Compound	l/nm	t/° C	d_1/nm	d_2/nm	d_3/nm
2,2-BBCO	1.51	125	1.35	0.546	0.532
3,3-BBCO	1.76	175	1.59	0.549	0.537
4,4-BBCO	2.01	100	1.75	0.541	—
5,5-BBCO	2.25	75	1.92	0.542	0.523
6,6-BBCO	2.50	75	2.12	0.540	0.521
7,7-BBCO	2.75	75	2.33	0.535	0.521
8,8-BBCO	3.00	100	2.59	0.533	0.520

homologues show at least three sharp rings on a flat film photograph. The inner ring is due to the spacing d_1 of the smectic layers. Values between 85 and 90% of the molecular lengths l, determined with Dreiding models, were observed (Table 2). This reflection appears in the second ($d = 0.679$ nm) and in the third order ($d = 0.453$ nm) only for 2,2-BBCO.

The values d_2 and d_3 for the two outer rings are very similar (Fig. 1) and seem to coincide for 4,4-BBCO. An additional outer ring ($d_4 = 0.473$ and 0.506 nm) with a very small intensity could be detected for 5,5-BBCO and 4,4-BBCO, resp.

Because of the sharp reflections the classification as an S_A phase can be discarded. The same is true for the S_B phase, which should show only one outer ring. S_E phases should show three outer rings (110, 200 and 210 according to Doucet et al. [6]) of comparable intensity. It is of course possible to calculate lattice parameters which yield the observed two d values for the 110 and 200 reflections, if the compound shows only two outer reflections. However, the indexing of the third outer ring of 5,5-BBCO with small index values (210, 111 or 201) is impossible and for most BBCOs the third outer reflection is missing. On the other hand it has to be taken into account that the BBCOs have another symmetry (3-fold axis along the long molecular axis) than liquid crystals with benzene rings. Therefore it may be possible that the intensity ratios of the reflections are different because of a different orientation or symmetry of the molecules in the unit cell. In order to classify the smectic phases investigations on the miscibility with other smectic liquid crystals have to be performed.

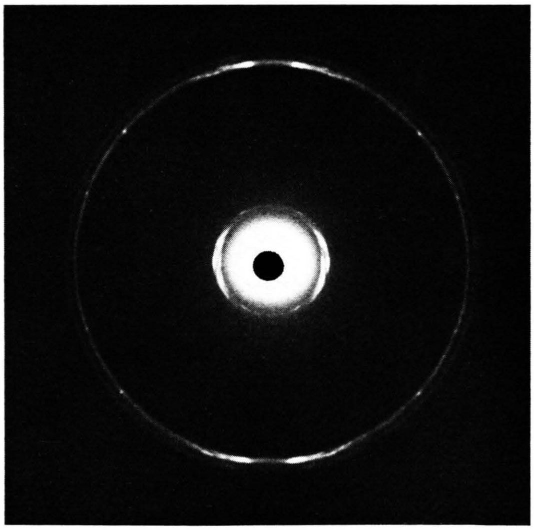


Fig. 1. X-ray diffraction pattern of the smectic phase of 5,5-BBCO at 75 °C after an exposure time of 1 h. The third outer ring is not visible on this photograph.

The formation of broad smectic phases has shown that the bibicyclooctane system is a well suited core for liquid crystals and 2,2-BBCO is, to the best of our knowledge, the liquid crystal with the smallest molecular length which has ever been synthesized.

Experimental

The ketones I were commercial products (Aldrich). Compounds II and III were prepared as described in Ref. [7], IV and V as described in [8], VI as described in [3], and VII and VIII as described in [9].

Properties of the octyl derivatives: II: b.p. 217 °C at 0.1 mm Hg; III: could not be obtained crystalline; IV: b.p. 165 °C at 0.1 mm Hg; VI: m.p. 53 °C, b.p. 107 °C at 0.1 mm Hg, MS(EI) m/e 238(45), 209(95), 167(40), 153(65), 125(100).

1-Iodo-4-n-pentyl-bicyclo[2.2.2]octane. A solution of 12.4 g (0.063 mole) of 1-bicyclo[2.2.2]-octanol and 75 ml of 57% hydroiodic acid was refluxed in 150 ml of acetic acid. After 1 h, the mixture was poured on ice and extracted with ether. The aqueous solution was neutralized with potassium hydroxide and further extracted with ether. The combined extracts were washed with aqueous solutions of sodium bicarbonate, sodium thiosulfate and water. After drying over magnesium sulfate the concentration in vacuo afforded 18.5 g of a brown oil. The crude product was distilled under reduced pressure to give 17 g (88%) of 1-iodo-4-n-pentyl-bicyclo[2.2.2]octane.

Properties of the iodo derivatives VII: CH_3: m.p. 76 °C (Ref. [10]: 71 °C); C_2H_5: m.p. 31 °C; C_3H_7: m.p. 61 °C; C_4H_9: b.p. 81 °C at 0.1 mm Hg;

C_5H_{11}: b.p. 101 °C at 0.3 mm Hg; C_6H_{13}: b.p. 105 °C at 0.1 mm Hg; C_7H_{15}: b.p. 114 °C at 0.1 mm Hg; C_8H_{17}: b.p. 135 °C at 0.1 mm Hg, MS(EI) m/e 221(65), 109(100).

4,4'-Di-n-pentyl-bibicyclo[2.2.2]octane. A flask with 2.7 g (0.11 mole) of magnesium turnings was flame dried and charged with 9.1g (0.07 mole) of anhydrous nickel chloride and 17 g (0.055 mole) of 1-iodo-4-n-pentyl-bicyclo[2.2.2]octane. After adding 50 ml of ether the mixture was refluxed under argon for 14 h. The reaction mixture was treated with water, filtered and washed further with water, ethanol, and heptane. The organic solvents were evaporated from the combined filtrates. Filtration and washing with water and acetone afforded the crude product which was recrystallized from ether/acetone to give 5.5 g (55%) of 4,4'-di-n-pentyl-bibicyclo[2.2.2]octane.

Properties of the BBCOs: Analytical data and transition temperatures are given in Table 1, MS(EI): M^+, $(M\text{-ethyl})^+$, $(M\text{-alkyl})^+$.

The transition temperatures were determined by DSC measurements (Perkin-Elmer, DSC 2) and with a polarizing microscope equipped with a hot stage. X-ray patterns were recorded with CuKα radiation on a flat film. The samples were contained in thin walled glass tubes of 0.5 mm diameter and were heated with an air stream.

[1] G. W. Gray and S. M. Kelly, J. Chem. Soc. Chem. Comm. **1979**, 974.

[2] G. W. Gray and S. M. Kelly, J. Chem. Soc. Chem. Comm. **1980**, 465.

[3] G. W. Gray and S. M. Kelly, J. Chem. Soc. Perkin II **1981**, 26.

[4] G. W. Gray, K. J. Harrison, J. A. Nash, J. Constant, D. S. Hulme, J. Kirton, and E. P. Raynes, Liquid Crystals and Ordered Fluids, ed. by J. F. Johnson and R. S. Porter, Plenum Press, New York 1974, p. 617.

[5] L. Pohl, R. Eidenschink, J. Krause, and G. Weber, Phys. Letters **65 A**, 169 (1978).

[6] J. Doucet, A. M. Levelut, M. Lambert, L. Liebert, and L. Strzelecki, J. Phys. Paris **36**, C1—13 (1975).

[7] A. Bruson and T. W. Riener, J. Amer. Chem. Soc. **64**, 2850 (1942).

[8] J. Cologne and R. Vuillemet, Bull. Soc. Chim. France, **1961**, 2235.

[9] H. E. Zimmermann, T. D. Goldmann, T. K. Hirzel, and S. P. Schmidt, J. Org. Chem. **45**, 3933 (1980).

[10] W. Kraus and H.-D. Gräf, Angew. Chem. **87**, 878 (1975).