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Deuterium labelled liquid crystalline compounds

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The synthesis of 4-(2'-methylbutyl)phenyl 4'*n*-heptylbiphenyl-4-carboxylate-d_{18} (7BEF5-d_{18}) is presented. The compound is intended to be used as a means of studying the collective modes of liquid crystals by the coherent inelastic neutron scattering technique. The 4'-*n*-heptylbiphenyl-4-carboxylic acid-d_{12}, a liquid crystalline intermediate was prepared as well; its acid chloride was coupled with 4-(2'-methylbutyl)phenol-d_6 to obtain the final product. The intermediates and final products were investigated by spectroscopic methods.

1. Introduction

Many liquid crystalline phases have positional ordering. The question arises as to the collective modes (for example phonons, librons, etc.) which exist in molecular crystals. The best method to study them is the coherent, inelastic neutron scattering technique. Until now two attempts have been made. First, a molecular crystal was melted into the liquid crystalline phase [1]. In the second case the compound (7BEF5) [2] was cooled down from the isotropic phase in a magnetic field yielding an oriented sample. Unfortunately the hydrogen atoms of the molecule disturb the scattering, however, this could be avoided using deuteriated substances. We decided, therefore, to synthesize the deuteriated compound 4-(2'-methylbutyl)phenyl 4'-*n*-heptyl-biphenyl-4-carboxylate-d_{18} (7BEF5-d_{18}).

The neutron diffraction method requires a large quantity (1-5 g) of compound studied, so we had to search for a very cheap method for the synthesis of this compound.

The synthesis of the proton analogue, 4-(2'methylbutyl)phenyl 4'*n*-heptylbiphenyl-4-carboxylate (7BEF5) has been published [3]. 4-*n*-Alkyl-4'-bromobiphenyls were prepared which were cyanated and later hydrolysed to the corresponding acids. This procedure led to 4'-*n*-heptylbiphenyl-4-carboxylic acid in 10-20 per cent yield.

Another possibility was to prepare the nitro derivative of the acyl-biphenyls. After separation of the isomers the nitro group was reduced by the Huang-Minlon method. The obtained amine was converted by diazonium tetrafluoroborate to

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4′-alkyl-4-cyanobiphenyl. The overall yield was 10–17 per cent [4]; this process should also involve hydrolysis of the cyano derivative.

According to another method 4′-alkyl-4-bromobiphenyl was prepared via 4-acyl-4-bromobiphenyl; its hydrazone was decomposed by sodium *tert*-butoxide [5].

An improved method was published for the 4′-*n*-alkyl-4-cyanobiphenyls where the biphenyl was acylated and the formed ketone reduced by the Huang–Minlon method. The obtained 4-*n*-alkylbiphenyl was converted to 4-iodo-4′-*n*-alkylbiphenyl and later cyanated [6].

According to another variant the biphenyl was acylated with the appropriate alkyl carboxylic acid chloride, the ketone formed here was reduced with the Huang–Minlon procedure. The alkylbiphenyl obtained was reacted with acetic acid chloride and this acetophenone derivative was converted to alkylbiphenyl carboxylic acid by the haloform reaction with 23 per cent total yield [7].

We chose this latter procedure with some modifications for the synthesis of 4-*n*-heptylbiphenyl carboxylic acid. It allowed us to preserve the original deuterium content during the synthesis and some new positions were also deuteriated.

The other key intermediate compound was 4-(2′-methylbutyl)phenol. Its synthesis has been published [3]. Anisol was the starting material which was acylated with 2-methylbutyric acid chloride. The ketone obtained was reduced with lithium aluminium hydride in the presence of aluminium chloride; it led to the partial cleavage of the protecting group. The total cleavage of the methyl group was carried out by a longer acidic treatment. This method has been improved in our laboratory giving higher yield for the deuteriated derivative.

All the steps of the synthesis were first tested by preparation of the proton analogues. The intermediates of the synthesis were checked by infrared, nuclear magnetic resonance and mass spectroscopy.

2. Experimental

Infrared spectra were taken with a Nicolet 170 SX FT-IR spectrometer in KBr pellets. ^{1}H NMR spectra were recorded on a Varian XL-400 spectrometer at 25°C, the chemical shifts (δ) are referred to internal tetramethylsilane. ^{1}H assignments, if necessary, were performed with the aid of homonuclear spin decoupling experiments. To determine the deuterium content, in some cases mole equivalent menthol was given as internal reference. Mass spectra were taken with a KRATOS MS-25-RFA instrument with the following settings: ion accelerating voltage 4 kV, ionizing voltage 70 eV, trap current 100 μA, direct introduction, 200°C. Thin-layer chromatography was carried out on Kieselgel 60 F_{254} plates for different eluent systems given later. Melting points (uncorrected) were determined using a polarising microscope equipped with a Boetius hot stage.

2.1. *Synthesis*

Biphenyl-d_{10} (**1**): Biphenyl (10·0 g, 65 mmol) was mixed with anhydrous $AlCl_3$ (2·0 g, 15 mmol) and trifluoroacetic acid-d_1 (15 g, 130 mmol) prepared from trifluoroacetic anhydride after adding the theoretical amount of D_2O. It was allowed to stand at room temperature for two weeks or refluxed for 20 h. The trifluoroacetic acid was then distilled off and the whole procedure repeated with another 15 ml of CF_3COOD several times. Finally the CF_3COOH was distilled off, benzene (10 ml) and later DCl/D_2O (10 per cent) was then added dropwise with cooling. After separation the organic layer was dried with K_2CO_3 and evaporated. The residue was crystallized from ethanol yielding 8·4 g (84 per cent) of product. Its melting point (mp) was: 70–71°C. $C_{12}D_{10}=164$, ^1H NMR ($CDCl_3$): Menthol was used as internal standard, the amount of deuteriation was 78 per cent.

4-n-Heptanoyl-biphenyl-d$_9$ (**2**): In a nitrogen atmosphere anhydrous aluminium chloride (7·91 g, 59·25 mmol) was suspended in carbondisulphide (CS_2) (15 ml), then *n*-heptanoic acid chloride (8·96 g, 74·75 mmol) in 10 ml of CS_2 and finally **1** (8·2 g, 50·93 mmol) in 10 ml of CS_2 was added dropwise. After complete addition the reaction mixture was refluxed for 5 h. The solvent was distilled off, the resultant greenish-black complex was decomposed by addition of D_2O with vigorous stirring and external heating. The precipitate was filtered off, and washed with ethanol several times in a nitrogen atmosphere until the filtrate became neutral. Thin layer chromatography: Kieselgel 60 F_{254} plates were eluted with ethyl acetate. At R_f 0·42 a yellow spot formed after spraying with 2,4-dinitrophenylhydrazine (0·4 per cent) in HCl (36 per cent) and heating at 100°C for some minutes. $C_{19}D_9H_{13}O=275$, 11·64 g (82·56 per cent), mp: 86·5–87°C. IR (KBr): 2990–2800 ($\nu C_{Al}H$), 2260 ($\nu C_{Ar}D$), 1675 ($\nu C{=}O$), 1575 ($\nu C_{Ar}C_{Ar}$), 1290 cm^{-1} ($\nu C_{Ar}–\underset{\cdot\cdot}{C}–C_{Al}$). ν, stretching vibration: C_{Ar}, aromatic carbon atom, C_{Al}, aliphatic carbon atom; D, deuterium, $\nu C_{Ar}C_{Ar}$, aromatic sceletal vibration, $–\underset{\cdot\cdot}{C}–$, carbonyl carbon atom; γ, out of plane deformation vibration. ^1H NMR ($CDCl_3$): 0·9(3 H, t), 1·3–1·8(8 H, m), 2·98 ppm 2 H, m). MS *m/z*: 275 M, 190 M–C_6H_{13} detectable, deuterium content did not change during the reaction (79 per cent).

4-n-Heptanoyl-biphenyl-d$_{11}$ (**3**): **2** (10·0 g, 36·36 mmol) was mixed with CF_3COOD (15 g, 130·4 mmol) and allowed to stand for 4 weeks at room temperature or refluxed for 40 h. After evaporation of trifluoroacetic acid the residue was treated with D_2O, filtered off and washed until it became neutral. 9·8 g (98 per cent), mp: 85–86°C. $C_{19}D_{11}H_{11}O{=}227$. IR (KBr): 2990–2800 ($\nu C_{Al}H$), 2260 ($\nu C_{Ar}D$), 2120 ($\nu C_{Al}D$), 1670 ($\nu C{=}O$), 1575 ($\nu C_{Ar}A_{Ar}$), 1275 cm^{-1} ($\nu C_{Ar}–\underset{\cdot\cdot}{C}–C_{Al}$). ^1H NMR ($CDCl_3$): 0·9(3 H, t), 1·3–1·8(8 H,m), 2·98 ppm (0·5 H,m). MS *m/z*: 277 M, detectable. As established from the isotopic profile of the molecular ion and M–[CO–C_6D_4–C_6D_5] fragment ion, a 98 per cent exchange reaction took place at the –CH_2 group neighbouring the –C=O group.

4-n-Heptyl-biphenyl-d$_{13}$ (**4**): A solution of anhydrous aluminium trichloride (24·8 g, 185 mmol) in super dry ether (50 ml) was added dropwise to a mixture of lithium aluminium deuteride (3·33 g, 79·40 mmol) and super dry ether (60 ml) in a nitrogen atmosphere. A solution of **3** in carbon tetrachloride (150 ml) was addded with vigorous stirring and external cooling. After one hour stirring at room temperature, the mixture was refluxed for ten hours. After cooling to 0°C, 10 per cent DCl/D_2O (50 ml) was added slowly to the mixture. After separation, the organic layer was washed with D_2O (30 ml). Finally anhydrous K_2CO_3 was added in small portions. After 1 hour it was filtered off and the solvent evaporated. The residue was distilled: bp 134–6°C 0·2 mmHg. 5·86 g (67·5 per cent). On standing at room temperature it became crystalline. mp: 26·5–27°C. $C_{19}D_{13}H_{11}=265$. IR (KBr): 2990–2800 ($\nu C_{Al}H$), 2260 ($\nu C_{Ar}D$), 2188, 2095 ($\nu C_{Al}D$), 1575 cm^{-1} ($\nu C_{Ar}C_{Ar}$). ^1H NMR ($CDCl_3$): 0·89(3 H,t), 1·25–1·40(8 H,m) 1·62 ppm (0·5 H,m) MS *m/z*: 265 M, detectable. The isotopic profile of the molecular ion and the M–[CD_2–C_6D_4–C_6D_5] fragment ion indicated that the overall amount of deuteriation was 85 per cent.

4-n-Heptyl-4′-acetylbiphenyl-d$_{12}$ (**5**): Aluminium chloride (5·6 g, 42·3 mmol) was dissolved in 1,1-dichloroethane (25 ml) cooled to 0°C and acetyl chloride (2·4 g, 21·32 mmol) and then **4** (5·65 g, 21·32 mmol) were added dropwise to the mixture. It was left to warm up to room temperature and to stand for 12 h. The reaction mixture was cooled to 0°C and 30 ml of DCl/D_2O (10 per cent) was added dropwise. After stirring for 1 hour the greenish brown complex turned into a yellow solution. The layers were separated, washed consecutively with D_2O, 2 per cent $NaOH/D_2O$ and again with D_2O. The organic layer was dried with anhydrous $MgSO_4$ and evaporated. The residue was crystallized from ethanol. 4·7 g, (71·8 per cent) mp: 86–86·5°C. $C_{21}D_{12}H_{14}O$=306. IR (KBr): 2990–2800 ($\nu C_{Al}H$), 2280, 2250 ($\nu C_{Ar}D$), 2180, 2080 ($\nu C_{Al}D$), 1675 ($\nu C{=}O$), 1575 ($\nu C_{Ar}C_{Ar}$), 1265 cm^{-1} ($\nu C_{Ar}\text{–}\underset{..}{C}\text{–}C_{Al}$). ^1H NMR ($CDCl_3$): 0·89(3 H, t), 1·25–1·40(8 H, m), 1·62(0·5 H, m), 2·64 ppm (3 H,s). MS *m*/*z*: 306 M detectable, amount of deuteriation is 80·8 per cent.

4'-n-Heptylbiphenyl-4-carboxylic acid-d_{12} (**6**): 12·53 g of sodium was dissolved in 160 g of heavy water and chlorine gas was introduced at 0°C. This mixture was used for the oxidation of **5** (3·9 g, 12·74 mmol) according to the method described in [7]. 3·3 g (85 per cent). Phase sequence of this liquid crystal is on cooling: I 262°C N 240°C S_C 156°C C. $C_{20}D_{12}H_{12}O_2 = 308$. IR (KBr): 3200–2000 ($\nu OH$), 2990–2800 ($\nu C_{Al}H$), 2260, 2245 ($\nu C_{Ar}D$), 2185, 2090 ($\nu C_{Al}D$), 1675 ($\nu C{=}O$), 1580 ($\nu C_{Ar}C_{Ar}$), 1290 ($\nu C_{Ar}\underset{..}{C}\text{–}O$), 950 cm^{-1} (γOH). ^1H NMR ($CDCl_3$): 0·9(3 H,t), 1·25–1·40(8 H,m) 1·62 ppm(0·5 H,m). MS: The amount of deuteriation was proved to be unchanged compared with **5**.

4'-n-Heptylbiphenyl-4-carboxylic acid chloride-d_{12} (**7**): 3·3 g (10·70 mmol) **6** was mixed with 8 g of $SOCl_2$ and reacted with standard methods. The obtained **7** was used without purification.

Anisole-d_5 (**9**): Phenol-d_6 (**8**) (7·15 g, 76·0 mmol), methyl iodide (11·48 g, 80·94 mmol) and potassium carbonate (12·44 g, 90·95 mmol) were refluxed in dry acetone for 36 h. 30 ml of water were added and the mixture extracted with petroleum ether (3 × 30 ml), the organic layer was extracted with Claisen alkali (3·5 g of KOH, 2·5 g of water, 10 ml of methyl alcohol), saturated sodium chloride solution (2 × 20 ml), dried with magnesium sulphate and distilled. Boiling point (bp): 150°C at normal pressure. 7·25 g (88 per cent). $C_7D_5H_3O = 103$.

4-(2'-Methylbutyl)anisole-d_6 (**10**): Aluminium trichloride (11·05 g, 82 mmol) was dissolved in 50 ml of dry petroleum ether (bp: 40–70°C) and 2-methylbutyric acid chloride (8·0 g, 66·4 mmol) in petroleum ether (50 ml) was added slowly at 0°C with vigorous stirring and finally a petroleum ether solution of **9** (7·0 g, 64·5 mmol) was also added. After 6 h stirring at room temperature the solvent was distilled off and super dry diethyl ether (100 ml) was added. The mixture was cooled to 0°C and lithium aluminium deuteride (4·2 g, 100 mmol) was added in small portions. After 6 h stirring 16 ml of a concentrated solution of magnesium sulphate in D_2O was added dropwise at 0°C. After filtration in a nitrogen atmosphere, the residue was washed with ether several times. The filtrate was evaporated and distilled. The reaction was followed by TLC on Kieselgel 60 F_{254} plates eluted with benzene, R_f 0·55 (**10**). Bp: 63°C/0·1 mmHg, 7 g (47·82 per cent). $C_{12}D_6H_{12}O = 184$. IR (KBr): 2835 ($\nu[CH_3\text{–}(O)]$), 2275m 2250 ($\nu C_{Ar}D$), 2180, 2135, 2095 ($\nu C_{Al}D$), 1590 ($\nu C_{Ar}C_{Ar}$), 1232 cm^{-1} ($\nu C_{Ar}\text{–}O\text{–}C_{Al}$). ^1H NMR ($CDCl_3$): 0·83(3 H, d), 0·9(3 H, t), 1·19, 1·42(2 H,m) 1·66(1 H,m), 3·78 ppm (3 H,s).

4-(2'-Methylbutyl)phenol–d_7 (**11**): **10** (5·3 g, 29·3 mmol) was added to a mixture of acetic acid anhydride (39 g), heavy water (5 g) and deuterium bromide in heavy water (47 per cent, 25 ml). This mixture was refluxed. The reaction was followed by TLC on Kieselgel 60 F_{254} plates eluted with benzene, R_f 0·34 (**11**). After the reaction was completed, the acids were distilled off. The residue was dissolved in benzene and sodium hydrocarbonate was added slowly. After one hour it was filtered off, the solvent was evaporated and the oil was distilled. Bp: 80°C/0·15 mmHg. 3·1 g, (63·2 per cent). $C_{11}D_7H_9O = 171$.

4-(2′-Methylbutyl)phenyl-4′-n-heptylbiphenyl carboxylate-d_{18} (7BEF5-d_{18}): In dry benzene solution (15 ml) **7** (2·06 g, 6·31 mmol) was reacted with **11** (1·07 g, 6·31 mmol) in the presence of pyridine (2·25 ml) at room temperature. The reaction was followed by TLC. D_2O was added after the reaction proceeded. The organic layer was extracted with DCl/D_2O (2 per cent), $NaHCO_3$ (5 per cent) in D_2O, and D_2O, dried on magnesium sulphate and the solvent was removed. The crude product was purified by flash chromatography on Kieselgel 60 (0·063–0·02 mm) (200 g) and the column eluted with chloroform : petroleum ether 1 : 1. Fractions of 20 ml each were collected. The column chromatography was followed by TLC using the same solvent. The fractions containing the compound with R_f 0·88 were evaporated and the residue was crystallized from ethanol. 1·6 g (55·1 per cent). The phase sequence of this liquid crystal is on cooling: I 147·2°C N 137°C S_A 67°C S_B 57°C S_G 40°C C. $C_{31}D_{18}H_{20}O_2 = 460$. IR (KBr): 2260 ($\nu C_{Ar}D$), 2190, 2135, 2090 ($\nu C_{Al}D$), 1730 ($\nu C{=}O$), 1588 ($\nu C_{Ar}C_{Ar}$), 1265 cm^{-1} ($\nu C_{Ar}{-}C{-}O$). ^1H NMR ($CDCl_3$): 0·87(3 H, d), 0·89(3 H, t), 0·92(3 H, t), 1·19, 1·42 (2 H, m) 1·25–1·36(8 H, m) 1·63(0·5 H, m), 1·64 ppm(1 H, m). MS *m*/*z*: 460 M, 373 M–$C_6D_2H_{11}$ detectable, the deuterium content of the molecular ion was 81·5 per cent.

4-(2′-Methylbutyl)phenyl-4′-n-heptylbiphenyl carboxylate (7BEF5): IR (KBr): 3065, 3045, 3030 ($\nu C_{Ar}H$), 2990–2800 ($\nu C_{Al}H$), 1730 ($\nu C{=}O$), 1605 ($\nu C_{Ar}C_{Al}$) 1270 cm^{-1} ($\nu C_{Ar}{-}\underset{..}{C}{-}O$). MS *m*/*z*: 442 M, 357 M-C_6H_{13}.

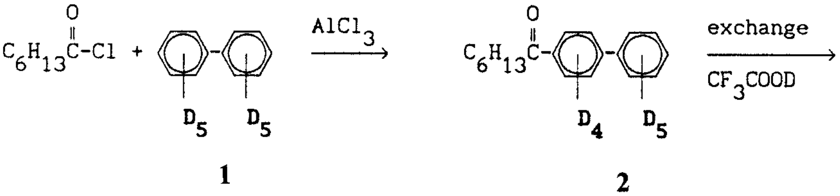
3. Results and discussion

The best procedure for the synthesis of 7BEF5-d_{18} is illustrated in figure 1. Biphenyl-d_{10} (**1**) was acylated by the Friedel–Crafts method with 4-*n*-heptanoic acid chloride leading to 4-*n*-heptanoyl-biphenyl-d_9 (**2**).

In preliminary experiments the exchange reactions were studied. Hydrogen atoms in the methylene groups in the neighbourhood of the carbonyl group are loosened. These hydrogens can easily be exchanged by deuterium atoms. This exchange reaction (see figure 2) was carried out with trifluoroacetic acid-d_1 in 4-*n*-heptanoyl-biphenyl. According to mass spectral data two deuterium atoms were incorporated.

Reducing this compound by the Huang–Minlon method (see figure 2), all the incorporated deuterium atoms were lost from the molecule. Although the proton-deuterium exchange is very slow in alkaline conditions, an exchange reaction took place in the undesirable direction probably due to the long heat treatment in a proton rich media. These results turned our attention to lithium aluminium deuteride ($LiAlD_4$) which allows further deuteriation on the carbon atom close to the core and preserves the deuterium atoms already present in **3**.

The aromatic carboxylic acid chlorides can be prepared in one step [8] by the Friedel–Crafts method using oxalyl chloride as the acylating agent. We have studied this method comparing it with a longer, three step synthetic route as depicted in figure 1. The one step method led to several by-products which were difficult to remove. The obtained 7BEF5 needed a more effective cleaning procedure giving a low yield. Therefore we followed the three step method for the preparation of 7BEF5-d_{18}.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D5
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2
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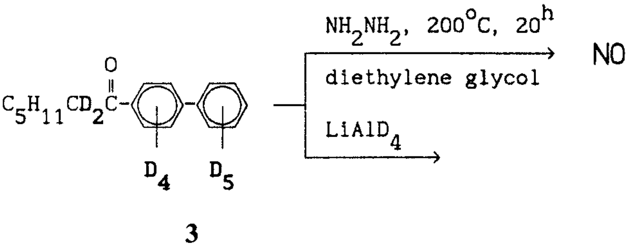
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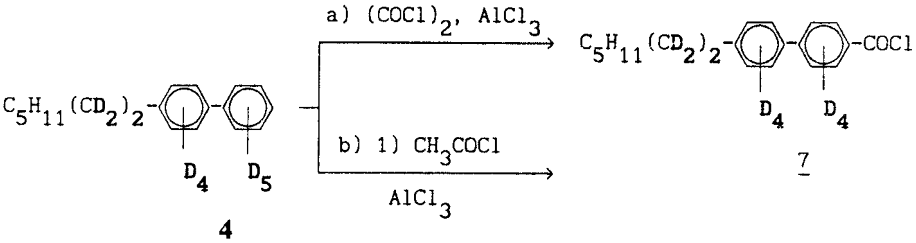
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D4
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D4
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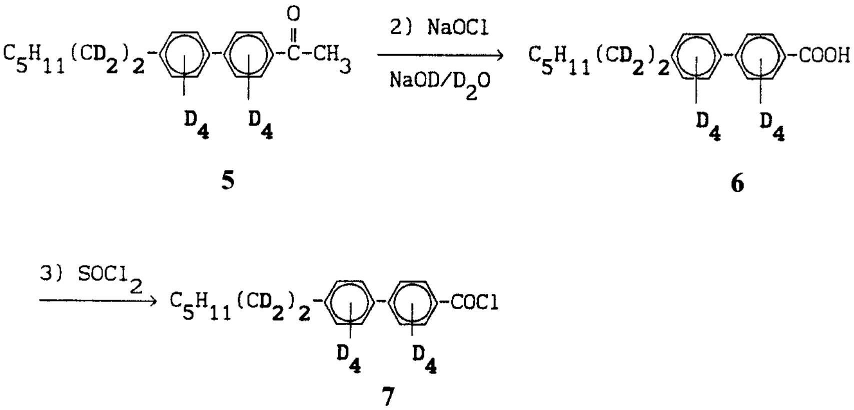
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D4
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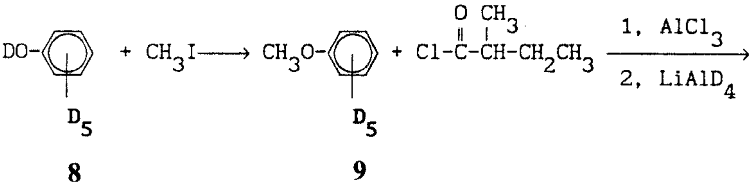
D4
7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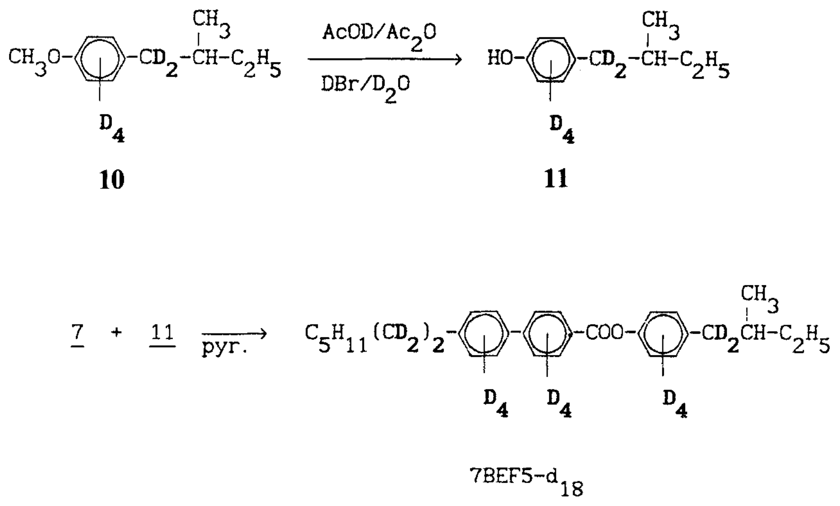

10 **11**

7BEF5-d18

Figure 1. Scheme of the synthesis of 7BEF5-d_{18}.

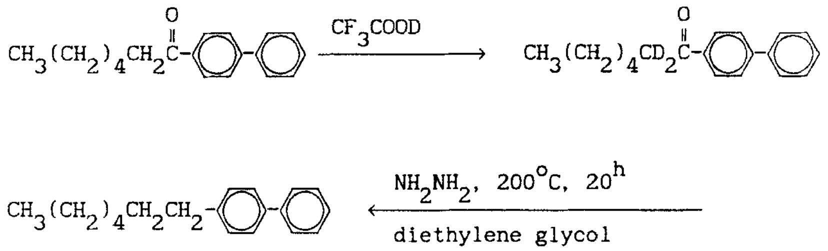

Figure 2. Investigation of the exchange reaction and reduction.

The method for the preparation of 4-(2'methylbutyl)anisole given in [3] has been improved. We did not isolate the ketone formed in the acylation process between anisole and 2-methylbutyric acid chloride. After changing the solvent LiAlD$_4$ was added to the reaction mixture and the resulting **10** was isolated.

Another problem was the protection of the phenolic OH group. If benzyl is the protecting group its catalytic cleavage would need deuterium gas. The protection of the phenolic OH group by its methyl ether derivative is another possibility. The question arises: do we have to use CD$_3$I or can we preserve the deuterium atoms on the benzene ring if we use CH$_3$I? Furthermore does CH$_3$ dilute the deuterium content of **11** by undesirable exchanges? Since the deuteriated variant is very expensive we have used CH$_3$I. The cleavage of the methyl ether needed strong acidic media and no undesirable exchange was observed on the benzene ring during the preparation of **8–11**.

The compounds were investigated by spectroscopic methods. In the IR spectra of the intermediates it is remarkable, that the aromatic sceletal vibrational bands of the deuteriated species were shifted from about 1600 cm^{-1} (proton analogues) to 1590–1575 cm^{-1}, as a consequence of the increased mass.

The ^{1}H NMR (400 MHz) spectra of the protonated and deuteriated compounds were compared. The starting biphenyl and phenol were deuteriated in 78 per cent and 95 per cent, respectively. The amount of deuteriation of the benzene rings in the final product is also around this value. According to the spectral data, a remarkable loss of the deuterium content did not occur during the synthesis. The proton signals in the NMR spectrum of 7BEF5 at 2·65, 1·63 and 2·64 ppm disappeared totally from the spectra of 7BEF5-d_{18} confirming the $\sim$ 99 per cent deuteriation rate at the postions α, β and γ, respectively (see figure 3), in the alkyl chains.

The mass spectra of 7BEF5 and 7BEF5-d_{18} were compared also. Deuterium content calculations were based on the comparison of the isotopic patterns of the molecular ions and some of the characteristic ions of the labelled and unlabelled intermediates and final products where no scrambling of the proton and deuterium atoms were detected. The main fragmentation routes of the deuteriated and protonated 7BEF5-d_{18} and 7BEF5 are given in figures 3 and 4, respectively. The overall deuterium content of the molecular ion of 7BEF5-d_{18} was 81·5 per cent. The same value was found for the 4-*n*-heptyl-biphenyl-4′-carbonyl-d_{12} moiety; this means

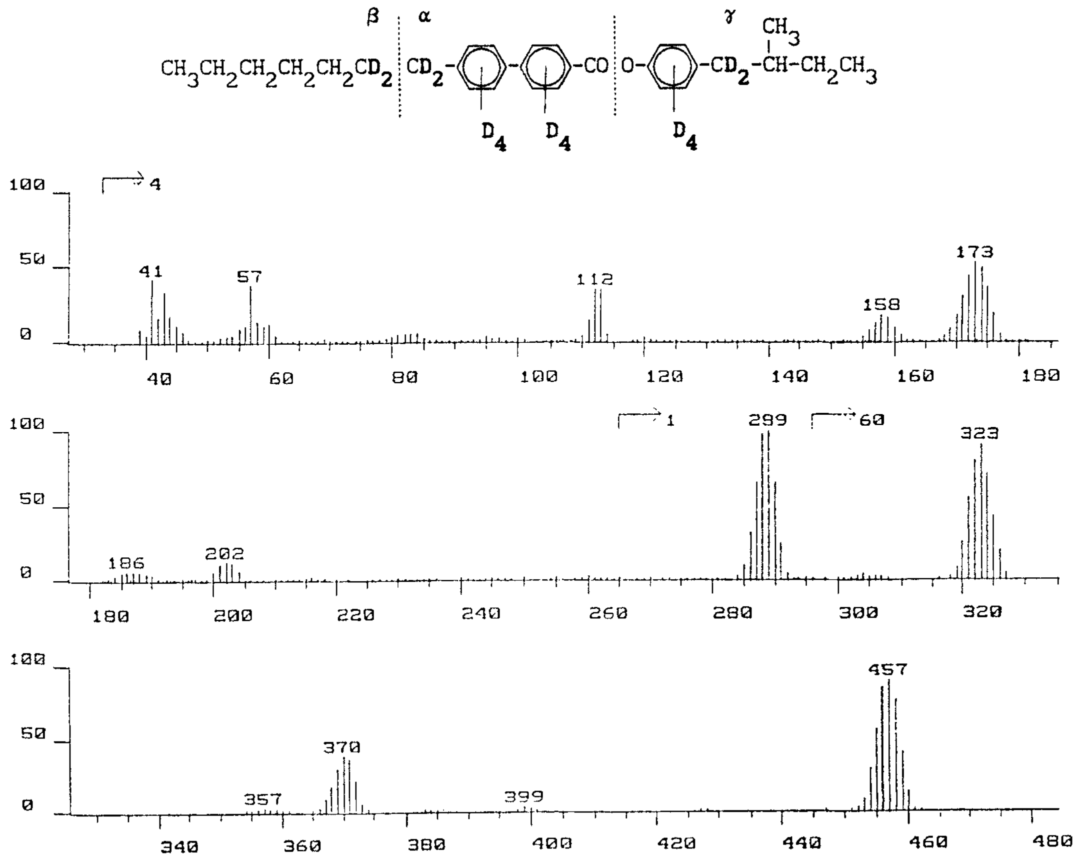

Figure 3. Mass spectrum and main fragmentations of 7BEF5-d_{18}.

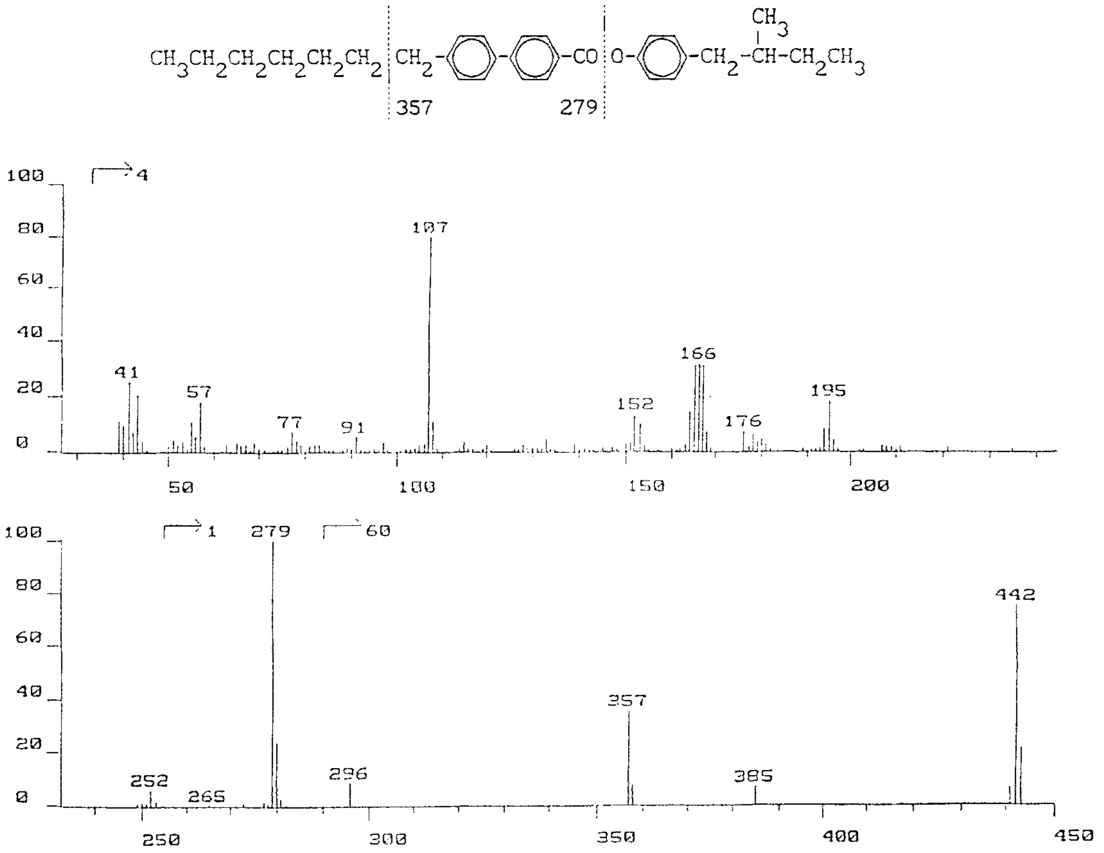

Figure 4. Mass spectrum and main fragmentations of 7BEF5.

no considerable loss of the original deuterium content on the benzene rings occurred during the synthetic steps.

The procedure described above allows the synthesis of a liquid crystalline compound which is labelled by deuterium atoms on the core system and on the carbon atoms of the alkyl chains near to the core. The neutron scattering measurements are under preparation.

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