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Specifically deuteriated intermediates for the synthesis of liquid crystals and liquid-crystalline polymers

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Invited Article

Specifically deuteriated intermediates for the synthesis of liquid crystals and liquid-crystalline polymers

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The recent developments in solid state N.M.R. techniques have rendered deuterium a most attractive nucleus for use in the study of liquid crystals and other ordered systems. Its application often requires that the deuterium be positioned at specific sites in the molecule. Here, the preparation of such specifically labelled compounds for use in liquid crystal research is discussed. It is shown that many deuteriated liquid crystals can be prepared from a limited set of labelled intermediates. Strategies for the labelling of such intermediates in both aromatic and aliphatic sites based on experience gained in the author's laboratory during the last years are discussed. In the experimental section more than fifty procedures for obtaining specifically deuteriated intermediates and mesogens are described in detail.

1. Introduction

Deuterium N.M.R. of labelled liquid crystals has proved to be a most powerful tool for the investigation and characterization of their mesomorphic properties [1–3]. Analysis of the deuterium spectra can provide detailed information on the structure, symmetry and domain distribution of the mesophase, as well as on the molecular ordering within the mesophase and the conformation and dynamics of the mesogenic molecules. The complete characterization of such systems usually necessitates the recording of deuterium spectra of several deuteriated species, each specifically labelled in different sites of the molecule. Thus, spectra from the aromatic deuterons provide information concerning the rigid part of the molecule while signals from aliphatic deuterons reflect the conformational equilibria of the flexible chains. In addition, dynamic parameters for different parts of the mesogenic molecules can often be derived from the N.M.R. lineshape [4] or relaxation rates [5]. These properties in thermotropic, lyotropic and polymeric liquid crystals have been extensively investigated in recent years by several research groups [6–24]. Interesting details on molecular dynamics in mesogenic systems may also be obtained from inelastic and elastic coherent neutron scattering experiments [25]. In order to eliminate the incoherent proton scattering partially or fully deuteriated liquid crystals may be required.

Here, I shall describe some new methods developed in our laboratory for the preparation of specifically deuteriated mesogens, including a variety of thermotropic, lyotropic and polymeric liquid crystals. There are various ways to present the subject; for example the syntheses can be presented according to the chemical structure of the mesogens, the synthetic procedures, or the class of liquid-crystalline mesophases.

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I have chosen an intermediate classification, based on common chemical building blocks of mesogenic molecules. Most thermotropic liquid crystals consist of aromatic cores to which flexible aliphatic chains are linked. In calamitic liquid crystals these cores usually consist of benzoic acid, biphenyl, terphenyl, azobenzene or azoxybenzene [26] units, while in discotics [27] they include benzene, triphenylene, truxene as well as anthraquinone and other moieties. More recently calamitic and discotic mesogens were also prepared with cycloaliphatic rather than aromatic cores [28, 29]. The more common lyotropic systems such as soaps, detergents, alcohols and phospholipids consist of aliphatic chains, although some less common lyotropic mesogens consist of aromatic cores to which polar side groups are attached. Examples of the latter include derivatives of chromone [30], flufenamic acid [31] and discotic-like molecules [32].

The chemical structure of many of these mesogenic compounds can be divided into a limited number of aromatic and aliphatic chemical building blocks from which the mesogenic molecules may be synthesized. I have therefore chosen to introduce the subject by reviewing procedures for specific labelling of such building blocks which serve as intermediates for the preparation of the desired liquid crystals. Clearly, the most suitable intermediate in terms of isotopic efficiency, economy in isotopic source and preparative procedure is chosen for deuteriation. Another important consideration concerns the possibility of back exchange during reaction steps which follow the deuteriation. Clearly the same conditions which allow deuteriation will also allow back exchange. Therefore, special care should be taken in any step where strong acids, strong bases or high temperatures are involved. In general there are two main procedures for deuterium labelling, namely, exchange and reduction. The combination of the intermediates into the final mesogenic product is then achieved by well-known synthetic routes which are described in the original literature concerning the synthesis of the mesogen.

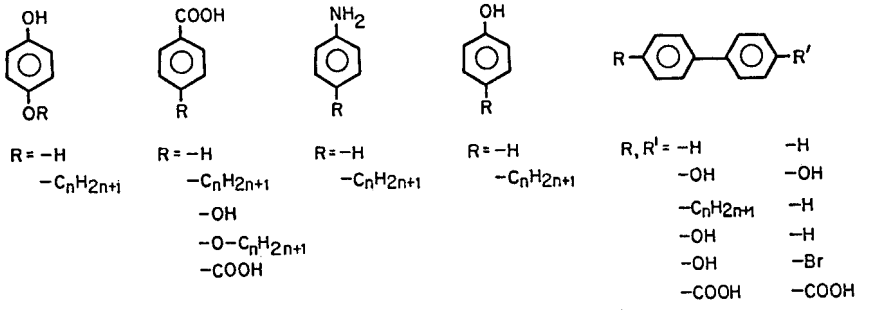
Therefore, the structure of the article is that in §2 aromatic intermediates and procedures for their specific deuteriation are discussed. These intermediates are most commonly deuteriated by exchange, using homogeneous acid catalysis either via mild refluxing, or under harsher high temperature—high pressure conditions. Heterogeneous catalysis with platinum as catalyst, as well as a number of alternative strategies for labelling various aromatic intermediates are also discussed. Section 3 contains an analogous discussion for labelling aliphatic building blocks. This includes procedures for perdeuteriation of fatty acids by catalytic exchange, as well as various routes for specific labelling either by exchange with D_2O of acidic hydrogens, or using a variety of chain extension techniques. Examples will be presented including, in particular, the specific labelling of various sites in aliphatic chains.

Finally, in §5 details of over fifty experimental procedures, the majority of which are the key reaction steps of §§2 and 3, are given for the benefit of those readers interested in the more practical aspect of the preparative work. The procedures described in the experimental section are referred to by (exp. No.) in §§2 and 3. These procedures are based on the experience accumulated in our laboratory over several years, during which literally hundreds of deuteriated liquid-crystalline compounds, including polymeric liquid crystals, have been prepared. Many of these procedures are presented for the first time. Some of them replace more cumbersome and less efficient procedures published earlier.

Before proceeding it is appropriate to mention certain relevant references in which details on deuteriation procedures have been reported. They include Neubert [33], and Boden, Bushby and Clark [34]. A treasure of valuable reactions concerning deuteriation of 4-alkyl-4′-cyanobiphenyls can be found in papers by Gray, Emsley, Luckhurst, Boden, Beckmann and co-workers [35–39]. The specific labelling of chains in lyotropic liquid crystals is described in several papers by Griffin, Seelig, Reeves, Charvolin and co-workers [40–43, 19]. The specific deuteriation of a variety of thermotropic and lyotropic liquid crystals performed in the author's laboratory have also been reported [44–56].

2. Aromatic building blocks

The common aromatic intermediates in the synthesis of low molar mass liquid crystals and polymeric liquid crystals are phenol, benzoic acid, benzaldehyde, aniline, biphenyl, and their parasubstituted alkyl, alkoxy- or hydroxy derivatives, as well as terephthalic acid;

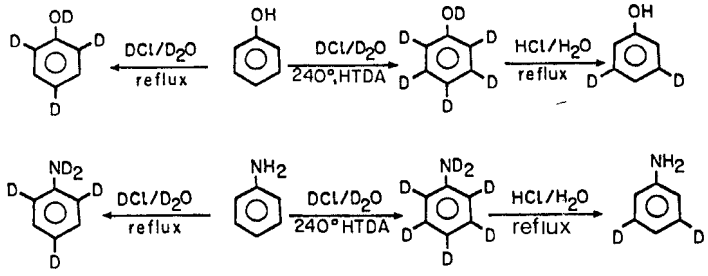


These intermediates serve as precursors in the preparation of many liquid crystalline mesogens, for example; *n*-alkoxy-benzylidene-*p*-*n*-alkyl-anilines (no.m) [7], *p,p′*-disubstituted azo- and azoxybenzenes [34], *p,p′*-disubstituted phenylbenzoates [26], terephthalidene-bis-4-alkylanilines [1], phenyl-4-benzoyloxybenzoate derivatives [26], 4-*n*-alkyl-and 4-*n*-alkoxy-4′-cyanobiphenyls [36] and also, in many main-chain and side-chain polymeric liquid crystals [57].

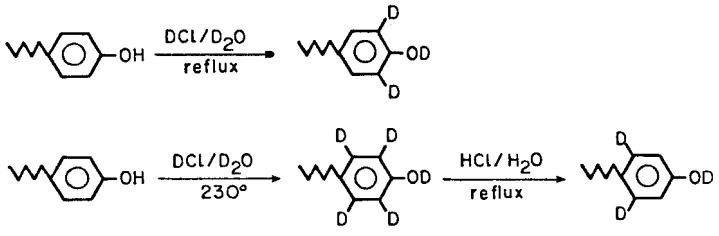
2.1. *Phenol, aniline and their para-substituted derivatives*

Unsubstituted aniline and phenol can be specifically labelled in the ortho and para-positions by acid catalyzed exchange under reflux in dilute DCl/D_2O. If the reaction is performed at high temperatures (230–250°C) in dilute acid under pressure (HTDA) the meta positions will also undergo exchange [58, 59]. Both reactions are efficient, fast, selective for the aromatic hydrogens and give very good chemical and isotopic yields. The HTDA reaction must be performed in an acid resistant high pressure vessel, for example, a tantalum or a glass lined Parr Hastelloy B container. Depending on the size of the pressure bomb, the procedure can readily be scaled up to 50 grams, or more, of the substrate. The combination of the mild reflux procedure with the HTDA method and making use of the possibility to back-exchange the deuterons with HCl/H_2O, means that a variety of isotropic species either perdeuteriated

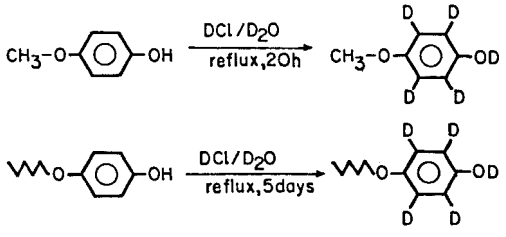
(exp. 1.3) or specifically labelled can be obtained. For example,



In para-substituted phenol and aniline the response to exchange will depend on the nature of the substituent. On reflux in DCl/D_2O 4-alkylphenols and 4-alkyl-anilines undergo exchange in the ortho positions and become perdeuterated in the aromatic positions under HTDA treatment. Thus, including back exchange with HCl/H_2O the three types of isotopomers, ortho, meta and complete aromatic deuteriation, can be prepared. For example, the preparation schemes for the various aromatic isotopomers of 4-*n*-pentylphenol (exp. 1.1, 1.2) are given;

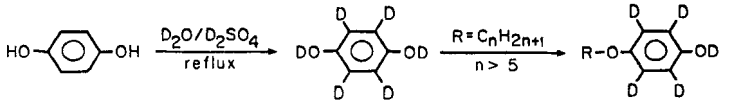


4-alkoxyphenols will undergo perdeuteriation in the aromatic sites by refluxing in DCl/D_2O. The exchange rate in the meta position decreases significantly, however, as the alkoxy-chain is increased in size. Thus, perdeuteriation to 96 at. per cent of the aromatic sites in 4-methoxyphenol takes some 20 hours, while for 4-pentyloxyphenol it requires approximately 5 days (exp. 1.8);

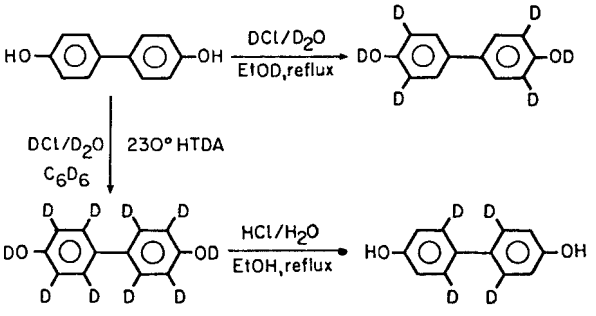


Deuteriation of 4-alkoxyphenols with more than five carbon atoms in the aliphatic chains is therefore preferably achieved by the monoalkylation of perdeuteriated hydroquinone. The latter can be prepared by exchange either with a base or under acidic conditions. On a preparative scale, hydroquinone (*p*-hydroxyphenol) is best deuteriated by reflux in D_2O containing catalytic amounts of D_2SO_4 (exp. 1.9) [62]. A precise description of the monoalkylation of hydroquinone is given by Keller and Liebert [33 (*a*)]. In order to avoid unwanted back exchange of the aromatic deuterons (in the case of perdeutero-hydroquinone) the reagents and solvents used in the alkylation have to be deuteriated (CH_3CH_2OD, D_2O, KOD). It should be noted

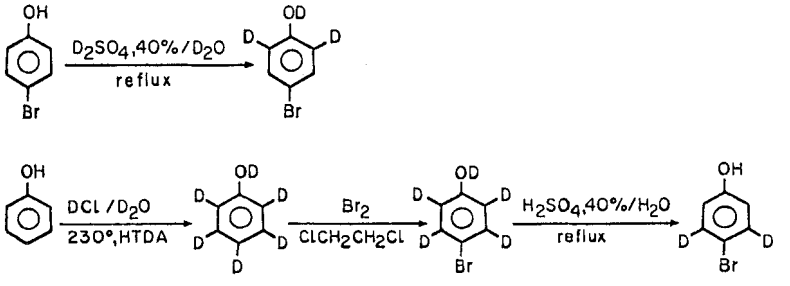
that the HTDA method of labelling 4-alkoxy-aromatic derivatives fails because of cleavage of the ether bond.



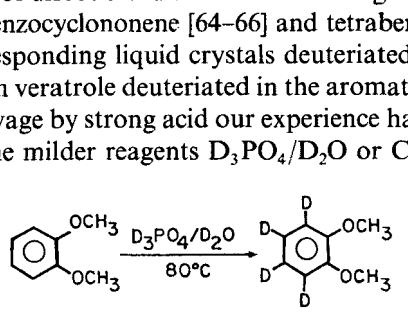
A common intermediate for many liquid crystalline monomers and polymers is 4,4′-biphenol (4,4′-dihydroxybiphenyl) [26, 57, 60]. It can also be deuteriated ortho to the hydroxy-groups by refluxing in DCl/D_2O (exp. 1.12). To increase the solubility of the reactant, EtOD is added until the 4,4′-biphenol is dissolved. Complete exchange of all the aromatic hydrogens can be realized using the HTDA-procedure with added benzene-d_6 to increase the biphenol solubility (exp. 1.11). Back exchange of the perdeuteriated 4,4′-biphenol results in 2,6,2′,6′-d_4-4,4′-biphenol (exp. 1.13);



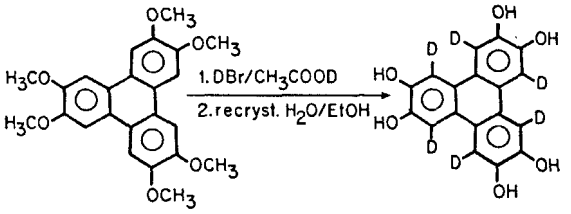
Another acid catalysed reaction which was successfully applied to prepare 4-bromophenol-2,6-d_2, involves D_2SO_4/D_2O [33]. To obtain the meta labelled *p*-bromophenol we start with the perdeuterated phenol, prepared by the HTDA method (exp. 1.3), followed by bromination [61] (exp. 1.4) and back exchange;



Ortho-dihydroxy benzene and its dimethylether (veratrole) are essential intermediates in the synthesis of discotic and discotic-like mesogens such as the derivatives of triphenylene [63], tribenzocyclononene [64–66] and tetrabenzocyclododecatetraenes [67]. To obtain the corresponding liquid crystals deuteriated in the aromatic sites it is convenient to start with veratrole deuteriated in the aromatic sites (exp. 1.20). Since ethers are subject to cleavage by strong acid our experience has been that deuteriation can be achieved using the milder reagents D_3PO_4/D_2O or CF_3COOD;



In certain cases, aromatic deuteriation can be achieved by hydrolysis under strong acidic conditions. For example, hexamethoxytriphenylene demethylated by DBr/CH_3COOD under reflux produces hexahydroxytriphenylene deuteriated in the unsubstituted aromatic sites [44];



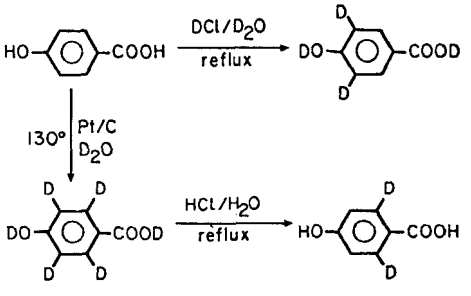
The same product can also be obtained by refluxing the hexamethoxy-derivative in CF_3COOD followed by cleaving the ether bonds with BBr_3 [68].

We end this section with two short comments. One is that the HTDA-method is not suitable for halogenated phenols, anilines or aromatic acids. Our experience showed either inefficient exchange or decomposition. The second is a warning against treating fluorinated compounds with HTDA, since under these conditions small amounts of HF which may be formed will destroy tantalum high pressure vessels.

2.2. *Benzoic acid and its para-substituted derivatives*

As indicated previously *p*-substituted benzoic acids and benzaldehydes are frequently used as precursors in the synthesis of liquid crystals. However, since aldehydes are usually obtained (exp. 1.19, 1.27, 1.28) by reduction of the acid and subsequent oxidation of the corresponding alcohol, we limit the discussion to benzoic acid and *p*-substituted derivatives. Unsubstituted benzoic acid cannot be labelled by DCl/D_2O under reflux, but will undergo perdeuteriation by HTDA [58, 59]. Specific labelling can, however, be achieved by dehalogenation of the corresponding halogenated benzoic acids [72]. A special procedure was recently published for the specific labelling of benzoic acid in the ortho-positions using rhodium-chloride as a catalyst [69].

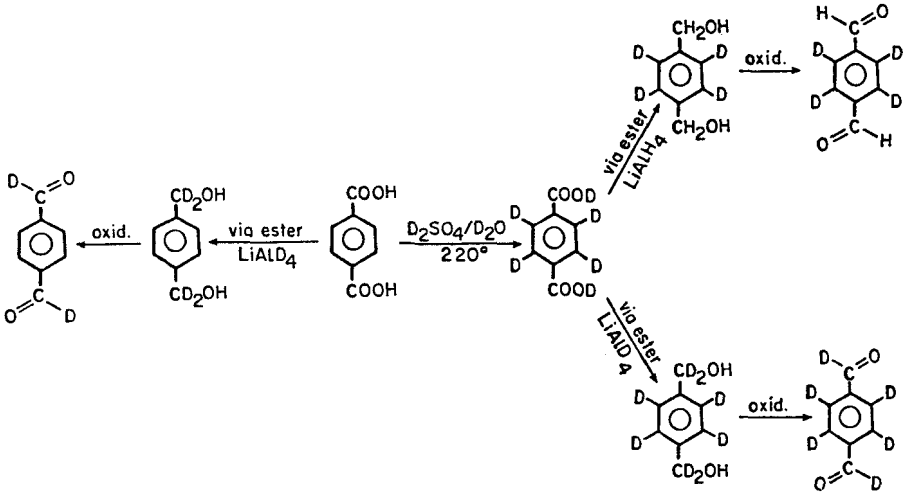
Para-hydroxybenzoic acid is an important intermediate in the preparation of monomeric and polymeric liquid crystals [26, 70]. Specific labelling in the meta position is preferably obtained by reflux with DCl/D_2O (exp. 1.22). We found that perdeuteriation can be accomplished by 10 per cent Pt on carbon (Pt/C) as catalyst using D_2O as the deuterium source (exp. 1.20). Specific ortho-deuteriation can be achieved by back exchange with HCl/H_2O (exp. 1.21);



The heterogeneous catalyst, Pt/C with D_2O, has proved useful in perdeuteriation of both aromatic and aliphatic compounds. In the experimental section, examples are

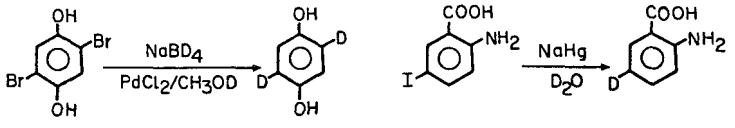
given for liquid crystal intermediates such as biphenyl (exp. 2.9) or 4-*n*-pentylbiphenyl (exp. 2.10). For aromatic acids, when performed at moderate temperatures (130°C), the reaction is particularly efficient, free of side reactions and results in very high isotopic and chemical yields. We have successfully used it for perdeuteriation of *p*-toluic acid, anthranilic acid and biphenyl-4,4′-dicarboxylic acid (exp. 1.18), as well as for 2,5-dialkoxyterephthalic acid (with 1 to 14 carbon atoms in the aliphatic chains). At higher temperatures (160°C) the α-hydrogens in the alkoxy side chains of the latter compound are also exchanged [71].

Aromatic acids can also be deuteriated using D_2SO_4/D_2O, although in many cases they will undergo various degrees of sulphonation. An important exception is terephthalic acid (exp. 1.17) for which it is found that D_2SO_4/D_2O is an excellent deuteriation reagent at 200°C. A variety of terephthaldehyde isotopomers can be derived from the labelled acid via the terephtalic acid diester by reduction to the corresponding alcohols followed by oxidation with Pb $(CH_3COO)_4$ or concentrated nitric acid (exp. 1.19);



2.3. *Specific labelling by direct synthesis*

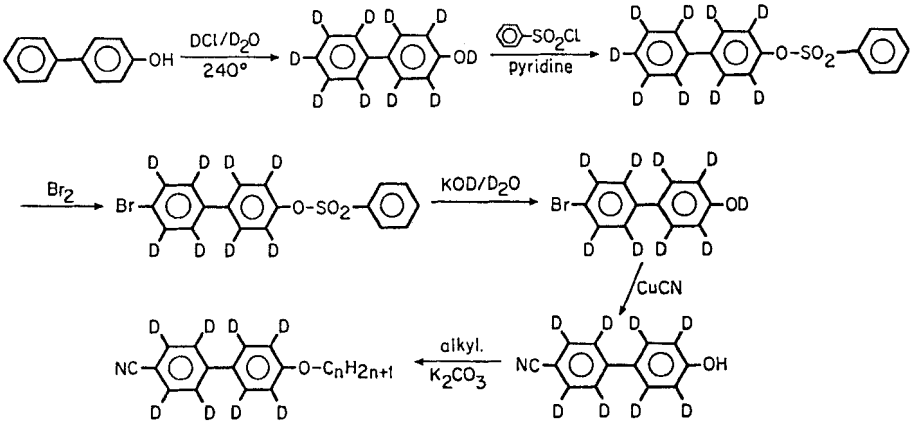
Specifically deuteriated aromatic species in which one of several equivalent hydrogens is labelled, cannot be prepared by catalytic exchange. Such intermediates must be prepared by direct synthesis, for example, by the dehalogenation of the corresponding halogen-derivatives. In certain cases where organometallic compounds, for example Grignard or lithiated derivatives, can be prepared, quenching with D_2O is recommended. An alternative method, involves exchange of a halogen compound with deuterium gas and a metal as catalyst. In this case however, one should be aware of possible scrambling side reactions. Alternatively $NaBD_4/CH_3OD$ with $PdCl_2$ as catalyst [72, 73], zinc/copper-alloy/D_2O [74] as well as sodiumamalgam 5 per cent in D_2O [51] can be used for selective reductive dehalogenation by deuterium. The dehalogenation with $NaBD_4$ was applied for 2-*d*, 3-*d*, and 4-*d*-benzoic acids [72]. Two additional examples (exp. 1.10, 1.24) are:



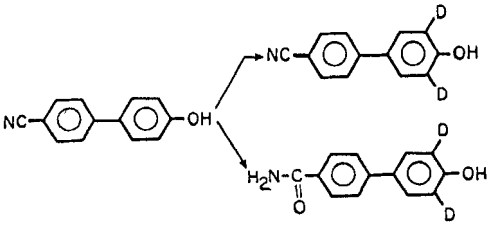
2.4. *Deuterated alkoxycyanobiphenyls*

To conclude this section describing the deuterium labelling of aromatic building blocks, I will briefly discuss in this sub-section the specific labelling of the aromatic sites in 4-alkoxy-4′-cyanobiphenyl and in the next sub-section, of the lyotropic mesogen diethylammonium flufenamate (DEAF) [51].

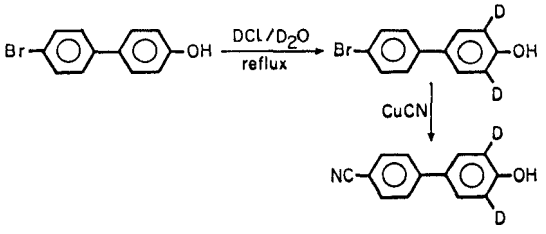
Cyanobiphenyls belong to the more extensively studied liquid-crystalline systems because of their relatively simple molecular structure and the convenient temperature ranges of their mesophases. Several deuterium N.M.R. studies of alkyl-cyanobiphenyl labelled in aliphatic and aromatic sites have been published which also contain experimental details [35–39]. On the other hand, very little work on the corresponding alkoxy compounds has been published [11, 13]. This is probably due to the fact that perdeuteriation of 4-hydroxy-4′-cyanobiphenyl cannot be achieved by exchange of the normal compound. Even 4-bromo-4′-hydroxybiphenyl will not undergo exchange in acidic solution or with Pt/C. We have to look, therefore, for another intermediate which is stable under the conditions of the hydrogen-deuterium exchange reaction. Such an intermediate was found to be 4-phenylphenol which, like phenol, will exchange all the hydrogens by HTDA (exp. 2.1). To obtain 4-hydroxy-4′-bromobiphenyl the hydroxy-group is first protected by benzenesulfonate [75] (exp. 2.2) followed by bromination with liquid bromine (exp. 2.3) and saponification with KOD in D_2O/dioxane (exp. 2.4). Cyanation and alkylation is finally performed in the usual manner [76] (exp. 2.5, 2.7, 2.8). It should be noted that deuteriated 4-hydroxy-4′-cyanobiphenyl is an intermediate for the α,ω-bis-(4.4′-cyanobiphenyloxy)-alkanes [77] and has been used in side-chain polysiloxane and polyacrylate liquid crystals as the mesogenic sub-unit [78].



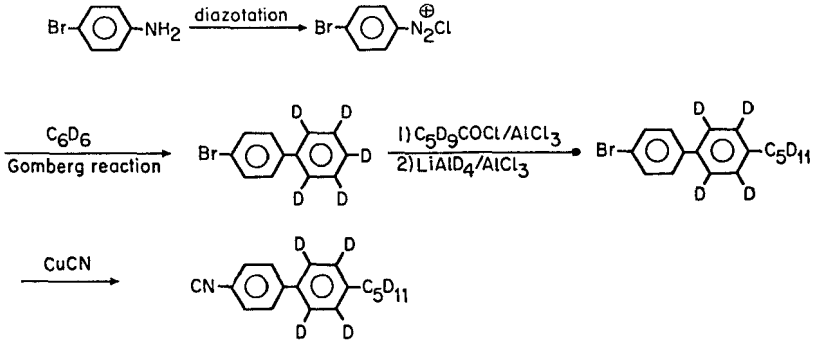
Only two reports on specifically labelled alkoxycyanobiphenyls in the aromatic rings have been published to date. They describe the preparation of 3,5-d_2-4-hydroxy-4′-cyanobiphenyl by exchange of the normal compound with CF_3COOD. However the yield was low due to side-reaction products in particular, 4-(hydroxyphenyl)-benzamide [11, 77], which is obtained by partial hydrolysis;



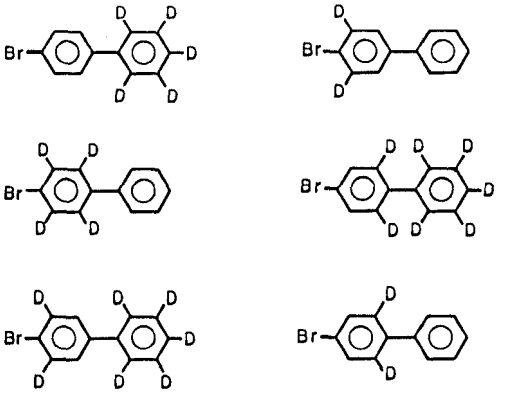
This difficulty can easily be circumvented by starting with a precursor of the 4-hydroxy-4′-cyanobiphenyl, namely 4-hydroxy-4′-bromobiphenyl, which readily exchanges ortho to the hydroxy-group using DCl/D_2O with a high yield and no side reactions (exp. equiv. to 2.6). It is finally converted to the cyano-compound by cyanation using CuCN.



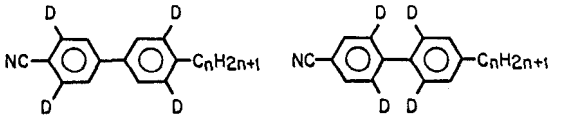
The method for the preparation of specifically labelled cyanobiphenyls, depends on whether asymmetric or symmetric substitution (with respect to the biphenyl moiety) is desired. As shown by Gray and Mosley [36, 38], asymmetrically labelled biphenyls can be prepared via 4-bromobiphenyl using the classical Gomberg-reaction. For example, to prepare 4-cyano-4′-pentyl-d_{11}-biphenyl 2′,3′,5′,6′-d_4 they started with bromoaniline and benzene-d_6 to obtain 4-bromobiphenyl in which the unsubstituted aromatic ring is deuteriated while the other is protonated. The 4′-alkyl derivative was then obtained by Friedel Crafts alkylation followed by reduction and cyanation;



This reaction scheme may be used to make other isotopomers of 4-bromobiphenyl from which many different specifically labelled alkylcyanobiphenyls can be prepared.



Symmetrically deuteriated alkylcyanobiphenyls, such as 3,3′,5,5′-d_4- or 2,2′,6,6′-d_4-, can be synthesized via the appropriate labelled biphenyls, for example,

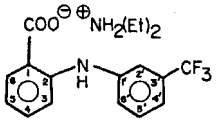


The latter compounds can be prepared in reasonable yield by coupling the Grignard-reagent of the specifically deuteriated bromobenzene (obtained from 4-bromo-aniline via the Sandmeyer-reaction) with cobaltous chloride [7]. Labelled biphenyl as well as bromobiphenyl can be transformed to *n*-alkanoylbiphenyl using aluminium chloride followed by reduction, bromination and cyanation as described earlier [36].

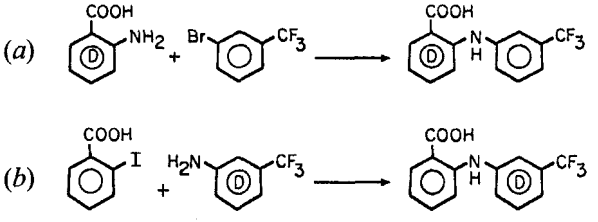
It is interesting to note that perdeuteriated 4-*n*-alkyl-4′-cyano-biphenyls can be prepared from 4-alkylbiphenyl perdeuteriated in the aromatic as well as in the aliphatic sites using Pt-catalyst; this is shown with perdeuteriated 4-*n*-pentylbiphenyl (exp. 2.10).

2.5. *Deuteriated flufenamic acid*

Aqueous solutions of the diethylammonium-salt of flufenamic acid (DEAF) give, over a wide temperature and concentration range, a stable lyomesophase [31],

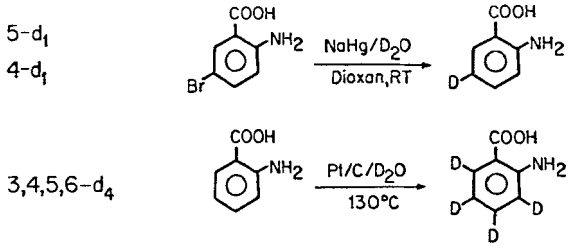


and its study by deuterium N.M.R. [51] required specific deuteriation of various aromatic sites. The acid can be prepared by either reacting ortho-aminobenzoic acid (anthranilic acid) with *m*-trifluoromethylbromobenzene (*a*), or reacting *o*-iodobenzoic acid with *m*-trifluoromethylaniline (*b*),

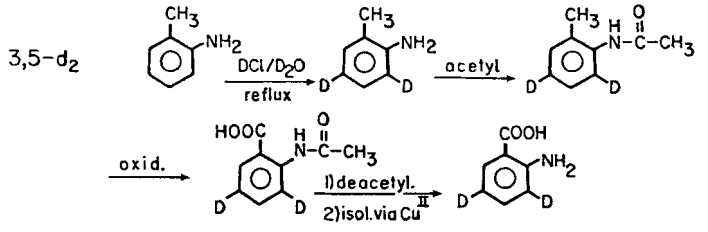


Thus there are four different intermediate building blocks; two for each of the two aromatic rings of flufenamic acid. From our previous discussion it is clear that suitable deuteriated intermediates could be either ortho-aminobenzoic acid (anthranilic acid) in scheme (*a*) or *m*-trifluoromethyl aniline in scheme (*b*). Anthranilic acid was specifically deuteriated by dehalogenation of the 4- and 5-halogen derivatives (exp. 1.23), while perdeuteriation was achieved using Pt/C catalysed exchange

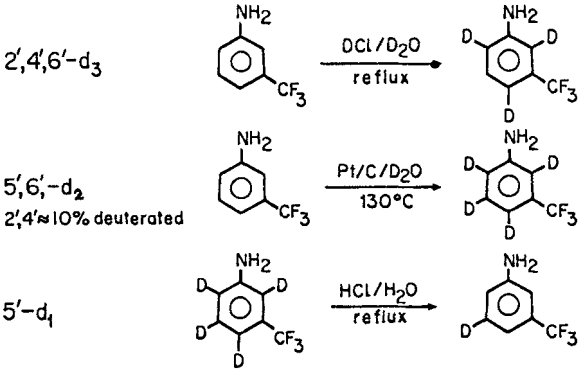
in D_2O;



Since the acid cannot be labelled ortho and para to the NH_2-group by exchange, a precursor of the anthranilic acid, namely *o*-toluidine, was used. The latter compound behaves like an aniline and can therefore be deuteriated in positions 3 and 5 by exchange with DCl/D_2O under reflux. The deuteriated *o*-toluidine was then used to prepare anthranilic acid via acylation, oxidation, deacetylation and finally was isolated as 3,5-d_2-anthranilic acid via a copper complex;



Deuteriation of the trifluoromethyl ring in the ortho- and para position was achieved by refluxing with DCl/D_2O (exp. 1.16), while perdeuteriation was accomplished by Pt/C catalysed exchange using D_2O. The enrichment level at sites 2′ and 4′ was somewhat less than in positions 5′ and 6′. Back exchange of the latter perdeuteriated aniline with HCl/H_2O left only the 5′ position labelled.



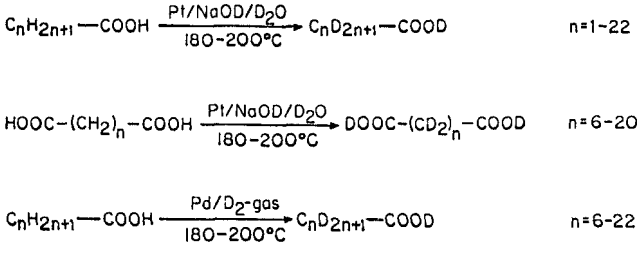
It should be noted that the phase transition temperatures of the deuteriated mesogens are often somewhat lower than the corresponding normal compound. A discussion of this effect may be found in [33] and other papers cited therein.

3. Aliphatic intermediates

Deuterium labelling of aliphatic chains in mesogenic compounds is usually achieved by synthetically linking the corresponding deuteriated aliphatic chain to the core of the molecule. Procedures for both the perdeuteriation as well as specific labelling of such aliphatic chains are described.

3.1. *Perdeuteriation*

The majority of perdeuteriation procedures of fatty acids have been described on a micromole scale using Adam's catalyst ($PtO_2 \cdot H_2O$). The published procedures usually require prereduction of the catalyst with deuterium gas, elimination of oxygen during the reaction and employing sodium peroxide to increase the exchange rate [80, 14]. A much simpler procedure for the perdeuteriation of fatty acids is to use Pt/C in $NaOD/D_2O$ at 180–200°C in a high pressure vessel. This procedure does not require prereduction and elimination of oxygen during the reaction. For fatty acids and α,ω-diacids containing up to twenty carbons, good isotopic yields can be obtained (exp. 3.1–3.4). Palladium on carbon as the catalyst and deuterium gas as the isotope source can be used for fatty acids with boiling points above 200°C [81] (exp. 3.5). This process is significantly slower and less economical but it offers an easy way to low level random deuteriation of high molecular weight fatty acids.

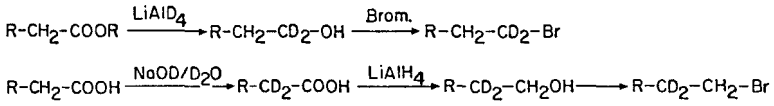


3.2. *Specific deuteriation*

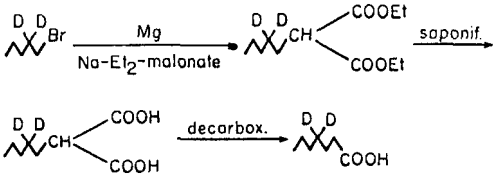
The complete interpretation of the deuterium N.M.R. spectra requires selective deuteriation and this normally involves a sequence of labelling and synthetic steps. Several procedures for obtaining such aliphatic chains have been described by DasGupta *et al.* [40], using the copper catalysed coupling of ω-bromo fatty acids and a labelled Grignard reagent, and by Boden *et al.* [34], using chain extension with malonic esters as well as Kolbe anodic oxidation. The deuteriation techniques used for labelling phospholipids and long chain fatty acids have been described in detail by Tulloch [82] and Rakoff [83]. In thermotropic liquid crystals the alkyl chains often contain less than twelve carbon atoms and so we shall refer mainly to the lower homologues of aliphatic acids, alcohols or halides; although the procedures can, in principal, be extended to the higher homologues. The reactions involve, for example, chain extensions by the carboxylation of alkylgrignards, decarboxylation of alkylmalonic acids or the homologation of alkylgrignards using α,ω-alkyldibromides. The same reactions can be applied to produce α,ω-dibromoalkanes 1-d_4 or 2-d_4 (exp. 5.1) which are used as flexible spacers in dimeric cyanobiphenyls [77] or discotic triphenylenes [68]. In all of these reactions, a specific position of the alkyl chain, usually the α or β positions requires labelling, with deuterium before the chain extension.

Alkylbromides labelled in the 1 position can be obtained by the bromination of the corresponding 1-d_2 alcohols which are prepared by the reduction of the ester using

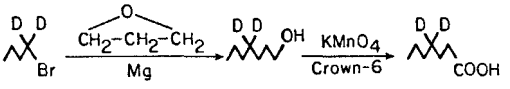
lithium aluminium deuteride. To prepare 2-d_2 alkylbromides an α-d_2 exchange of the corresponding acid is first performed, at 200°C in alkaline conditions (exp. 4.5, 4.6), followed by reduction and bromination.



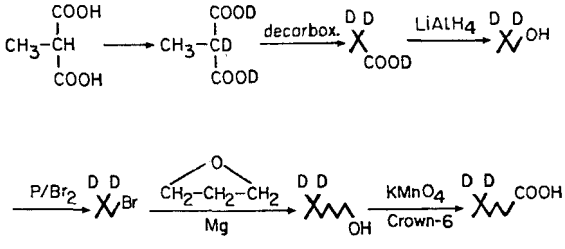
Labelling the carbon atoms 3 or 4 can be achieved by the chain extension of the 1 or 2 deuteriated bromides using diethylmalonate, followed by decarboxylation. An example of this is the preparation of 4-d_2-heptanoic acid from 2-d_2-pentylbromide;



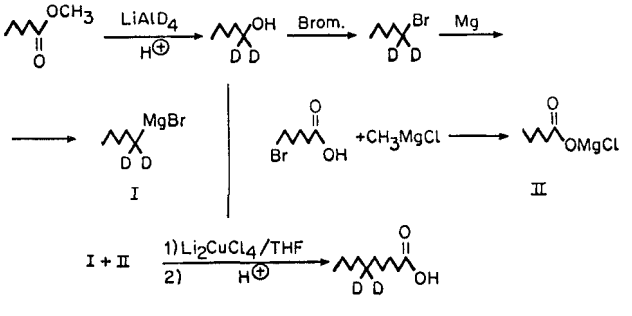
Alternatively, chain extension by three methylene units [84] can be obtained by reacting the Grignard reagent of the appropriate alkylbromide with trimethyleneoxide (exp. 4.1) followed by oxidation [85];



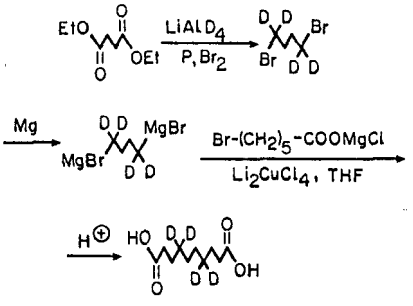
This method can also be used for labelling higher carbons along the chain using suitably deuteriated starting reagents. An example of this is the preparation of 5-d_2-hexanoic acid;



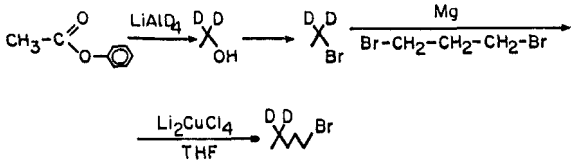
Labelling inner carbons of fatty acids can often be conveniently achieved by the chain extension of a deuteriated Grignard reagent using the appropriate ω-bromocarboxylic acid [40, 86, 87]/(exp. 4.2) according to the general scheme;



The Li_2CuCl_4-catalysed condensation shown in the last step was also used to prepare specifically double-deuteriated α,ω-di-carboxylic acids for example 4-d_2-7-d_2-decanedioic acid [88] (exp. 4.3). This compound serves as an intermediate in the preparation of labelled spacers in main-chain polymer liquid crystals [8].

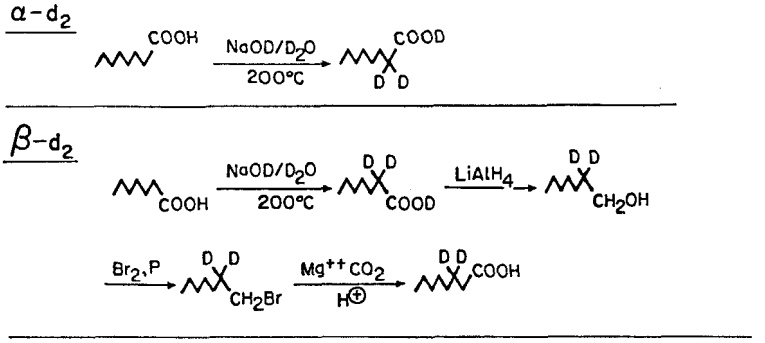


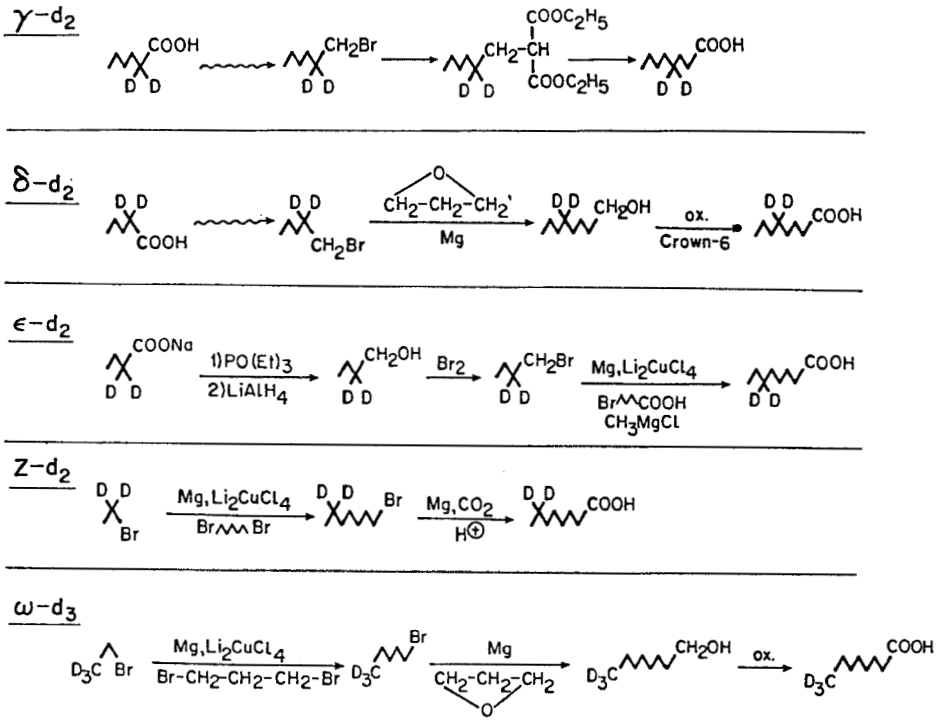
Another chain extension procedure used to obtain labelled alkylbromides is to react an alkyl-Grignard with an α,ω-alkyldibromide [89, 90] containing more than two carbon atoms, using Li_2CuCl_4 (exp. 4.4). An example of this method involves the preparation of 4-d_2-pentylbromide;



Depending on whether the starting alkyl-Grignard or the α,ω-alkyl-dibromide is deuteriated, a range of deuterium labelling along the chain is possible. For example, ω-d_2-pentylbromide can be obtained by the homologation of ω-d_3-ethylbromide with α,ω-dibromopropane. If we start with 1-d_2-ethylbromide, then 4-d_2-pentylbromide will be the homologation product. The analogous reaction of ethylbromide with 1,3-d_4-α,ω-dibromopropane ($BrCD_2$-CH_2CD_2-Br) results in 1,3-d_4-pentylbromide. This reaction was recently used for the preparation of 7,7-d_2-1-bromohexadecane by the homologation of the Grignard of 1-d_2-decylbromide with 1,6-dibromohexane. The product of this reaction was used for the deuteriation of stiff macromolecules with flexible side chains [92].

Reaction scheme for specifically deuteriated octanoic acid





To complete this section, a schematic overview of the procedures used in the preparation of labelled octanoic acids having specific deuteriation on each of the methylene and methyl groups is given. These isotopic species were prepared for the synthesis of the corresponding deuteriated discotic hexaoctanoyloxytriphenylene liquid crystals [93].

4. Conclusion

In this paper, various procedures for the specific deuteriation of intermediates used in the synthesis of liquid crystals have been discussed. There are several schemes which prove to be particularly useful because of their high specificity, high yield, synthetic simplicity and economy of the isotopic source. One of these general schemes involves the homogeneous acid catalysed exchange in which D_2O serve as the deuterium pool. This reaction can readily be used to label substituted phenols and anilines. Another important scheme involves Pt/C as the heterogeneous catalyst for exchange with D_2O. This method is particularly useful for aromatic and aliphatic acids. These main schemes together with a variety of conventional organic procedures can be used to specifically label the majority of the important intermediates employed in the synthesis of liquid-crystalline compounds. In cases where the common intermediate cannot be deuteriated directly, there are often alternative routes in which its deuteriation is achieved via a precursor molecule. This applies, in particular, in the specific labelling of aliphatic chains which can be prepared by proper chain elongation techniques from shorter fragments. In §§2 and 3, it is shown that a judicious choice of starting materials and reaction schemes allows essentially all the known thermotropic, lyotropic and polymeric liquid crystals to be specifically deuteriated in various sites of the molecule.

5. Experimental

This section presents the laboratory procedures for many of the key reaction steps described in §§2 and 3. The first subsection (5.1) describes the labelling of aromatic intermediates, followed by (5.2) a description of a series of reaction steps to obtain labelled cyanoalkoxy- and cyanoalkylbiphenyls. In 5.3, the preparation of fully deuteriated fatty acids and α,ω-dioic acids is given while in 5.4, the preparation of a series of specifically deuteriated chain intermediates is described. The section is completed with two examples of preparing deuteriated spacers for polymeric liquid crystals. In following these procedures usual safety precautions should be strictly followed. In particular, when a high pressure vessel is used it should never be filled to more than 40 per cent of its total volume. Such safety precautions can be found in standard laboratory manuals (see for example [94]).

5.1. *Aromatic intermediates*

1.1. *4-n-Pentylphenol-2,3,5,6-d_4*

4-*n*-Pentylphenol (Eastman Kodak, 5g) was heated in a tantalum high pressure vessel with 5 per cent DCl in D_2O (70 ml) at 230°C for 50 hours. After cooling the phases were separated; the aqueous phase was extracted twice with ether; the organic extracts combined and dried. After distillation *p-n*-pentylphenol-d_4 (4·5 g; m.p. = 21–23°C) was obtained. The deuteriation grade of the aromatic sites was 96 per cent.

1.2. *4-n-Pentylphenol-2,6-d_2*

4-*n*-Pentylphenol was heated with 10 per cent DCl in D_2O (70 ml) under reflux for fifty hours. The work-up was performed in the way described previously (1.1) yielding 4·5 g of *p-n*-pentylphenol-2,6-d_2. N.M.R. analysis indicated complete deuteriation ortho to the phenolic OH-group. The corresponding 3,5-d_2-phenol was obtained by back exchange of *p-n*-pentylphenol-2,3,5,6-d_4 with HCl/H_2O.

1.3. *Phenol-d_6*

A mixture of phenol (30 g) and DCl in D_2O (4 per cent, 100 ml) was heated with stirring in a tantalum high pressure vessel (300 ml volume) at 220°C for seventy hours. After cooling the phases were separated and a second exchange was performed under identical conditions using a fresh DCl/D_2O solution. The product was isolated, distilled and subjected to a third exchange. A final distillation resulted in perdeuteriated phenol (m/z = 99 (100 per cent), 98 (15 per cent). m.p. = 38–39°C).

1.4. *p-Bromophenol-d_4*

To a solution of phenol-d_6 (24 g) in ethylenedichloride (50 ml) bromine (34 g in ethylenedichloride) was added dropwise at 0°C over a period of three hours. The reaction mixture was stirred for a further hour and the solvent removed by distillation. Perdeuteriated bromophenol was distilled through a small column (b.p. 120–124°C, 15 torr; yield = 36 g; m.p. = 63–64°C.)

1.5. *4-Cyanophenol-d_4 (4-hydroxy-benzonitrile-2,3,5,6-d_4)*

To 4-bromophenol-d_4 (10 g) dissolved in D.M.F. (70 ml), was added CuCN (5·2 g). The stirred mixture was refluxed for 20 hours. The usual work up with ferric chloride

in D_2O/DCl yielded after distillation using Kugelrohr apparatus, 4-cyanophenol-d_4 (4·5 g; m.p. = 109–111°C). The deuteriation was found to be 96–98 per cent (^{1}H-N.M.R.).

1.6. *4-Cyanophenol 2,6-d_2 and*
1.7. *4-Cyanophenol-3,5-d_2*

4-Cyanophenol-2,6-d_2 was prepared from 4-bromophenol-2,6-d_2 by the acid catalyzed exchange of 4-bromophenol in 40 per cent D_2SO_4/D_2O under reflux, while 4-cyanophenol-3·5-d_2 was prepared by back exchanging 4-bromo-phenol-d_4 in 40 per cent H_2SO_4/H_2O, followed by cyanation with CuCN.

1.8. *4-Methoxyphenol-2,3,5,6-d_4*

p-Methoxyphenol (10 g) was refluxed in DCl/D_2O (5 per cent, 100 ml) for 24 hours. After cooling, the product was extracted with ether. The combined ether extracts were washed with saturated sodium chloride solution, dried over sodium sulphate and the solvent was removed on the rotary evaporator. Kugelrohr distillation (10 torr, 150°C) yielded 9 g of 4-methoxyphenol-2,3,5,6-d_4. ^{1}H-N.M.R. indicated a deuteriation grade of the aromatic hydrogens greater than 96 per cent. Using the same reaction, *p*-ethoxyphenol-d_4 was prepared; however, the hydrogens ortho to the phenolic group exchange rapidly under reflux conditions, while the exchange rate for the meta hydrogens is considerably slower. 4-Pentyloxy-phenol-2,3,5,6-d_4 (m.p. = 55–56°C) requires approximately 5 days refluxing conditions to exchange all the aromatic hydrogens.

1.9. *1,4-Hydroquinone-d_6*

Hydroquinone (30 g) was dissolved in D_2O (100 ml) and concentrated D_2SO_4 (2 ml) and refluxed for 5 days. The deuteriated hydroquinone crystallizes on cooling was isolated and used for a second exchange under the same conditions. Mass-spectra as well as ^{1}H-N.M.R. compared with the protonated hydroquinone indicated a deuteriation grade of 97 per cent (m.p. = 173–175°C). The chemical yield after the second exchange was 75 per cent.

1.10. *1,4-Hydroquinone-2,5-d_2*

2,5-Dibromohydroquinone (0·84 g) was dissolved in CH_3OD (20 ml) and $PdCl_2$ (1·3 g) was added slowly. To this mixture was added $NaBD_4$ (0·9 g) in small portions under constant stirring for 20 min at room temperature. Stirring was continued for further four hours. After hydrolysis (2N HCl) and extraction with ether, 0·28 g (75 per cent) 2,5-d_2-hydroquinone was isolated. The precise labelling of the aromatic sites was established by the proton-carbon and deuteron-carbon splitting patterns of their N.M.R. spectra.

1.11. *4,4′-Dihydroxybiphenyl 2,2′,3,3′,5,5′,6,6′-d_8-(OD)$_2$*

A mixture of 4,4-biphenol (3 g), benzene-d_6 (10 ml 99 per cent deuteriated) and DCl/D_2O (5 per cent, 80 ml) was heated with stirring under HTDA-conditions at 230°C for 60 hours. After work up perdeuterated 4,4′-biphenol (2·9 g; m.p. = 275–276°C) was obtained.

1.12. *4,4'-Dihydroxybiphenyl-3,5,3',5'-d_4-(OD)$_2$*

4,4-Biphenol (3 g) dissolved in ethanol-OD (200 ml) was heated under reflux with DCl 20 per cent in D_2O (80 ml) for 3 days. After evaporation and drying of the residue, the ^{1}H-N.M.R. indicated a complete exchange ortho to the hydroxy groups.

1.13. *4,4'-Dihydroxybiphenyl-2,6,2',6'-d_4*

This compound was prepared using the method described in (exp. 1.12), using perdeuteriated 4,4'-biphenol, HCl, EtOH and H_2O.

1.14. *4-n-Heptylaniline-2,6-d_2*

4-*n*-Heptylaniline (3 g) was refluxed for 50 hours with DCl/D_2O (5 per cent, 70 ml). The hydrochloric acid was neutralized by solid potassium carbonate; the aniline extracted with ether, dried and distilled. *p-n*-Heptylaniline-2,6-d_2 (90 per cent yield, 95 per cent deuteriation) was obtained.

1.15. *p-n-Heptylaniline-2,3,5,6-d_4*

Under HTDA-conditions, DCl/D_2O (5 per cent, 70 ml), the heptylaniline was heated with stirring at 250°C. After work up described in (1.14) ring deuteriated 4-*n*-heptylaniline-2·3·5·6-d_4 (b.p. = 136–138°C/1 mm.) was obtained by distillation. The chemical yield was 80 per cent and N.M.R. showed a complete absence of aromatic hydrogens.

1.16. *m-Trifluoromethylaniline-2,4,6-d_3*

m-Trifluoromethylaniline (20 g) was converted to the aniline hydrochloride in EtOH by adding HCl. The alcohol was evaporated and the solution cooled to 0°C; the hydrochloride salt precipitated. It was filtered, dried, dissolved in D_2O (70 ml) and this was refluxed for 24 hours. The D_2O was then removed by distillation, and the exchange repeated three times, each time using fresh D_2O. Solid potassium carbonate was added; the aniline extracted with ether and washed with H_2O. *m*-trifluoro-methyl-aniline-2,4,6-d_3 (15 g, b.p. = 185°C) was obtained and ^{1}H-N.M.R. showed one aromatic resonance (meta, 1 H).

1.17. *Terephthalic acid-d_6 (perdeuteriated)*

1,4-Benzenedicarboxylic acid (terephthalic acid) (10 g) dissolved in D_2SO_4 (92–95 per cent, 200 ml) was heated with stirring at 220°C. The D_2SO_4 was diluted to 92–95 per cent with D_2O. The coloured solution was kept at this temperature for 24 hours and allowed to cool. The crystallized terephthalic acid was filtered through a porous glass-plate, washed with a small amount of D_2O and exposed to a second exchange under identical conditions using fresh D_2SO_4/D_2O. The perdeuteriated terephthalic acid (9 g m.p. > 300°C) obtained was 98 per cent labelled on the aromatic ring (^{1}H-N.M.R.: 60 MHz/DMF-d_7).

1.18. *Biphenyl-4,4'-dicarboxylic acid (perdeuteriated)*

The dicarboxylic acid (2 g) in D_2O (50 ml) containing NaOH (0·75 g as pellets) and Pt/C (1 g) was heated under constant stirring in a stainless steel high pressure vessel to 200°C for five days. The cooled solution was acidified with HCl. The precipitated

biphenyl-4,4′-dicarboxylic acid was isolated (1·8 g; m.p. > 300°C) and analyses by N.M.R. indicated deuteriation of all the aromatic hydrogens to better than 96 per cent.

1.19. *Terephthaldehyde-methin-d_2*

To terephthalyalcohol 1,4-CD_2OH (7 g, obtained by reduction of dimethyl-terephthalat with $LiAlD_4$), was slowly added nitric acid (HNO_3 d = 1·4, 20 g); the temperature was kept between 15–20°C. The dialcohol dissolved slowly and after 20 minutes the oxidation was stopped using a large excess of H_2O whereupon the deuteriated dialdehyde precipitates. After filtration and successive washings with water, it was recrystallized from H_2O. The sublimed terephthaldehyde-methin-d_2 (6 g; m.p. = 114–115°C; m/z = 136) showed no methin resonances by ^{1}H-N.M.R. In the same manner perdeuteriated terephthaldehyde was prepared from terephthalic-acid-d_6.

1.20. *1,2-Dimethoxybenzene-3,4,5,6-d_4*

To 1,2-dimethoxybenzene (24 g) was added D_3PO_4 (85 per cent in D_2O) and the reaction mixture was stirred vigorously and heated at 80°C for 40 hours. The cooled mixture was extracted three times with ether; the solvent was evaporated and the residue distilled under reduced pressure yielding the deuteriated product (10 torr; b.p. = 140–145°C; 23 g). The deuteriation grade of the aromatic sites was better than 96 per cent. No deuteriation of the methyl groups was detected.

1.21. *4-Hydroxybenzoic acid-d_6 (perdeuteriated)*

4-Hydroxybenzoic acid (8 g) was introduced into a thick glass-tube (volume approximately 250 ml) together with D_2O (100 g) and platinum on carbon (10 per cent, 1 g). The air was pumped out, while the contents were frozen at −30°C; the vial was sealed. The tube was shaken for 6 days at 130°C in a commercial laboratory heating oven. It was opened at room temperature; the reheated solution was filtered from the catalyst and evaporated giving approximately 90 per cent deuteriated product. After a second exchange procedure the deuteriation was better than 98 per cent in the aromatic sites. The yield of 4-hydroxybenzoic acid-d_6 (m.p. = 213–215°C) was 7·2 g.

1.22. *4-Hydroxybenzoic acid-2,6-d_2 and*
1.23. *4-Hydroxybenzoic acid-3,5-d_2*

The perdeuteriated acid (5·7 g), described in (1.21) was back exchanged by refluxing in 5 per cent HCl (80 g) for 24 hours. The 2,6-d_2-4-hydroxybenzoic acid (5·1 g), crystallized on cooling. The ^{1}H-N.M.R. spectra has a single resonance at 6·8 p.p.m. The specificity of the exchange is better than 95 per cent. *p*-Hydroxybenzoic acid-3,5-d_2 can be prepared in the same manner by refluxing 4-hydroxybenzoic acid in DCl/D_2O.

1.24. *Anthranilic acid-5-d_1*

2-Amino-5-iodobenzoic acid was dissolved in dry dioxane (80 ml) and D_2O (80 ml). Sodiumamalgam (5 per cent sodium, 50 g) was added slowly and stirred at room temperature for 2 days. The solution was separated from the mercury and

evaporated to dryness. After acidification by acetic acid, the copper complex was precipitated using an aqueous solution of copper(II) acetate. The filtered and washed complex was suspended in water whilst hydrogensulphide precipitated and coppersulphide. The coppersulphide was separated, and 5-d_1-anthranilic acid was evaporated to dryness (2·1 g; m.p. = 144–146°C; m/z = 138). The ^{2}H-N.M.R. spectrum of the final lyotropic mesophase, 5-d_1-flufenamic acid/diethylammonium salt/H_2O, showed one doublet, indicating a precise deuteriation without any scrambling on the 5-position.

1.25. *Pentyloxy-d_{11}-bromobenzene-d_4*

Perdeuteriated *n*-pentylbromide (prepared via perdeuteriation of pentanoic acid, reduction by $LiAlD_4$ to *n*-pentanol-d_{11} and conversion to the bromide-d_{11}, 30 g) and *p*-bromophenol-d_4 (35 g) in dry acetone (50 ml) and pulverized K_2CO_3 (28 g) were refluxed for 18 hours. The work up of the alkylation yielded 4-pentyloxy-d_{11}-*p*-bromobenzene-d_4. It was distilled at 160°C/0·1 torr.

1.26. *4-Pentyloxy-d_{11}-benzoic acid-d_4*

A mixture of magnesium (2·5 g) and pentyloxy-d_{11}-bromobenzene-d_4 (24·5 g) in diethyl ether was refluxed for 2 hours and then carboxylated at −20°C; work up in the usual manner yielded 4-pentyloxy-d_{11}-benzoic acid-d_4 (11 g). The acid can also be prepared by the alkylation of perdeuteriated *p*-hydroxybenzoic acid.

1.27. *4-Pentyloxy-d_{11}-benzylalcohol-d_6 and*
1.28. *4-Pentyloxy-d_{11}-benzaldehyde-d_5*

The benzyl alcohol was prepared by the reduction of the acid using $LiAlD_4$ in ether; after hydrolysis the product was distilled and oxydized. *p*-Pentyloxy-d_{11}-benzylalcohol-d_6 (4 g) was dissolved in pyridine (dried over molecular sieves) and stirred with lead tetraacetate overnight at room temperature. The pyridine was removed under reduced pressure; the residue was stirred with ether, filtered, concentrated and the perdeuteriated 4-pentyloxybenzaldehyde (3·2 g) was vacuum distilled in a Kugelrohr apparatus.

5.2. *Aromatic intermediates for cyanoalkoxybiphenyls and cyanoalkylbiphenyls*
2.1. *4-Hydroxybiphenyl-d_{10}-(perdeuteriated)*

4-Hydroxybiphenyl (15 g) was stirred and heated at 230–240°C under HDTA conditions (tantalum vessel) together with DCl/D_2O (5 per cent DCl in D_2O 99·8 per cent, 100 ml) for 4 days. The cooled mixtured was separated by filtration and a second exchange under the same conditions was performed. The final purification was achieved using sublimation (115°C, 10^{-3} torr). The ^{1}H-N.M.R. 60 MHz spectrum of 4-hydroxy-biphenyl-d_{10} (14 g; m.p. = 165–166°C; m/z = 180) using the protonated compound as the reference, showed no hydrogen resonances.

2.2. *Biphenyl-d_9-4-phenylsulphonate*

To 4-hydroxybiphenyl-d_9 (20 g, 0·11 mole) dissolved in dry pyridine (250 ml), benzenesulphonylchloride (22·8 g, 0·129 mole) was added dropwise while the temperature was kept at 10°C. The mixture was then heated for 30 min to 60°C,

followed by a reflux period of 40 min. The solution was concentrated (under reduced pressure) to approximately 10 per cent of the original volume. By diluting the residue with equal parts of H_2O and 10 per cent HCl the sulphonic acid ester was separated as a crystalline product. Recrystallization from EtOH/H_2O yielded biphenyl-d_9-4-phenylsulphonate (26 g, 76 per cent; m.p. = 103–104°C).

2.3. *4-Bromobiphenyl-d_8-4′-phenylsulphonate*

To biphenyl-d_9-phenylsulphonate (10 g) was added bromine (7·6 g) dropwise at room temperature within 10 min. The DBr evolved was pumped off by applying a weak vacuum (600 torr); the mixture was allowed to stand for 15 min, followed by heating and stirring at 80°C for 10 min. The resulting oil was cooled and recrystallized from EtOH to give 4-bromobiphenyl-d_8-4′phenyl-sulphonate (m.p.: 79–81°C) in 83 per cent yield.

2.4. *4-Hydroxy-4′-bromobiphenyl-d_8*

The deuteriated phenylsulphonate was saponified in a 1 : 1 mixture of *p*-dioxane/D_2O (each 200 g) with potassium hydroxide pellets (20 g). After cooling the phases were separated and the dioxane was washed three times with D_2O. The KOD/D_2O phase was extracted with ether. The combined aqueous phases were cooled and acidified with 20 per cent H_2SO_4/H_2O and the product was filtered off. 4-Hydroxy-4′-bromobiphenyl-d_8 (7 g; m.p.: 169–170°C) was recrystallized from EtOH/H_2O.

2.5. *4-Hydroxy-4′-cyanobiphenyl-d_8*

The cyanation was performed in the usual manner: thus, 4-hydroxy-4′-bromobiphenyl-d_8 (5 g) and CuCN (2·8 g) in dry dimethylformamide (75 ml) were refluxed for 18 hours. The mixture was worked up with ferric chloride but D_2O and DCl were used instead of the protonated material. After recrystallization from EtOH/H_2O, 4-hydroxy-4′cyanobiphenyl-d_8 (3·3 g, 83 per cent) was obtained (m.p.: 198–199°C; m/z = 203). The ^{1}H-N.M.R. spectrum of the product compared with the protonated one and showed a deuteriation grade better than 97 per cent.

2.6. *4-Hydroxy-4′-bromobiphenyl-2,6,2′,6′,3′,5′,-d_6 (back-exchange)*

The perdeuteriated 4-hydroxy-4′-bromobiphenyl (1 g) dissolved in toluene (10 ml) was refluxed with concentrated HCl/H_2O (1 : 1, 200 ml) for 24 hours. Thin layer chromatography indicated the stability towards such treatment. The phases were separated, followed by the extraction of the aqueous layer. The combined organic phases were evaporated yielding 4-hydroxy-4′-bromobiphenyl-d_6 (m.p. = 168–170°C); the ortho-positions to the hydroxy group are back exchanged by hydrogens.

2.7. *4-Methoxy-4′-cyano-2,6,2′,6′,3′,5′,-d_6-diphenyl*

This was synthesized by the alkylation of 4-hydroxy-4′-cyano-2,6,2′,3′,5′,-d_6-biphenyl with methyl iodide in a conventional manner in cyclohexanone using potassium carbonate as the base. From the integrals of the ^{1}H-N.M.R.-spectrum of the isolated and purified methoxyderivative, the back exchange of the ortho deuterons to the methoxy group (see prep. above) was found to be better than 98 per cent (m/z = 215 (100 per cent).).

2.8. *4-Ω-d_3-Pentyloxy-4'-cyanobiphenyl-d_8*

To 4-hydroxy-4'-cyanobiphenyl-d_8 (0·6 g) dissolved in cyclohexanone (15 ml), pulverized potassium carbonate (2 g) and Ω-d_3-pentylbromide (1·4 g) were added. The mixture was refluxed at 160°C for 20 hours. The cooled mixture was filtered to remove potassium bromide and excess potassium carbonate. The residue was washed with ether, the solvent removed by vacuum distillation and the remaining oil was distilled in a Kugelrohr apparatus at 10^{-3} torr/200°C. A chromatographic purification on silica-gel 60 followed using CH_2Cl_2 as eluent. After a second distillation the yield was 0·5 g 4-Ω-d_3-pentyloxy-4'-cyanobiphenyl-d_8. Thin layer chromatography on silica gel/CH_2Cl_2 reveals one spot. The products (literature value, undeuteriated product, 67·5°C) (m/z = 276 (100 per cent)) clearing temperature was 65·5–66°C.

2.9. *Biphenyl-d_{10} and p-terphenyl-d_{14}-(perdeuteriated)*

Biphenyl (10 g), D_2O (100 ml) and platinum on carbon (10 per cent, 1 g) were heated and stirred in a stainless steel pressure vessel for 8 days at 200°C. The product was isolated by filtration, purified by distillation and subject to a second exchange under the same conditions. The final product (9 g) was checked using N.M.R. spectroscopy (compared to the protonated one) and was found to be better than 98 per cent deuteriated. In the same manner *p*-terphenyl was perdeuteriated at 250°C.

2.10. *4-n-Pentylbiphenyl-d_{20}-(perdeuteriated)*

4-*n*-Pentylbiphenyl (5 g), D_2O (50 ml) and platinum on carbon (10 per cent, 1 g) were heated and stirred in a stainless steel pressure vessel at 240°C for 7 days. The product was separated and distilled. It was deuteriated in the chain and in the aromatic sites to better than 95 per cent. Pentylcyanobiphenyl was obtained by iodation and cyanation as described elsewhere [36].

5.3. *Perdeuteriated fatty and α,ω-dioic acids*

3.1. *Perdeutero-octanoic acid*

Octanoic acid (15 g), sodium hydroxide pellets (6 g), D_2O (99·9 per cent, 100 ml) and the catalyst platinum on carbon (10 per cent, 5 g) were heated and stirred in a stainless steel high pressure vessel at 180°C for 7 days. The acid was isolated by acidification, extracted with ether and distilled giving randomly 85 per cent deuteriated octanoic acid. After a second exchange reaction under identical conditions the isolated *n*-octanoic acid was perdeuteriated (12 g, D = 97 per cent). Reduction of the perdeuteriated octanoic acid was performed using $LiAlD_4$ in ether. The deuteriated octanol was brominated with bromine and red phosphorous to give *n*-octylbromide-d_{17} (D = 97 per cent; yield 80 per cent; B.p. = 196–199°C).

3.2. *Perdeutero-palmitic acid (hexadecanoic acid)*

Palmitic acid (20 g), sodium hydroxide pellets (4 g), D_2O (120 ml) and platinum on carbon (10 per cent, 4 g) were heated together in a stainless steel 300 ml high pressure vessel with Teflon fittings at 200°C for 6 days. The water was evaporated by distillation and the dried sodium palmitate was exchanged on a second run with D_2O (120 ml) and another fresh amount of catalyst (Pt/C 10 per cent, 1 g) for 10 more days. After a third exchange under the same conditions, acidification, filtration and final distillation, 18 g of perdeuteriated hexadecanoic acid (m.p. protonated = 61–64°C,

m.p. perdeuteriated = 54–56°C) was obtained. ^{1}H-N.M.R. and mass spectroscopy indicated a deuteriation grade better than 99 per cent.

3.3. *Perdeutero-hexanedioic acid (adipic acid)*

Adipic acid (Fluka, 3 g), sodium hydroxide pellets, (two mole equivalents and 10 per cent excess), D_2O (99·9 per cent, 40 ml) and platinum on carbon (10 per cent, 1·2 g) were heated and stirred together in a stainless steel pressure container at 180°C for 9 days. It should be stressed that tantalum pressure vessels are not suitable under alkaline conditions! After cooling, the content of the vessel was filtered, acidified and evaporated. The residue was distilled in a Kugelrohr apparatus at 170°C/10^{-3} torr giving hexanedioic acid chain-perdeuteriated (2·25 g; m.p. 150°C; ^{1}H-N.M.R./D.M.S.O = 95 per cent random deuteriation). This procedure was applied to adipic to docosanedioic acid; the optimum exchange temperature varies a little between 180°C and 220°C among the various dioic acids. If there is a small decarboxylation taking place then the temperature has to be decreased and the exchange time increased.

3.4. *Perdeutero-tetradecanedioic acid*

Tetradecandioic acid (5 g), sodium hydroxide pellets (1·7 g, two mol equivalents + 10 per cent), Pt/carbon (10 per cent, 2 g) and D_2O (100 ml) were heated and stirred at 190°C for 9 days. The mixture was cooled to 80°C and filtered from the catalyst. The solution was acidified with hydrochloric acid, the precipitated dioic acid filtered, washed with water, dried and finally distilled in a Kugelrohr apparatus at 10^{-3} torr. The deuterium content of the tetradecanedioic acid (4·5 g) was approximately 94–96 per cent. After a second exchange under the same conditions it was better than 98 per cent.

3.5. *Lauric acid (dodecanoic acid gas-phase exchange)*

Lauric acid (20 g) was placed in an exchange cell fitted with a gas inlet (porous glass), heated and stirred together with palladium on charcoal (10 per cent, 0·5 g). The temperature was kept at 195°C while deuterium gas was bubbled through the melt (approximately 25 ml/min). After 5 days the deuterium content was found to be around 50 per cent. There is a constant loss of material due to the carrier effect of the deuterium gas. After 12 days approximately 95 per cent deuterium was found. The total consumption of deuterium gas was in the region of 400 litres. The traces of hydrocarbon formed are separated by distillation. The final yield was 7 g random deuteriated lauric acid (m.p. 39–41°C), this is quite low in comparison to the yields of the other methods described above.

5.4. *Specifically deuterated fatty acids and derivatives*

4.1. *4-d_2-Hexanoic acid*

The Grignard from *n*-propylbromide-1-d_2 (14 g) was refluxed for 1 hour and cooled to room temperature. Trimethyleneoxide (7 g) in ether (20 ml) was added dropwise and the mixture was refluxed and stirred for 1 hour. Dry benzene (130 ml) was added and the ether continously distilled off by raising the temperature of the oil bath gradually to approximately 80°C. The pasty mass obtained was refluxed for 4 hours. The cool mixture was hydrolysed with water and the phases were separated. The aqueous phase was extracted repeatedly with ether, the organic phases combined,

the solvents removed and the 4-d_2-hexanol distilled (6·9 g, b.p. 155°C). The alcohol was oxidized by potassium permanganate in benzene and 18-dicyclohexyl-crown-6 to the 4-d_2-hexanoic acid. The ^{1}H-N.M.R., spectrum (360 MHz in $CDCl_3$) showed a deuteriation grade of 97 per cent in the 4-position. The acid was used to prepare hexahexanoyl-gamma-d_2-oxybenzene.

4.2. *8-d_2-Dodecanoic acid*

n-Pentylbromide-1-d_2 (8 g, prepared by the reduction of methylpentanoate using $LiAlD_4$ and subsequent bromination) was converted to the Grignard and refluxed for 1 hour. To Ω-bromoheptanoic acid (10 g) in dry THF (100 ml) methylmagnesium-chloride in THF (17 ml, 3 molar) was added carefully. When the gas evolution stopped, the catalyst (0·58 g $CuCl_2$ and 0·29 g LiCl in 18 ml THF) was added. To the stirred cooled mixture at −30°C the Grignard was slowly added. The solution was kept at −30°C for one hour, stirred at room temperature overnight and was quenched with cold sulphuric acid (2N, 200 ml). After extractions using ether, purification by potassium hydroxide extraction, reacidification and again extractions with ether 8-d_2-dodecanoic acid (5·5 g; m/z = 202, 100 per cent; 201, 2 per cent). In order to obtain a very pure product, esterification and saponification is recommended [40].

4.3. *4-d_2-7-d_2-Decanedioic acid* [88]

Magnesium turnings (3 g, activated with a trace of iodine) and 1,4-dibromo-1,4-d_4-butane in THF (30 ml) were slowly added under constant boiling. The mixture was diluted with dry THF, the excess magnesium removed and kept under nitrogen. Ω-bromopropionic acid (22 g) in THF (120 ml) was cooled to −30°C and methyl-magnesiumchloride (50 ml of a 3 molar solution in THF) was added dropwise while the reaction temperature was kept below −20°C. The catalyst dilithium tetra-chlorocuprate (0·8 g $CuCl_2$, 0·4 g LiCl in 16 ml THF) was added and the deuteriated Grignard reagent was added slowly at −20°C. The mixture was kept for a further 90 minutes at −20°C and finally stirred at room temperature for 15 hours. It was hydrolysed using sulphuric acid and extracted several times with ether. The combined ether extracts were washed with saturated sodium chloride solution and several times with dilute potassium hydroxide solution. The combined aqueous phases were acidified with sulphuric acid until the pH was 2–3. 4-d_2-7-d_2-decanedioic acid (sebacic acid) precipitated and isolated (m.p. 132°C, 2·6 g.)

4.4. *ω-d_3-Pentylbromide*

2-d_3-Ethylbromide (CD_3CH_2Br 14 g, prepared from CD_3COOD by reduction to 2-d_3-ethylalcohol followed by conversion to the bromide) was reacted with mag-nesium (3·1 g) in THF (20 ml). The solution with the catalyst, (140 mg LiCl and 110 mg $CuCl_2$) in water-free THF (80 ml) was prepared and 1·3-dibromopropane (28 g) was added. The mixture was kept at 5°C and the Grignard solution of CD_3CH_2Br was added dropwise (exothermic) ensuring that the temperature did not exceed 10°C. After this addition the reaction was stirred slowly while warming to room temperature within 2 hours. The reaction mixture was hydrolysed using diluted hydrochloric acid, the phases were separated and the aqueous phase extracted with ether. After washing and drying, the solvent was rectified on a Vigreux column. The product (13 g; b.p. 125–145°C) was distilled in a micro column (having 15 theoretical plates) yielding 5-d_3-pentylbromide (8·4 g, 43 per cent; b.p. 127–130°C).

4.5. *α-d_2-Oleic acid (cis-9-octadecenoic acid-α-d_2)*

Oleic acid (10 g), sodium hydroxide pellets (1·5 g) and D_2O (99·8 per cent, 40 ml) were heated and stirred in a stainless steel pressure vessel at 200°C for 4 days. The usual work up gave oleic acid-α-d_2. The ^{1}N-N.M.R. spectrum (360 MHz/$CDCl_3$) revealed the complete absence of α-hydrogens.

4.6. *α,α′-d_4-Dodecanedioic acid*

Dodecanedioic acid (25 g), sodium hydroxide pellets (7 g) and D_2O were heated in a stainless steel high pressure vessel with Teflon fittings at 200°C for 4 days. The depleted D_2O was distilled off and the solid residue was used for a second exchange with fresh D_2O (80 ml). The isolated acid was distilled yielding α,α′-d_4-dodecanedioic acid (12 g; approximately 97 per cent deuteriated; m.p. 127–128°C).

5.5. *Spacers for dimeric and polymeric liquid crystals*

5.1. *1,6-Hexanediol-1,6-d_4 and 1,6-dibromohexane-1,6-d_4*

The dimethylester of adipic acid (35 g) dissolved in ether was added slowly to a stirred mixture of $LiAlD_4$ (10 g) in ether (400 ml). The reaction was kept for 5 hours at room temperature and refluxed overnight. The mixture was hydrolysed, filtered and the aqueous phase was salted out and extracted with ether. Distillation of the product (10^{-3} torr) gave 1,6-hexanediol-1,6-d_4 (m.p. 35–38°C). The diol-d_4- (18·5 g) was brominated with red phosphorous and bromine. After distillation at 20 torr 1,6-dibromohexane-1,6-d_4 (25·3 g) was obtained.

5.2. *1-1-d_2-1-Hydroxy-6-bromohexane* [91]

To $LiAlD_4$ (7 g) in ether, a solution of ω-bromohexanoic acid-benzylester (67·5 g) in ether was slowly added ensuring that constant boiling occurred. The stirring was continued at room temperature for 6 hours and finally refluxed for 30 minutes. Hydrolysis with water and sulphuric acid, extraction with ether and destillation resulted in a 62 per cent yield (b.p. 73°C (0·1 torr); $n_D^{20} = 1{\cdot}4815$).

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