Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 19 Oct 2010.

To cite this article: Mary E. Neubert (1985): Synthesis of Some Deuterated Aromatic Mesomorphic Compounds Used in Broad-Line ^{2}H-NMR Studies, Molecular Crystals and Liquid Crystals, 129:4, 327-373

To link to this article: http://dx.doi.org/10.1080/00268948508085038

Mol. Cryst. Liq. Cryst., 1985, Vol. 129, pp. 327–374
0026-8941/85/1294–0327/$30.00/0

Synthesis of Some Deuterated Aromatic Mesomorphic Compounds Used in Broad-Line ^{2}H-NMR Studies†

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(*Received December 20, 1984*)

Twenty-one deuterated mesogens of the following types: HOAB (perdeuterated chains), 4-alkoxybenzoic acids (perdeuterated chain and acid deuteron), 7S5 and 8S5 (perdeuterated alkoxy chain), 4-alkoxybenzylidene-4′-alkylanilines (2 or 4 deuterons in the aniline ring, 2-α-deuterons on the alkyl chain and perdeuterated alkyl or alkoxy chain) and TBBA (perdeuterated alkyl chains or anil deuterons) were prepared for use in broad line ^{2}H-NMR by using standard literature methods. The required 4-alkoxybenzoic acids, aldehydes and anilines with perdeuterated chains were prepared by alkylation of the appropriate 4-substituted phenol. The acid proton in the 4-alkoxybenzoic acids was replaced with a deuteron either by basic hydrolysis of the ester or acid chloride or by base-catalyzed exchange on the acid. Two deuterons were incorporated into the aniline ring ortho to the amino group by exchange in dilute H_2SO_4. Four ring deuterons, two α-chain deuterons or a perdeuterated chain were incorporated into 4-alkylanilines by the following sequence of steps: Friedel-Crafts acylation of benzene with an acid chloride, catalytic reduction, Friedel-Crafts acylation with oxalyl chloride, hydrolysis in base and a Schmidt rearrangement in H_2SO_4. New deuteration equipment was designed for the catalytic reduction using deuterium. IR, NMR and MS were used to determine the deuterium content in these compounds. Small differences in mesophase transition temperatures were observed for mesogens containing perdeuterated alkyl or alkoxy chains.

INTRODUCTION

During the last 12 years, the deuterated mesogens listed in Table I were synthesized and their mesophases studied using broad-line ^{2}H-NMR by J. W. Doane and his group. Various factors were con-

†Presented in part at the 187th National Meeting of the American Chemical Society, St. Louis, MO, April 1984; Abstr. No. Coll. 37.

sidered in choosing to study these particular compounds. These included the mesomorphic properties of the mesogens, the synthetic feasibility of preparing the compound and the availability and cost of required deuterated reagents. References for Doane's published ^{2}H-NMR data are given in Table I.

A simplified designation has been adopted for the thioesters and anils to facilitate communications about these materials. These abbreviations not only define the number of deuteriums present but also their location. The designations for the corresponding non-deuterated mesogens which have already been used in the literature are also used in the abbreviation for this system. The non-deuterated thioesters IV are called $\overline{n}$Sm systems. Chain deuterons are indicated in parentheses by a capital C following by d_n with n = the number

TABLE I

Deuterated Mesogens Prepared for Broad-line ^{2}H-NMR Studies

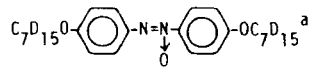
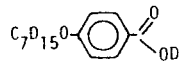
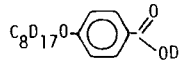
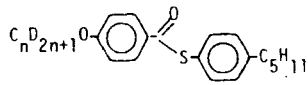
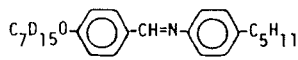
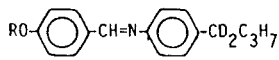
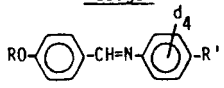
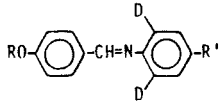
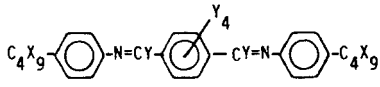
Number	Mesogen	Designation	^{2}H-NMR Reference No.
I.		HOAB-d_{30}	1-4
II.		70BA-d_{16}	4-6
III.		00BA-d_{18}	7
IV.			
	a. n=7	$\overline{7}$S5(Cd_{15})[b]	
	b. n=8	$\overline{8}$S5(Cd_{17})	8
V.		70.5(Cd_{15})	
VI.			
	a. R=CH_3	10.4(C'α-d_2)	9,10
	b. R=C_9H_{21}	90.4(C'α-d_2)	11

TABLE I (*continued*)

Table I (cont'd)

Number	Mesogen	Designation	^{2}H-NMR Reference No.
VII.			
	R / R'		
	a. CH_3 / C_4H_9	10.4(R'd_4)	9,10
	b. C_4H_9 / C_7H_{15}	40.7(R'd_4)	12-14
	c. C_4H_9 / C_8H_{17}	40.8(R'd_4)	15
	d. C_4H_9 / C_8D_{17}	40.8(R'd_4)	11
	e. C_5H_{11} / C_7H_{15}	50.7(R'd_4)	11
	f. C_9H_{21} / C_4H_9	90.4(R'd_4)[c]	
VIII.			
	R / R'		
	a. C_4H_9 / C_2D_5	40.2(C'd_5,R'2,6-d_2)	
	b. C_7H_{15} / C_2D_5	70.2(C'd_5,R'2,6-d_2)	
	c. CH_3 / C_4H_9	10.4(R'2,6-d_2)	
	d. C_7H_5 / C_4H_9	70.4(R'2,6-d_2)	
	e. C_7H_5 / C_7H_5	70.7(R'2,6-d_2)	
IX.			
	a. X=D, Y=H	TBBA-d_{18}	
	b. X=H, Y=D	TBBA-d_6	

[a] This material was recovered from the ^{2}H-NMR studies, recrystallized and used by J.A. Janik (Institute of Nuclear Physics, Krakow, Poland) in his neutron scattering studies.

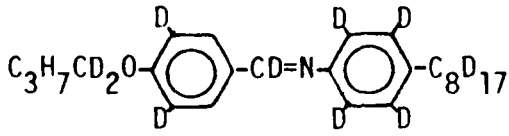
[b] This material crystallized too quickly in ^{2}H-NMR studies of the S_C phase to obtain any results.

[c] Isotope purity was not high enough to obtain a simple ^{2}H-NMR spectrum with this sample.

of deuterons. If the chain is on the thiol ring a prime is added to the C. Thus, compound IVa is $\overline{7}S5(Cd_{15})$ and if the deuterated chain were on the other ring it would be $\overline{7}S5(C'd_{11})$. A partially deuterated chain is indicated by using the Greek letters to denote position. Thus compound VIa is 10.4(C'α-d_2). Ring deuterons are designated by a capitol R followed by numbers for their location and d_n. When the ring is

fully deuterated these numbers are dropped. Thus, compound VIIa is 10.4(R'd_4) and VIIIc is 10.4(R'2,6-d_2). A combination of chain and ring deuteriums can be designated as for VIIIa as 40.2(C'd_5,R'2,6-d_2). This leaves only one deuterium to consider i.e. the anil which can be indicated as Ad.

This system is useful only if a few positions are deuterated for the abbreviations become too long if too many deuterons are added. Such an example is as follows:



40.8(Cα-d_2, R2,6-d_2, Ad, R'-d_4, C'd_{17}).

SYNTHESIS

These mesogens were prepared using the appropriate deuterated intermediates by standard methods available in the literature for preparing the analogous non-deuterated materials as shown in Figure 1. HOAB-d_{30} (I) was prepared in a yield of 84% from the deuterated 4-alkoxyaniline **1** using a method similar to that reported for the synthesis of the corresponding dialkyl compound in the presence of hydrogen peroxide.[16] The thioesters IV were prepared by esterification of the acid chloride of **2** with the thiol **3** according to our

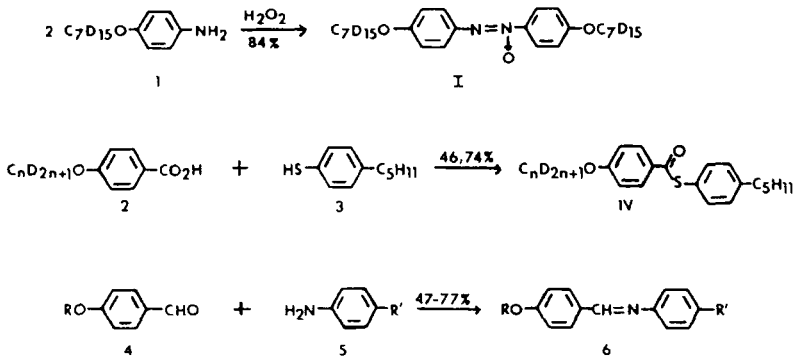
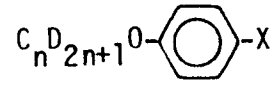


FIGURE 1 Synthetic methods for deuterated mesogens.

published procedure in a maxumum yield of 74%.[17] At the time we prepared these materials the carbodiimide method had not been developed. It would now be the method of choice since it avoids the need to prepare the acid chloride. A large variety of deuterated anils and dianils (V-IX) were prepared by reaction of the aldehyde **4** with aniline **5** in the presence of molecular sieves to remove water formed in this reaction. Deuterium was incorporated either into the aldehyde **4** or the aniline **5**. All of the ring deuterium incorporation was done on the aniline half of these anils since it was easier to prepare the deuterated anilines that the aldehydes from benzene.

To prepare the deuterated liquid crystals listed in Table I, these synthetic schemes required the synthesis of the deuterated intermediates listed in Table II. The synthetic problems involved can be divided into 3 general types:

1. Synthesis of a chain deuterated 4-substituted alkoxybenzene where X is the appropriate functional group:



for intermediates **1**, **2**, and **12**.

2. A method for preparing 4-alkylanilines which allows for incorporation of deuterium into the α-methylene group (**28**), the entire alkyl chain (**29d** and **30a**) and four ring deuterons (**29**).

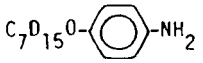
3. Exchange of only two protons in the aromatic ring of 4-alkylanilines (**30**). Perdeuterated terephthaldehyde **31** was commercially available and therefore, did not have to be prepared.

Synthetic methods used to prepare deuterated materials have special requirements not found in the synthesis of non-deuterated materials because of the high cost of the required starting deuterated reagents, either in money or time. This requires small scale reactions and a synthetic sequence which yields only the desired product in high yields. Yields are highest in a synthetic sequence that uses a minimum number of reactions, gives only the desired product and involves simple work-up procedures. Preferably this sequence should use the least costly deuterated reagents and introduction of deuterium near the end of the synthesis.

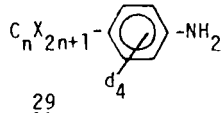
Our earilier work on developing better synthetic methods for alkylating 4-substituted alkoxybenzenes[18] provided good procedures for preparing the chain perdeuterated alkoxy intermediates **1**, **2** and **12** as shown in Figure 2. Chain perdeuterated 4-heptyloxyaniline **1** was

TABLE II

Required Deuterated Intermediates

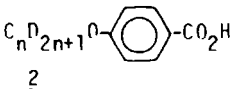


1

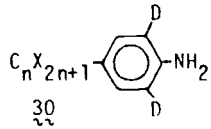


29

a. n=4, X=H
b. n=7, X=H
c. n=8, X=H
d. n=8, X=D

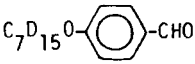


2

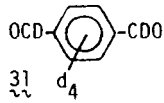


30

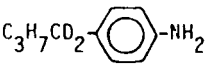
a. n=2, X=D
b. n=4, X=H
c. n=7, X=H



12



31



28

prepared by alkylation of 4-hydroxyacetanilide **7** with perdeuterated heptyl bromide (obtained from Merck Sharp and Dohme†) in the presence of base using anhydrous conditions followed by hydrolysis of the resulting amide **8**. Purified yields of 86 and 68% respectively were isolated. Similarly the chain perdeuterated 4-heptyl and octyl-oxybenzoic acids **2** were prepared by alkylating 4-hydroxybenzoic acid

†All perdeuterated alkyl halides were obtained from Merck and checked by NMR and mass spectra for isotope purity. No hydrogenated material could be detected.

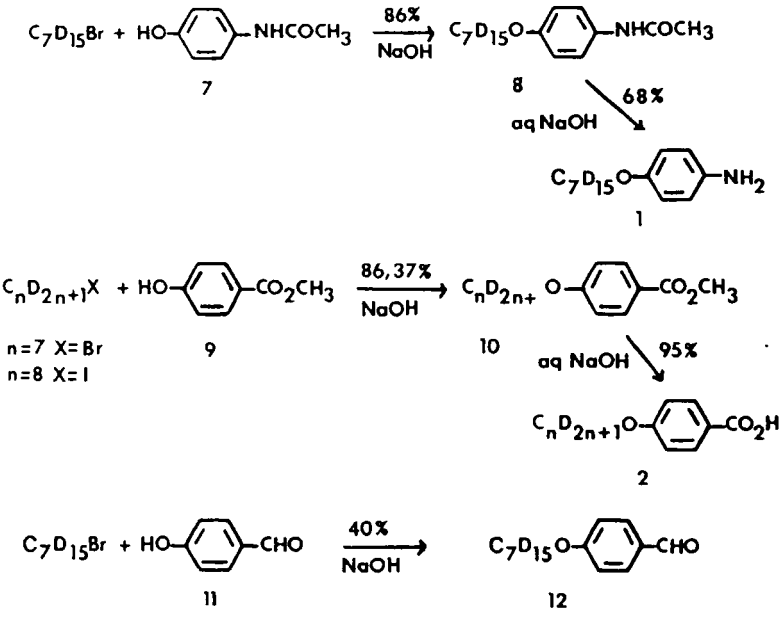


FIGURE 2 Synthetic methods for deuterated 4-substituted alkoxybenzenes.

methyl ester **9** followed by hydrolysis and the aldehyde **12** by alkylation of 4-hydroxybenzaldehyde **11**.

Initially, high pressure catalytic deuterium exchange in D_2O was investigated as a possible method for preparing the perdeuterated 4-alkylanilines in one step. Aniline-d_7 has been prepared by such an exchange in D_2O[19-22] and similar conditions have been used to prepare perdeuterated fatty acids.[23-26] Attempts were made to apply this method to 4-alkylanilines to try to exchange both the ring and chain protons simultaneously. However, no exchange seemed to occur as determined by mass spectrometry and at the high temperatures employed, a lot of tar was formed. Similar results were obtained using either propylbenzene or 4-propylacetanilide. Extensive studies of such catalytic deuterium exchanges on alkylbenzenes have been reported by Garnett's group.[27-30] These studies show that steric hindrance between the ortho aromatic protons and the chain protons does not favor catalytic deuterium exchange readily in the position ortho to the alkyl chain or in the chain itself. Some exchange did occur on both the ring and the chain but this was not complete. Exchange on the chain seems to decrease with increased distance from the ring. Consequently catalytic deuterium exchange as a synthetic route to perdeuterated 4-alkylanilines was abandoned.

Deuterium was incorporated either in the ring and/or the chain of 4-alkylanilines by synthesizing these anilines from either aniline or benzene using deuterated materials. Initially, aniline-d_5 was used to prepare ring-d_4-alkylanilines by the method diagrammed in Figure 3. The aniline was acylated to give acetanilide **13** which was then acylated again in a Friedel-Crafts reaction to the ketone **16**. A Wolff-Kishner reduction of this ketone gave the aniline **15**. Although this method allows for introduction of a perdeuterated chain or deuterium into the α-position, it suffers from a number of disadvantages. The maximum yield in the Friedel-Crafts reaction with non-deuterated materials is 50%.[31] 4-n-Heptylaniline-d_4 (**29b**) was prepared in this manner in an overall yield of 12.5% with only a 35% yield in the Friedel-Crafts reaction. Additionally, in order to reduce the ketone **16** in the Wolff-Kishner reaction with deuterium, all the reagents would have to be deuterated i.e. the hydrazine, KOH and water. This problem can be avoided by using a catalytic reduction to the alkylacetanilide **14** followed by basic hydrolysis but the low yield in the Friedel-Crafts reaction made it necessary to design a totally new synthesis.

A better method for preparing these 4-alkylanilines was developed by doing a Schmidt rearrangement on the 4-alkylbenzoic acid **20** to the aniline **19** (Figure 4). These acids are readily available in high yields by Friedel-Crafts acylation of alkylbenzenes **18** with oxalyl

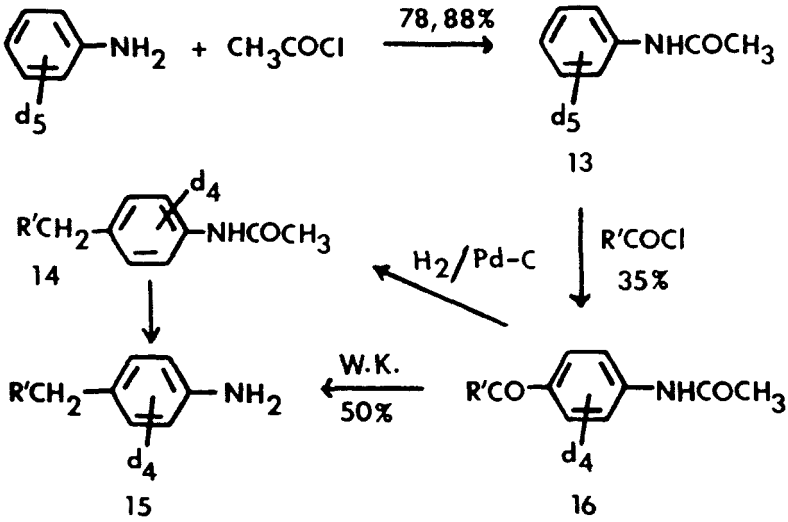


FIGURE 3 Method 1 for preparing ring deuterated 4-alkylanilines.

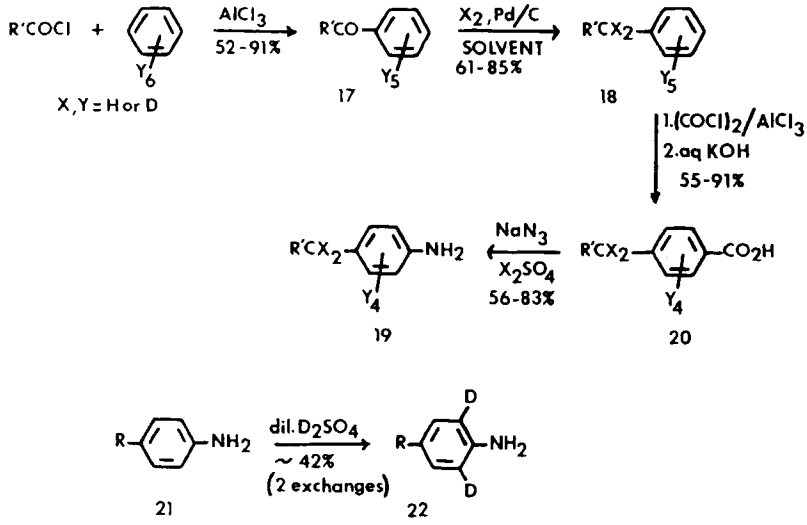


FIGURE 4 Method 2 for preparing deuterated 4-alkylanilines.

chloride[32] followed by basic hydrolysis of the acid chloride. The alkyl benzenes **18** were prepared from the ketones **17** by a catalytic reduction and the ketones through a Friedel-Crafts acylation of benzene. This method allows for deuterium incorporation in both the ring and the chain (either perdeuterated or deuterated in the α-position). All these reactions gave good yields of the desired product and required few manipulations in the work-up procedures. Initially, the formation of large amounts of precipitated K_2SO_4 in the Schmidt reaction during the work-up procedure produced a lower yield of the aniline **19** as it clung to the salt. This problem was avoided by using ammonium hydroxide for neutralization and a larger volume of H_2O.

Use of a catalytic reduction of the ketone presented a larger problem when deuterium was used. These catalytic reductions were done using a Parr apparatus when hydrogen was used. However, the storage tank for the hydrogen gas is relatively large on this equipment and would therefore require a large amount of expensive deuterium to fill and maintain the needed 50 psi. An even greater problem was that our Parr apparatus is regularly used for hydrogenations and we could not afford to have it tied up for deuterations only. Constant replacement of the hydrogen with deuterium and vice-versa would not only be costly but undoubtedly lead to isotope contamination. Therefore, a smaller tank set-up was designed to hold the deuterium gas. This was patterned after the Parr apparatus and attached to the

Parr shaker. It consists of a Whitey 150cc sample cylinder with 1/4″ female pipe threads **h** strapped to a wooden board **i** with pipe strapping **g** for stabilization (Figure 5). A needle valve **d** with 2-1/4″ male pipe threads was inserted on each side (**d**). A 1/4″ female pipe threaded cross **c** was added to one needle valve and a T connector with two 1/4″ female pipe threads and a 1/4″ Swagelok hose connector **k** on the other valve. To the cross **c** was added a large Monel process gauge **f** for accurate pressure reading of small amounts (pressure range = 0–100 in one psi divisions), a 1/4″ Swagelok 1/4″ hose connector with a male pipe thread **e** on one end and a 1/4″ needle valve with a hose connector on the other **b**. To the connector **k** was added a pressure gauge reading 0–100 psi in 2 psi divisions. Thick walled plastic tubing (diameter = 1/4″, thickness 1/16″) able to withstand at least 100 psi was used to connect this tank to an aspirator via **e** and a 3-way stopcock, to the Parr shaker holding a 250 ml Parr bottle via **a** and to a deuterium tank via **m**. Lecture bottles of deuterium are the best tanks to use on this equipment since they contain a large amount of gas under high pressure in a small volume. However, some suppliers have discontinued this size and offer only F tanks containing various amounts of deuterium. These F tanks have less deuterium in a large volume and therefore under less pressure so that the tank with the smallest amount of deuterium cannot be used for many reductions since total reduction of the ketone could not be obtained at pressures <25 psi.

A number of factors seemed to affect obtaining complete reduction of the ketone **17** to the alkylbenzene **18**. Reduction seemed to go easiest in acetic acid (or DOAc if D_2 was used) but this could not be separated from most of the alkylbenzenes by distillation. The acetic acid had to be neutralized to isolate the product. Complete reduction was achieved in absolute ethanol (or EtOD) if enough catalyst was used and it had a high activity. Old off-the-shelf catalyst gave poor results. Catalyst (10% Pd/C) obtained from Strem Chemicals Co. gave consistently good results; ~600 mg/0.01 mole was used. No

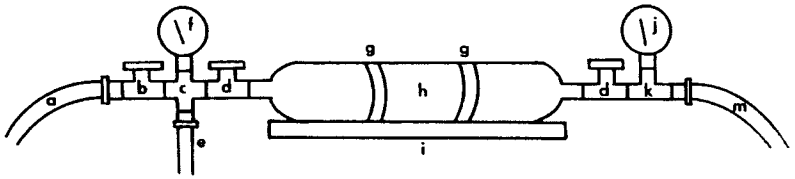
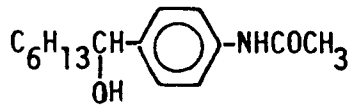


FIGURE 5 Catalytic deuteration apparatus.

extensive studies were done to determine if less of this more active catalyst could be used and still achieve complete reduction. Reduction of shorter chain ketones created a new problem. When the acetyl ketone **17** ($R = CH_3$) was reduced in ethanol, very low yields of ethylbenzene could be isolated. A very careful distillation of the reduction solution through a combination of Widmer and Vigreux columns without separation indicated than an azeotrope was formed between the alkylbenzene and the alcohol. This was true for other alcohols such as methanol as well. The problem was resolved by using tetrahydrofuran (THF) as the solvent. In one reduction of the ketone **17** with $R = CD_3$ in THF, no loss of β-deuterons seemed to occur. In a second run which had been sluggish because of a low deuterium pressure, some exchange seemed to occur as shown by ^{2}H-NMR. More reactions need to be done in THF to determine if deuterated THF needs to be used; it seems it should not be necessary.

Conceivably no solvent need be used with the acylbenzenes since they are liquids and excess ketone could be used as the solvent at least when the alkyl chain did not contain deuterium. However, two problems occurred when an attempt to do this was made. When no excess ketone was used, the mixture with the catalyst was too thick to shake well which is important for obtaining complete reduction and the acylbenzene and/or alkylbenzene caused the stopper used on the Parr apparatus to expand so much that it was difficult to remove from the bottle. The amount of solvent used was varied according to the amount of material to be reduced. Even the smaller 250 ml Parr bottle is too large for a 1-2g scale run so additional solvent was added to obtain adequate shaking. No effect on the reduction seemed to occur as a result of this dilution.

Reductions were done using an initial pressure of 50 psi. As deuterium was consumed as indicated on the bottle gauge, additional gas was added to maintain this pressure. Although the largest pressure drop was observed within the first hour, reduction was continued for another 16 hr to ensure completion. Incomplete reduction could be detected by TLC (in $CHCl_3$) by the appearance of a spot with $R_f \sim 0.42$ below that for the starting ketone with $R_f \sim 0.65$ and the alkylbenzene with $R_f \sim 0.78$ as well as by the appearance of a hydroxyl absorption in the IR spectrum. This is probably due to the presence of the α-hydroxy intermediate **25** (X = D Figure 6). Although this alcohol was not isolated in the reduction of the acylbenzenes, the alcohol **32** was obtained from an incomplete reduction of the corresponding α-ketone, purified by recrystallization and identified by



32

NMR and MS. TLC of this material also showed a spot with an R_f value < than that of both the starting ketone and the final product. During the course of these studies, Gray's group reported reducing the α-keto group of acylbiphenyls to the corresponding alkylbiphenyls containing a perdeutero chain using lithium aluminum deuteride (LAD).[33] However, this material was contaminated with small amounts of the corresponding olefinic intermediate **27** which was difficult to remove from the desired alkylbiphenyl. No such material was detected in these reductions with palladium but since these olefins are difficult to differentiate from the product, the presence of small amounts cannot be eliminated since no attempt was made to detect this intermediate by gas chromatography. Usually when TLC of the isolated material indicated that reduction was incomplete, it was repeated to obtain only the alkylbenzene.

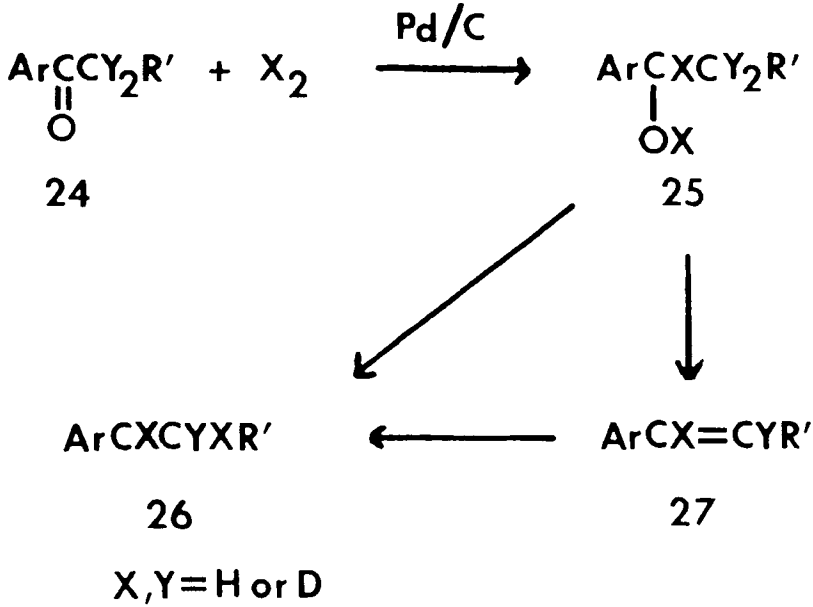


FIGURE 6 Possible mechanisms for catalytic reduction of aromatic α-alkylketones.

As long as the alkyl chain of the ketone contained the same hydrogen isotope as that added in the reduction i.e. X = Y (Figure 6) there was no need to be concerned about incorporation of hydrogen or deuterium into the β-position via the possible olefin intermediate **27**. However, when X ≠ Y incorporation can occur in the β-position if the olefin is an intermediate. In ^{2}H-NMR studies of the α-deuterated anils VI, additional chain deuterons were found. In one instance these were reported to be in the γ-position[11] but it is hard to imagine how deuterium would be incorporated in this position and not in the β-one. Possibly, these materials were contaminated with some impurity. Although some studies of the mechanism of reduction of alkyl α-ketones have been done, these were concerned with rate studies rather than identifying the intermediates.[34-36] Conceivably reduction could proceed directly from the alcohol **25** to the alkane **26**. Additional studies are necessary to resolve this problem.

Incorporation of only two ring deuterons into the 4-alkylanilines was accomplished by acid catalyzed exchange. Previous studies had shown that deuterons are incorporated ortho to the amino group in dilute D_2SO_4[37] but the results in concd D_2SO_4 are less well defined.[37,38] Dilute acid catalyzed exchange was tried using 4-*n*-butylaniline. Refluxing a solution of this aniline in 50% D_2SO_4 for 70 hr gave incorporation of deuterium of ~80% ortho to the amino group. No exchange ortho to the alkyl group could be detected by NMR. A second exchange increased this to 85%. Since the second exchange increased the deuterium content by only ~5%, only one exchange was used in subsequent reactions to aviod material losses. Deterium incorporation was not increased by using deuterated bases in the work-up procedure. A deuterium incorporation of 70-80% was found to be sufficient for broadline ^{2}H-NMR studies. The exchange time was reduced to 24 hr with no effect on the amount of exchange. As in the Schmidt reaction, yields were increased to 75-80% (purified) by using ammonium hydroxide rather than potassium hydroxide in the work-up procedure. All the ring-d_2 anilines required in this work were prepared in this manner.

When butylaniline was refluxed in concd H_2SO_4 for 17 hr, a lot of decomposition occurred but the isolated aniline showed ~47% deuterium incorporation in both positions. However, only about 9.7% of deuterium was incorporated ortho to the butyl group and 6.5% ortho to the amino group when the exchange was done at either room temperature or 60° for 24 hr. Extending this time to 48 hr (at room temperature) gave ~48.3% exchange ortho to the butyl group and ~55.0% ortho to the amino group. The difference between the two

positions might not be real considering the inaccuracy in determining these percentages. Such results indicate that exchange in concd D_2SO_4 is useless for incorporating either two or four deuterons into the aromatic ring.

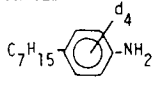
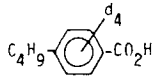
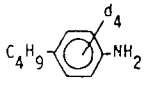
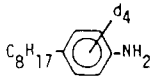
Incorporation of deuterons in the position ortho to the amino group in both dilute and concentrated acid suggests that at least some of the amino group remains unprotonated since the ammonium group is a meta director whereas the amino group is ortho-para directing. Additionally, the alkyl group is a ring activator and an ortho, para director. In dilute acid, the influence of the amino group seems to predominate but in concentrated acid, both the amino and alkyl groups seem to have an equal effect.

Various preliminary deuterium exchanges on possible aniline precursors and 4-substituted alkoxybenzenes were also tried. These indicated that synthetically useful exchange occurs only when a ring activating substituent is present. When two substituents were present, one which is a strong ring activator (o, p-director) and the other a strong deactivator (m-director), no exchange seemed to occur. For example, acid catalyzed exchange on either 4-alkoxybenzoic acid or benzaldehyde using deuterated acetic acid did not occur despite a literature report claiming the incorporation of two deuterons ortho to the alkoxy group in this acid under these same conditions.[39] Although several attempts were made to repeat this result, NMR showed no deuterium incorporation. Possibly, acetic acid is not a strong enough acid but concentrated D_2SO_4 might cleave the alkoxy group. As is generally true with aromatic electrophilic substitutions, when two ring activators were present with one much stronger that the other, the stronger one determined the location of the deuterium. Acid catalyzed exchange on both 4-alkylanilines and 4-bromophenols gave exchange ortho to the amino and hydroxy groups, respectively. No deuterium ortho to the other substituent could be detected. In order for deuterium exchange to be useful in the synthesis of deuterated compounds, it should be easy to do and have a high percentage of exchange. This seems best achieved by using a compound that contains a strong ring activator and no strong deactivating groups.

To obtain a maximum percentage of deuterium in the final product of a synthesis scheme also requires avoiding exchange of the incorporated deuterons with protons in reagents or solvents used in reactions following incorporation. This calls for some knowledge of reaction mechanisms and which protons are exchangeable. The isotropic purity of a few of the alkylanilines and a benzoic acid were estimated by NMR (Table III). Some ring protons were found in both positions in the aniline prepared via Friedel-Crafts acylation of

TABLE III

Hydrogen Exchange on 4-Alkyl-ring-d_4 Compounds

Compound	Method	Estimated (nmr) % Ring Protons
	1	9.25 ortho to R 11.1 ortho to NH_2
	2	4.8 ortho to R 4.8 ortho to CO_2H
	2 using H_2SO_4	0 ortho to R 42.8 ortho to NH_2
	2 using D_2O(FC) and D_2SO_4 (Schmidt)	0

deuterated aniline. Smaller amounts were found also in both positions in the acid used in the Schmidt reaction. When this acid was converted to the aniline in concd H_2SO_4, a large percentage of protons were found ortho to the amino group but none ortho to the alkyl group which conflicts with the equal distribution of deuterium observed in both positions when exchange was done on 4-n-butylaniline in concd D_2SO_4. When D_2O was used to process the Friedel-Crafts reaction and D_2SO_4 was used in the Schmidt reaction, no ring protons were detected. The difference between the percentages for the C_4 aniline and acid for the protons ortho to the alkyl group suggests that these protons might be due to some impurity.

Undoubtedly, the easily exchangeable amino acid protons were also exchanged in many of these reactions but any deuterons incorporated in this manner could exchange just as easily with protons when exposed to air. Partially deuterated amino and hydroxy groups were sometimes observed but never fully deuterated ones. Since these protons (or deuterons) were lost during conversion to the liquid crystal, it did not matter which isotope was present. However, the mesomorphic 4-alkoxybenzoic acids II and III with an acid deuteron were of interest for ^{2}H-NMR studies. These were prepared by hydrolysis of the acid chloride or ester with deuterated base or by

deuterium exchange in base while carefully protecting the product from air.

To conserve deuterated intermediates in these syntheses not all of those prepared were purified nor spectral data obtained. Generally, purification was done on all the intermediates in a new reaction scheme and spectral data obtained to establish that there were no problems. Preliminary studies with non-deuterated materials were also done to try to maximize the yields and to determine which intermediates had to be purified. Usually, the 4-alkylbenzoic acids and anilines were not purified whereas the ketones, alkybenzenes and the final mesomorphic compounds always were. Purified yields of the mesogens were lower than when purified intermediates were used but the overall yields were probably higher. Typical experimental procedures for all syntheses are given in the experimental section.

ANALYTICAL METHODS

Good methods for preparing deuterated compounds are not very useful without a means for determining the location of the deuterons and the amount. Mass spectrometry (MS) has the advantage of requiring only a very small amount of material whereas high resolution proton NMR can easily provide both the location and the number of deuterons. Initially, an MS-12 instrument was used for MS analysis but several problems were encountered. Thomas has indicated in his book on deuterated compounds that the use of MS to determine the amount of deterium incorporation requires the assumption that the ease of fragmenting the C-D bond is the same as that for the C-H bond i.e. there is no isotope effect.[40] In studying the mass spectra for HOAB-d_{30} and its intermediates, an isotope effect was observed (Table IV). Peak intensities for the M+2, M+1, M+, M−1, and M−2 peaks were determined for both the deuterated and non-deuterated compounds **33-35**. The spectra were expanded as much as possible using the visicorder scans to minimize errors in measuring the peak heights and then the relative (to M+ peak) intensities calculated. All three deuterated compounds showed no aliphatic protons in their NMR spectra. Yet in the two intermediates **33** and **34**, the M-1 peak was 15-20% larger in the deuterated materials than in the non-deuterated ones and the M-2 peak was 2-3% larger. In compounds **35**, the differences were 44 and 13%, respectively. These results suggest that the C-D bond is broken much easier in the mass spectrometer than the C-H bond. This discouraged any further use

TABLE IV

Mass Spectrometry Isotope Effect

Compound	Number	X	Relative Peak Heights M+2	M+1	M+	M-1	M-2
$C_7X_{15}O$-(C$_6$H$_4$)-NHCOMe	33a	H	0.028	0.200	1	0.037	0
	33b	D	0.023	0.168	1	0.187	0.021
		Δ[a]	-0.055	-0.032		0.150	0.021
$C_7X_{15}O$-(C$_6$H$_4$)-NH_2	34a	H	0.020	0.173	1	0	0
	34b	D	0.024	0.181	1	0.198	0.031
		Δ[a]	0.004	0.008		0.198	0.031
$C_7X_{15}O$-(C$_6$H$_4$)-N=N(→O)-(C$_6$H$_4$)-OC_7X_{15}	35a	H	0.099	0.349	1	0	0
	35b	D	0.091	0.337	1	0.436	0.132
		Δ[a]	-0.008	-0.012		0.436	0.132

[a]Relative peak height difference for X=H and X=D.

of mass spectral data for quantitative deuterium analysis. Qualitative analysis was possible, however. Parent peaks were observed for most of the deuterated compounds prepared. Major fragments often helped confirm the structures especially when compared to the spectra for the non-deuterated compounds. However, determining the peak intensities accurately with such high molecular weight compounds was difficult to do using the MS-12 instrument so these data, presented in Table V, are limited for making comparisons between the deuterated and non-deuterated compounds.

NMR proved to be much more useful for deuterium analysis than MS. Although a larger sample is required, most of this can be recovered. Analysis for deuterons by NMR is a negative analysis, i.e. the absence of protons is detected rather that the presence of deuterons. Thus a useful analysis requires both a knowledge of the location of the various protons in the corresponding non-deuterated compounds and large enough differences in chemical shifts for those protons that are to be replaced by deuterons so that they can be distinguishable from the remaining protons. NMR spectra were obtained for the corresponding non-deuterated intermediates and many of the anils prepared in this work. Detailed data are presented in Tables VI and VII. Nearly all of the 1,4-disubstituted intermediates gave an NMR spectrum which showed a well defined pair of doublets

TABLE V

Mass Spectral Data for Deuterated Versus Non-deuterated Compounds

	X	Method[1]	Parent Peak m/e (rel. intensity)	Major Fragment Peaks m/e (rel. intensity, identification)
$C_7X_{15}O$-C$_6$H$_4$-NHCOCH$_3$	H	RS	249	
	D	CD	264(27.0)	152 (20.33, H_2N-C$_6$H$_4$-OD), 111 (7.45), 110 (100), 109 (6.98), 108 (7.10), 66 (7.57) and 43 (12.97).
$C_7X_{15}O$-C$_6$H$_4$-NH_2	H	RS	206	
	D	CD	222(11.49)	111 (9.68), 110 (100), 109 (16.64) and 108 (8.35).
$C_7X_{15}O$-C$_6$H$_4$-N=N(O)-C$_6$H$_4$-OC_7X_{15}	H	CD	426	409 (M-15), 124 (22.79), 123 (HO-C$_6$H$_4$-NO), 108 (22.84), 107 (100, HO-C$_6$H$_4$-N), 93 (41.53), 69 (11.70) and 65 (14.53).
	D	RS	456	
$C_8X_{15}O$-C$_6$H$_4$-CHO[2]	H	CD	234(56.93)	123 (100), 122 (HO-C$_6$H$_4$-CHO, 88.98), 121 (HO-C$_6$H$_4$-C$\equiv$O$^+$, 62.86), 110 (18.74), 71 (37.87), 70 (24.93), 57 (63.97), 56 (21.62), 55 (40.84), 43 (80.50) and 41 (75.63).

TABLE V (*continued*)

	D	CD	251(63.6)	123 (DO-⟨⟩-CHO, 81.76), 122 (DO-⟨⟩-C≡O, 60.20), 94 (13.63), 82 (46.65), 80 (31.07), 78 (20.19), 77 (13.77), 66 (100), 65 (13.70), 64 (29.70) and 62 (48.59).
$C_8X_{17}O$-⟨⟩-CO_2CH_3	D	CD	281(44.93)	155 (19.03), 154 (10.47), 153 (DO-⟨⟩-CO_2Me, 100), 123 (11.49), 122 (70.61), 107 (14.19) 91 (15.20), 82 (12.16), 66 (25.90) and 62 (15.65).
$C_8X_{17}O$-⟨⟩-CO_2H	D	CD	267(34.82)	141 (26.59), 140 (11.55), 139 (DO-⟨⟩-CO_2H, 100), 122 (DO-⟨⟩-$C\equiv O^+$, 17.06), 107 (12.47), 82 (21.77) and 62 (21.70).
$C_8X_{17}O$-⟨⟩-COCl	H	CD	268(~8)	233 (C_8H_7O-⟨⟩-$C\equiv O^+$, 52.91), 121 (HO-⟨⟩-$C\equiv O^+$, 100), 94 (10.47), 83 (12.91), 71 (29.65), 70 (26.05), 69 (23.37) and 65 (17.09).
	D	CD	285(26.7)	281 (22.2), 251 (8.9), 250 ($C_8D_{17}O$-⟨⟩-$C\equiv O^+$,

TABLE V (*continued*)

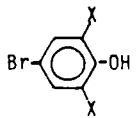
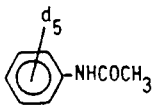
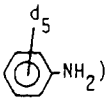
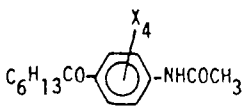
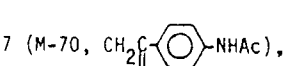
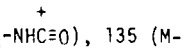
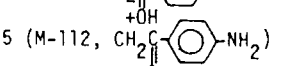
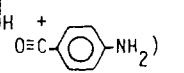
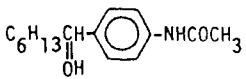
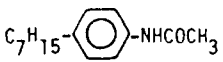
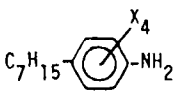
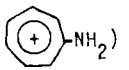
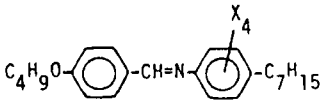
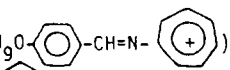
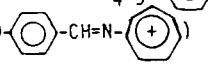
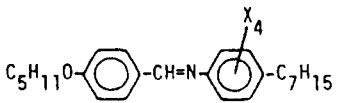
			287(8.9)	68.9), 249 (100), 248 (40.01), 243 (48.9), 122 (DO-⟨⟩-C≡O, 97.35), 96 (15.79), 94 (10.15), 82 (24.02), 80 (22.62) 78 (19.38), 66 (53.84), 64 (32.83) and 62 (40).
	H	CD	174(66.13)	93 (31.05, M-Br), 69 (8.47), 65 (82.66),
			72(63.31)	64 (14.11), 63 (25.81), 62 (14.52), 53 (11.69), 50 (12.90), 39 (55.24), 38 (23.79) and 37 (14.11).
	D	RS	176,174	
		RS	140	122 (M-18), 98 (M-42, )
	H	RS	247	190 (M-57, $C_6H_{13}CO$-Ph), 177 (M-70, ), 162 (M-85, ), 135 (M-112, ) and 120 (M-127, )
	D	RS	251	194 (M-57), 181 (M-70), 166 (M-85), 139 (M-112), 124 (M-127), 96

TABLE V (*continued*)

		RS	249	165, 164 (M-C_6H_{13}), 106, 94, 77.
	H	RS	233	192, 148, 107, 106, 78.
	H D	RS RS	191 195	106 (M-85, ) 110 (M-85)
	H	RS	351	266 (M-85, ) and 210 (M-141, )
	D	RS	355	270 (M-85) and 214 (M-141)
	H D	RS RS	365 369	280 (M-85) and 210 (M-155). 284 (M-85) and 214 (M-155)

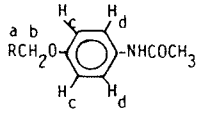
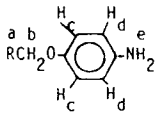
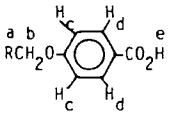
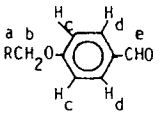
[1]RS = data obtained from a recorder scan.

CD = data obtained from a computer printout.

[2]This C_8 aldehyde was prepared as well as the C_7 homolog but never converted to a mesogen. Mass spectra data was obtained only for the C_8 homolog.

TABLE VI

NMR Data for 4-Substituted Alkoxybenzenes

Compound	δ[1]	Peak Multiplicity[2]	Proton Identification	J^3(Hz)
	7.90	s	e	--
	7.38	d	d	9.0
	6.80	d	c	9.0
	3.90	t	b	6.0
	2.10	s	f	--
	2.0-0.68	m	a	--
$CD^4(A)^5$				
	6.25-6.73	m	c,d	--
	3.76	t	b	6.0
	3.14	s	e	--
	2.0-0.70	m	a	--
CT(A)				
	9.50	s	e	--
	8.08	d	d	9.0
	6.90	d	c	9.0
	4.00	t	b	6.0
	2.00-1.60	m	a	--
CT(E)				
	9.56	s	e	--
	7.72	d	d	9.0
	6.89	d	c	9.0
	3.95	t	b	6.0
	2.0-0.68	m	a	--
CT(A)				

1. δ = Chemical shift in ppm.
2. s = Singlet, d = doublet, t = triplet, m = unresolved multiplet.
3. J = Coupling constant.
4. CD = $CDCl_3$, CT = CCl_4 used as solvents.
5. A = Varian A-60, E = Varian EM-360 instruments used.

TABLE VII

NMR Data for Intermediates for the Synthesis of 4-Alkylanilines

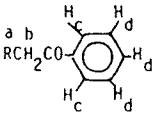
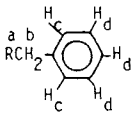
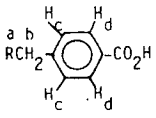
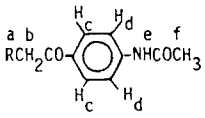
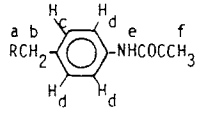
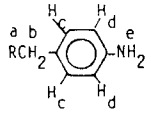
Compound	δ[1]	Peak Multiplicity[2]	Proton Identification	J^3(Hz)
	7.90	m	c	--
	7.40	m	d	--
	2.89	t	b	7.0
	2.0-0.7	m	a	--
$CT^4(D)^5$				

TABLE VII (*continued*)

Compound	δ[1]	Peak Multiplicity[2]	Proton Identification	J[3] (Hz)
	7.08	s	c,d	--
	2.58	t	b	7.0
	1.90	m	a	--
CT(E)				
	8.00	d	d	8.0
	7.20	d	c	8.0
	2.62	t	b	7.0
	2.0-0.60	m	a	--
CT(E)				
	8.20	s	e	--
	7.88	d	c	8.5
	7.52	d	d	8.5
	2.90	t	b	7.0
	2.18	s	f	--
	1.9-0.70	m	a	--
CD(A)				
	7.93	s	e	--
	7.33	d	c	8.5
	7.02	d	d	8.5
	2.53	t	b	7.0
	2.09	s	f	--
	1.88-0.61	m	a	--
	6.78	d	c	8.5
	6.47	d	d	8.5
	3.24	s	e	--
	2.42	t	b	7.0
	1.85-0.68	m	a	--
CT(A)				

1. δ = Chemical shift in ppm.
2. s = Singlet, d = doublet, t = triplet, m = unresolved multiplet.
3. J = Coupling constant.
4. CD = $CDCl_3$, CT = CCl_4 used as solvents.
5. A = Varian A-60, E = Varian EM-360 instruments used.
6. Peaks identified by comparison with Varian curve no. 239 for p-acetotoluidide ref. 42.

with J = 8.5-9.0 Hz for the aromatic protons. The ring substituents in these compounds affected the chemical shifts of these protons giving the order for protons ortho to CO_2H (8.08-8.00δ) > ketone (7.90-7.88) ≃ CO_2Me (7.83) > CHO (7.72) > NHCOMe (7.52-7.33) > RO ≃ -S- (6.90-6.75) > NH_2 (6.47-6.25).† When two substituents with nearly equal chemical shifts (ex RO and NH_2) were present, these two doublets overlapped making it difficult to differentiate the aromatic protons. When only one substituent was present, two complex multiplets were sometimes observed. In the keto benzenes, these could be differentiated by chemical shift and the different proton integrals, whereas in the alkylbenzenes the aromatic protons appeared as a singlet. This, however, did not create a serious problem since these protons could be differentiated later when the monosubstituted benzene was converted to a disubstituted compound. The methylene group in the alkyl chain which was adjacent either to an oxygen atom (δ4.00-3.76), a ketone group (2.90-2.89) or a benzene ring (2.62-2.42) always occurred as a triplet with J = 6-7 Hz. The remaining aliphatic chain protons occurred as an unresolved complex multiplet in the 2.0-0.60δ region.

Replacement of protons in these intermediates with deuterons caused total loss of the peak assigned for these protons in the NMR spectrum when 100% replacement was achieved. Partial exchange gave a peak for these protons but at a decreased intensity. Additionally, ring deuteration affected the splitting pattern of the aromatic protons. When only two protons were exchanged in a high percentage as when 4-n-butylaniline was exchanged in dilute H_2SO_4, one peak was observed for those protons ortho to the alkyl group and a doublet for those remaining protons ortho to the amino group. However, when less exchange occurred as when this aniline was treated with concentrated sulfuric acid, two sets of triplets were observed. One would expect a combination of the doublet observed when both sets of protons are present plus the singlet observed when one set is completely replaced by deuterium but apparently there is a limit to how much deuterated material can be present to be able to see this splitting as a triplet. Such an effect provided another indicator for the amount of exchange taking place. An approximate percentage of deuterium

†Since the chemical shifts for the protons ortho to the amino and methoxy groups were so similar, the chemical shift for protons ortho to the amino group (6.40δ) in 4-chloroaniline were compared with that for the protons ortho to the methoxy group (6.75) in 4-chloroanisole for help in making these assignments.

incorporation was determined by comparing proton integrals for those exchanged with those not exchanged. This assumes, of course, that no exchange occurred with the reference protons. The accuracy of these percentages is not high when the peak is small as would be the case when say 95% of the protons have been replaced with deuterons. There is also the problem that impurities can absorb in the same region. For example, $CDCl_3$ which is often used as a solvent for obtaining NMR spectra usually contains small amounts of $CHCl_3$ which shows a singlet at 7.25 in the aromatic proton region. Thus, use of this solvent can give an inaccurate percentage for deuterons incorporated into the aromatic ring. This problem was avoided by using CCl_4 as the solvent.

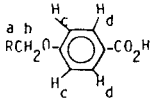
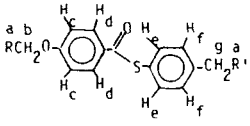
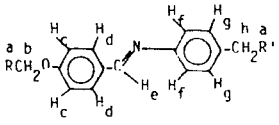
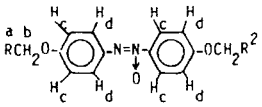
Those intermediates and mesogens prepared using a perdeuterated alkyl halide showed no detectable protons for the aliphatic chains which indicated that no exchange occurred in the syntheses of these compounds. The deuterium purity was not so high, however, in the 4-alkylanilines. This is because the ring deuterons are more readily exchanged under some of the conditions used in the synthetic scheme. Additionally, as mentioned earlier, incorporation of deuterium into the ring by acid-catalyzed exchange was never 100%. NMR proved very useful in determining which aromatic protons were exchanged in the reaction by comparing the proton integrals for the two aromatic proton absorptions. To determine if any exchange had occurred on the more intense absorption, its integral was compared with that for the α-methylene group and found to be essentially the same suggesting that no detectable exchange had occurred. This is how the percentages were estimated for materials listed in Table III.

Although the isotropic purity of the α-methylene protons could be estimated, this was not as accurate since the triplet is broader and therefore less intense than the aromatic doublets. Small percentages of isotropic contamination in the remaining alkyl chain could not be determined because of the complex multiplet which occurs for these protons. As mentioned earlier, ^{2}H-NMR suggested that some contamination might have occurred.

Even though no change in isotropic content was expected in the synthesis of the mesogens from the deuterated intermediates, NMR spectra were obtained to both confirm their structure and purity (see Table VIII for spectra for the protonated anils). Since these contain a combination of two ring components, the spectra were more difficult to intepret although most protons could be differentiated from each other. It was not always easy to assign all the aromatic peaks. This was achieved, however, by comparing spectra of a wide variety of

TABLE VIII

NMR Data for Non-deuterated Mesomorphic Compounds

Compound	Chemical Shift (δ)	Peak[1] Multiplicity	J(Hz)	Proton Identification
	8.06	d	9.0	d
	6.90	d	9.0	c
	4.00	t	6.0	b
	2.0-1.5	m	--	a
	7.91	d	9.0	d
	7.35	d	8.0	f
	7.10	d	8.0	e
	6.83	d	9.0	c
	3.95	t	6.0	b
	2.62	t	8.0	g
	2.0-0.60	m	--	a
	8.31	s	--	e
	7.75	d	9.0	d
	7.01	s	--	f,g
	6.80	d	9.0	c
	3.91	t	6.0	b
	2.58	t	7.0	h
	2.0-0.70	m	--	a
	8.20	d	9.0	d,d'
	6.83	d	9.0	c,c'
	3.95	t	5.5	b
	2.0-0.68	m	--	a

[1] s = Singlet, d = doublet, t = triplet.

[2] See Table IX for more details.

intermediates with those for an even wider set of mesogen curves. Before this collection was available, the aromatic peaks for the thiols, 4-alkylphenols and the thioesters were incorrectly assigned.[17] Detailed data for the intermediates discussed in this paper are presented in Tables VI and VII and for mesogens in Table VIII. A discussion of the chemical shift assignments for the ring protons in the thiols and thioesters will be discussed in a later paper.

Although the ring protons appeared as a set of two doublets in the spectrum for 4-alkylanilines, in the anil these protons became equal and occur as a singlet at ~7.01δ due to the effect of the imine double bond on the chemical shifts. This made it impossible to determine in which position the deuterons were located and also made it more difficult to estimate the amount since this singlet occurred near the doublet for the aromatic protons ortho to the alkoxy group on the aldehyde ring. Despite this, a reasonable estimate could be made as

long as $CDCl_3$ was not used as the solvent. The deuterium content estimated from the NMR spectrum obtained for the anils always agreed with that obtained for the precursor anilines.

The NMR spectrum for HOAB-d_{15} showed an additional splitting (Figure 7a) of the aromatic doublets from that observed for the non-deuterated material (Figure 7b). Both these curves were obtained using a Varian A-60 instrument but the HOAB-d_{30} curve had been obtained using $CDCl_3$ as the solvent whereas the curve for HOAB had been done in CCl_4. Initially, it was thought that this additional splitting was caused by the removal of some long distance ring chain coupling but the J constants for this new splitting is not the same for both sets of peaks. Therefore, it represents a difference in chemical shifts rather than a coupling between protons. These different shifts are due to the different effect of the N and the N → O on the ring protons. It was difficult to understand, however, why this did not occur in the spectrum for the protonated compound as well. To try to resolve this problem, both spectra were rerun in CCl_4 using a Varian EM-360 instrument since we no longer had the A-60. However, this new splitting was not observed in either sample (Figure 7c). When these samples were run again in the same manner using $CDCl_3$ as the solvent, the new splitting was observed for the proton doublet in the 8.2δ region but not for the doublet at 6.9δ (Figure 7d). This splitting was finally observed in both doublets when the curves were run in $CDCl_3$ on the Varian FT-80 instrument (Figure 7e).† Table IX presents the detailed data along with peak assignments. This data indicates that in $CDCl_3$ there is not only a difference in chemical shifts between the protons on rings B and C but that this difference is larger for the protons ortho to the azo group (i.e. d and d′) than those ortho to the alkoxy group (i.e. c and c′) as one would expect. This data also indicates that these differences occur only in $CDCl_3$ and that the resolution of the EM-360 instrument is not large enough to show the smaller additional splitting in the 6.9δ doublet.

Infrared spectra were routinely obtained on these deuterated compounds to determine if the proper compound had been prepared. When these were compared with curves for the corresponding hydrogen compounds interesting differences were observed. Some of these were useful in analyzing these compounds for deuterium content. The perdeuterated chains were easily detected by the presence

†Since a deuterated probe is needed to obtain a curve on the FT-80, CCl_4 was not tried.

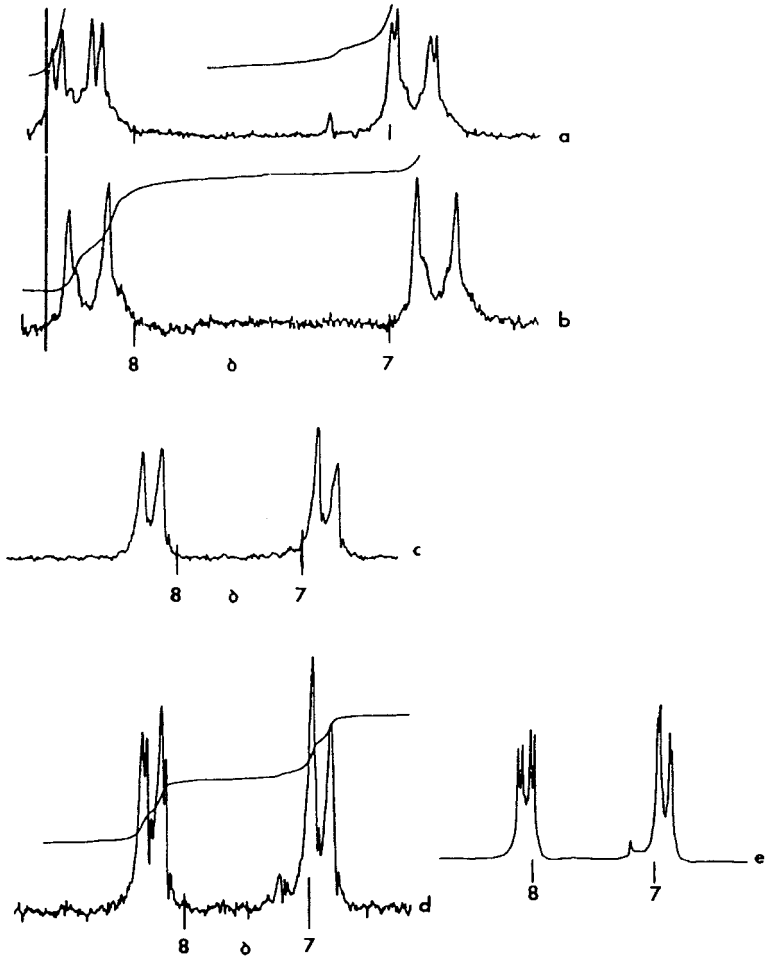
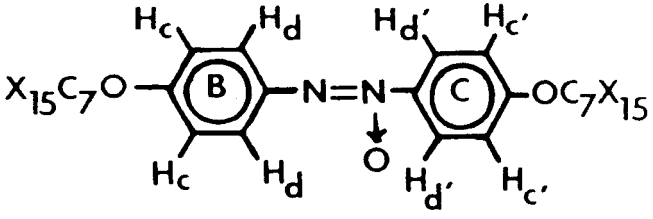


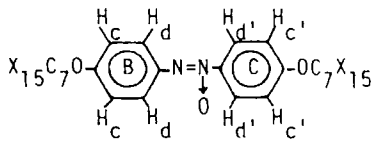
FIGURE 7 NMR spectra for



a. X = D in $CDCl_3$, A-60. b. X = H in CCl_4, A-60. c. X = H or D in CCl_4, EM-360. d. X = H or D in $CDCl_3$, EM-360. e. X = H or D in $CDCl_3$, FT-80.

TABLE IX

NMR Data for Aromatic Protons for



X	Solvent[1]	Instrument[2]	Chemical Shift (δ)	Peak Multiplicity[3]	J(Hz)	Proton Identification
H	CT	A	8.20	d	9.0	d,d'
H or D	CT	E	6.83	d	9.0	c,c'
D	CD	A	8.25	d	9.2	d'
H or D	CD	F	8.21	d	9.2	d
			6.92	d	9.2	c'
			6.90	d	9.2	c
H or D	CD	E	8.28[4]	d	9.0	d
			8.23[4]	d	9.0	d'
			6.90	d	9.0	c,c'

[1] CT = CCl_4, CD = $CDCl_3$

[2] A = A-60, E = EM-360, F = FT-80 Varian.

[3] d = Doublet.

[4] The accuracy in measuring such small differences in δ on an EM-360 curve is not as high as on A-60 or FT-80 curves.

of two sharp and intense C-D peaks at 2230 and 2120 cm^{-1} (Figure 8b). These occurred in the starting perdeuterated halides and acids and persisted without change through a synthesis. However, the shorter perdeuterated ethyl chain showed a more complex multiplet at 2230, 2180, 2130 and 2090 cm^{-1} (Figure 8a). This C-D absorption was too weak to be observed in the α only deuterated anilines. Additionally, a perdeuterated chain eliminated the aliphatic C-H absorptions at 2900-2000 cm^{-1} leaving only weak aromatic C-H absorptions or none at all when the ring was also deuterated.

The effect of deuterons on the aromatic ring absorptions was less well defined than on the chain. Changes were sometimes observed in the aromatic ring vibrations in the 1600 cm^{-1} region. Often a doublet occurred at 1600 and 1580 cm^{-1} and sometimes a shift occurred to a lower frequency in ring deuterated compounds. In the ring deuterated anilines **15**, two peaks were observed at 1620 and

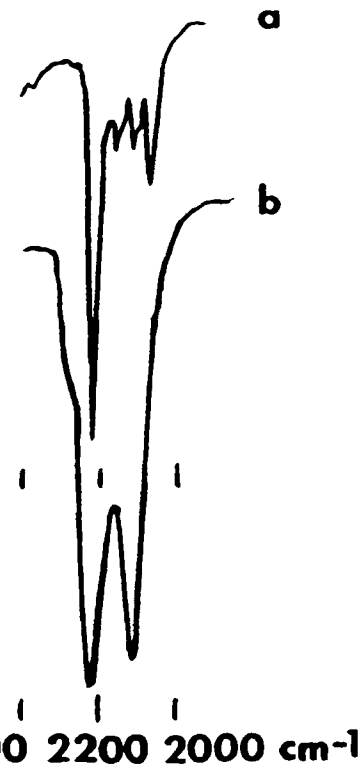


FIGURE 8 Infrared spectra (films) for perdeuterated alkyl chains in the 2200 cm^{-1} region (C-D stretch).

1590 (weaker) cm^{-1} whereas the non-deuterated compound showed only one peak at 1620 cm^{-1}. Spectra for the chain only deuterated alkyl anilines did not show this doublet. The presence of a doublet in this region did not mean, however, that the ring was deuterated. Other intermediates showed a doublet in this region for both the protonated and deuterated samples. For example, the IR spectra for the acids **20** with or without deuterium in the ring and/or the chain showed a doublet at 1600 and 1570 cm^{-1}.

Since several deuterated MBBA compounds were prepared containing deuterium in different positions on the aniline ring, the IR spectra of these compounds (VIa, VIIa and VIIIc) along with that for the non-deuterated material were studied in more detail using a Perkin-Elmer 283 instrument which provides better resolution than a routine analysis instrument. In the 3000 cm^{-1} region (C-H stretch, Figure 9) changes were observed in the intensity of some of the peaks. The weak doublet at ~2865 and ~2855 cm^{-1} showed a decreased intensity of the 2855 peak in the α-deuterated compound VIa (Figure 9b) but remained constant in the two ring deuterated compounds suggesting that this peak is at least partially due to chain C-H stretching. The intensity of the 2925 peak in the 2955, 2925 cm^{-1} doublet also decreased in this compound. Again no change was observed in the ring deuterated compounds (Figure 9c and d).

Obvious differences were also observed in the 1600 cm^{-1} region (in-plane ring vibrations, Figure 10). In MBBA, a poorly resolved intense doublet of equal intensities occurred at ~1608 and 1600 cm^{-1} flanked by two sharp and intense (but weaker) peaks at ~1628 and 1575 cm^{-1} (Figure 10a). In the α-deuterated compound (Figure 10b), the intensity of the 1608 cm^{-1} peak decreased whereas in the ring d_2 compound VIIIc (Figure 10c), the 1600 cm^{-1} peak decreased in intensity. This latter peak disappeared altogether in the ring-d_4 compound VIIa (Figure 10d) and the flanking peaks were less intense.

Obvious changes also occurred in the fingerprint region of all the IR spectra observed for the deuterated compounds. Differences were, of course, more obvious with an increasing number of deuterons. Generally, spectra became simpler but no attempt was made to analyze this region because of its complexity. Although the incorporation of deuterons into a compound causes obvious changes in their IR spectra, this method is not as useful for deuterium analysis as NMR. The number incorporated is difficult to determine, there is a lot of peak overlapping, and enough is still not yet known to assign peaks. However, since IR is often one of the first analytical tools used on a new compound for structure identification, it can, in many

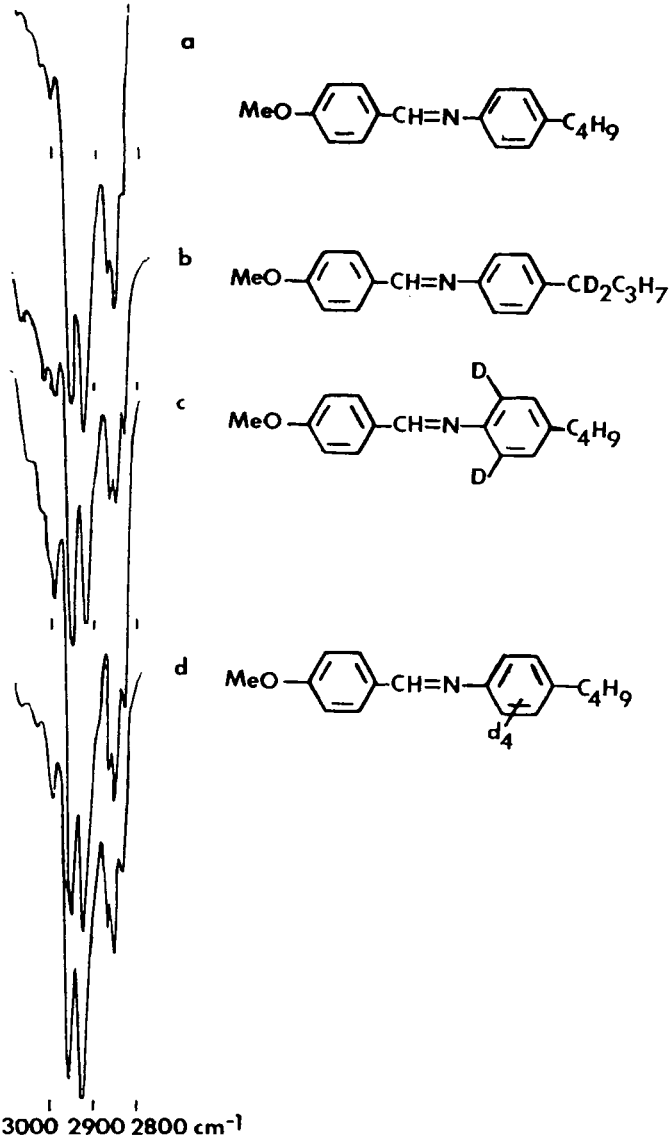


FIGURE 9 Infrared spectra (films) for deuterated MBBA Mesogens in the 3000 cm^{-1} region (C-H stretch) determined using a PE-283 instrument.

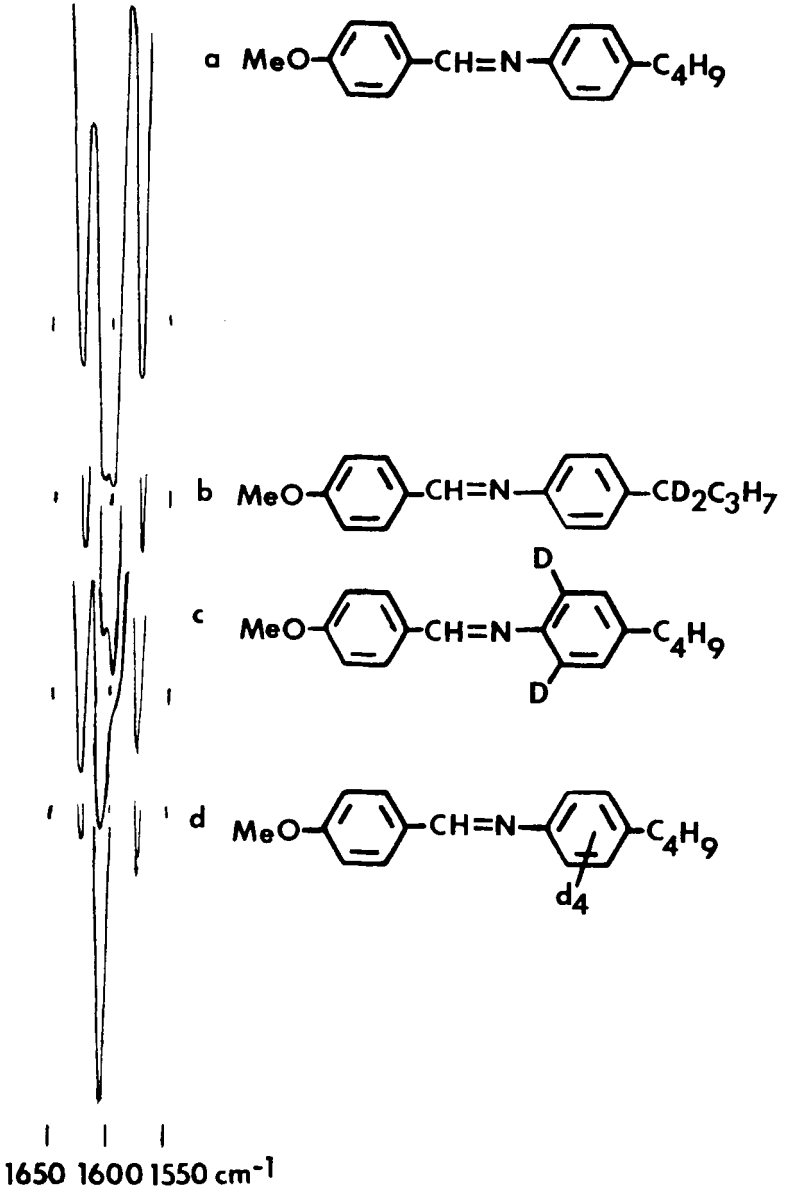


FIGURE 10 Infrared spectra (films) for deuterated MBBA mesogens in the 1600 cm^{-1} region (in-plane vibrations) determined using a PE-283 instrument.

instances, give a preliminary idea as to whether deuterium has been incorporated.

TRANSITION TEMPERATURES

A routine check of the transition temperatures of the deuterated mesogens containing a large number of deuterons indicated that these often differed from those found for the non-deuterated materials (Table X). However, this could be due to a difference in the purity of these compounds. Often the deuterated mesogens were not as extensively purified as the non-deuterated materials to avoid large losses. In order to determine if an isotope effect was present, samples of equal purity of both the deuterated and non-deuterated materials of the same mesogen were needed as well as a means for accurately determining these purities. The thioester, $\bar{7}$S5 was chosen since it can be purified by chromatography. High pressure liquid chromatography (HPLC) was used to determine the purities and to purify the deuterated compound. (The non-deuterated material was found to be sufficiently pure.) It has the advantage of requiring only small amounts of materials with minimum losses. These HPLC results are presented in Table XI. The estimated purities were 99.94% (H) and 99.95% (D). Three mesophase transitions were studied. The temperatures observed for $\bar{7}$S5 (Cd_{15}) were all 1.3-1.5° lower than those observed for $\bar{7}$S5. A comparison of the data for $\bar{7}$S5 (Cd_{15}) before and after chromatography shows a difference only in the melting temperatures. Thus, even in the recrystallized material, this isotope effect could be detected. That such an effect occurs in $\bar{7}$S5 does not mean, however, that it also occurs in other deuterated materials.

Gray and Mosely have reported observing isotope effects on transition temperatures in a number of deuterated biphenyl compounds.[43] Unlike $\bar{7}$S5 (Cd_{15}), no change in the melting transitions were observed in these compounds. Transition temperatures were observed to be $\pm$0.1-1.5° different from those for the hydrogen compounds. Although Gray and Mosely felt that the difference in polarizability of deuterium compared with hydrogen probably contributes to this isotope effect, they could not explain why both (+) and (−) effects were observed. They also indicated that since this effect is observed in ring as well as chain deuterated mesogens, Marcelja's explanation that it is caused by the effect of deuteration on the energy differences between the *trans* and *gauche* conformers of the alkyl chains[44] was eliminated.[45] Clearly, more studies are needed before an explanation can be provided for these seemingly conflicting data.

TABLE X

Transition Temperatures (°C) for Deuterated Mesogens[1]

Compound	X	Y	S	S_B	S_C	S_A	N	I
$C_7X_{15}O$-⟨⟩-CO_2Y	H	H			93-94		101-102	150-151
	D	D			88.1-89.6		92.9-94.1	141.5-142.2
$C_8X_{17}O$-⟨⟩-CO_2Y	D	D			99.6-100.6		105.5-105.8	145.6-147.2
	D	D			96.7-98.5		102.5-103.0	140.5-142.9
$C_7X_{15}O$-⟨⟩-N=N(→O)-⟨⟩-OC_7X_{15}	H				69.0-70.6		90.9-91.0	121.9-122.1
	D				62.0-73.7		93.5-93.6	121.4
$C_7X_{15}O$-⟨⟩-C(=O)-S-⟨⟩-C_5H_{11}	H				(36.5)[2]		50.7-51.7	82.6-82.7
	D				(35.0)		52.0-53.1	81.3
$C_8X_{17}O$-⟨⟩-C(=O)-S-⟨⟩-C_5H_{11}	H		(31.1-31.3)		(56.0-56.3)	58.0-58.6	62.7-63.5	86.5
	D				(53.5)		59.0	82.8-83.0
C_4H_9O-⟨⟩-CH=N-⟨Y_4⟩-C_8X_{17}	H	H	(12.4-12.6)	37.5-38.0		48.2-48.3	62.1	78.5-78.7
	D	D	(14.4-14.6)	35.5-36.4		50.4-50.6	64.1-64.2	78.3-78.5
			(14.7)	35.6-36.2		49.6-50.0	63.4-63.5	78.0-78.1
$C_7H_{15}O$-⟨⟩-CH=N-⟨Y, Y⟩-C_4H_9	H	H	32.6	--	63.9	65.2	74.5	76.5[3]
	H	D	--	--	63.0	64.2	74.0	76.1

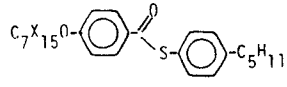
TABLE X (*continued*)

$C_7X_{15}O$-⟨⟩-CH=N-⟨⟩-C_5H_{11}	H	H	~21	59.1-59.3	64.6-65.0	68.7-68.9	79.9-80.0	83.5-83.7
	D	H		30.6-31.0	58.9	59.8	76.9	81.7-81.8
$C_7H_{15}O$-⟨⟩-CH=N-⟨⟩-C_7H_{15} (Y)	H	H	33.2	51	65.4	70.3	83	84[3]
	H	D	--	53.9	68.6	71.2-71.3	83.5	83.5-83.7
$C_5H_{11}O$-⟨⟩-CH=N-⟨⟩-C_7H_{15} (Y_4)	H	H	29.2	37.6	52.6	55.9	65.7	78.0
	H	D	19.8-21.3	38.5	53.2-53.6	56.2	64.9	78.8

1. Not all transition temperatures were determined for the deuterated materials.
2. ( ) indicates a monotropic transition.
3. Data taken from ref. 47.

TABLE XI

Transition Temperatures (°C) for



X	Purity	S_C	N	I
H	99.94	(36.5)[1]	50.7-51.7	82.6-82.7
D	99.75[2]	(35.0)	52.0-53.1	81.3
D	99.95	(35.0)	49.4-50.5	81.2-81.3
Difference		1.5°	1.3°	1.4°

1. ( ) indicates a monotropic transition.

2. Recrystallized material.

EXPERIMENTAL

All perdeuterated halides were obtained from MSD Isotopes, St. Louis, Missouri, Linde deuterium was used and other deuterated reagents were obtained from either MSD or Aldrich Chemical Company. Organic extracts were dried over anhyd Na_2SO_4 followed by Linde No. 4A molecular sieves. Anal-Tech silica gel GHLF 2.5 × 10 cm Uniplates® (250μ) and UV light were used for TLC. Melting points were determined using a Thomas-Hoover apparatus and are corrected.

A Perkins-Elmer model 700 or a Pye Unicam 3-200 IR instrument was used to obtain routine IR spectra. NMR data were collected using a Varian A-60 (A), EM-360 (E) or FT-80 (F) instrument with TMS as an internal standard using either $CDCl_3$ (CD) or CCl_4 (CT) as the solvent. Mass spectral (MS) data were collected using a Associated Electronics Industries Model MS-12 at 70 eV. Computer printouts were obtained when possible but accurate peak intensities for high m/e parent peak groups could not be obtained.

Transition temperatures were determined using a Leitz-Wetzler ortholux or a Leitz Laborlux 12 Pol polarizing microscope equipped with a calibrated, modified Mettler FP-2 heating stage at a rate of 2°/min. HPLC was done using a Perkin-Elmer instrument consisting of a series 3B microcomputer controlled pump module with a LC-75 UV (253.2nm) detector and autocontrol, a Sigma 10B data control

station and Rheodyne 7105-7110 injection valves with pneumatic actuators. An octadecylsilane/silica gel (C-18) stationary phase with 10mm particles was used for both analytical (PE 0258184, 0.26 × 25cm) and preparative (PE 80007050, 1.6 × 25cm) work. Samples were applied to the column in acetone and eluted with CH_3CN. A flow rate of 2 ml/min at 34° was used for analytical runs [R_t = 3.89 min for $\bar{7}S5$ (Cd_{15})] and 15 ml/min for preparatory work (R_t = 7.55 min). The central part of the peak at R_t = 7.55 was collected as the purified sample. The maximum column capacity for preparatory work was 55 mg.

NMR peak assignments for protons in these deuterated compounds are given in Tables VI-IX, MS data in Tables IV and V and transition temperatures for mesogens in Table X.

4-*n*-Heptyl-d_{15}-oxyacetanilide, 8

A soln of 3.89g (25.8 mmoles) of 4-hydroxyacetanilide, 1.03g (25.8 mmoles) NaOH, 6.62g Linde molecular sieves no. 4A in 25 ml each of anhyd benzene and freshly distilled DMF was refluxed for 1 hr using a Dean-Stark trap. *n*-Heptyl-d_{15}-bromide was added dropwise in 15 min and refluxing continued for 17 hr. The insoluble solids were removed from the hot rxn mixture by filtration through glass fiber filter paper and washed with ϕH. The solvent was removed from the filtrate *in vacuo* to give 8.57g of the crude product which was recrystallized from MeOH to give 4.40g (64.7%) of the desired anilide **10**: mp 77-86°; IR ($CHCl_3$) 3300, 3400 (wk d, NH); 2230, 2120 (med d, C-D) 1670 (str s, amide C=O); 1600 (wk s, Ar) and 1510 cm^{-1} (str s, Ar). A second crop (1.43g) was obtained from the filtrate to give a total yield of 85.7%. A small sample was recrystallized 2 more times to give an analytical sample: mp 84-86°; NMR showed no C_7H_{15} protons.

4-*n*-Heptyl-d_{15}-oxyaniline, 1

A soln of 5.70g (21.6 mmoles) of 4-*n*-heptyl-d_{15}-oxyacetanilide and 19.0g NaOH in 38 ml EtOH and 12 ml H_2O was refluxed 4 hr, poured onto ca 150 ml crushed ice and extracted with 3 × 100 ml Et_2O. The Et_2O layer was dried, filtered and the filtrate concentrated *in vacuo* to dryness to give 4.20g (88.4%) of crude product. Distillation of this material at 143° (1.5 mm) gave 3.27g (68.3%) of the desired aniline **1**: mp 43-46°, IR ($CHCl_3$) 3350 (wk, NH); 2230, 2120 (med d, C-D), 1610 (med s, Ar), 1510 (str s, Ar) and no C=O, and NMR showed no C_7H_{15} protons.

4,4′-*n*-*Bis*(heptyl-d_{15}-oxy)azoxybenzene, I

To a soln of 3.0g (13.5 mmole) of 4-*n*-heptyl-d_{15}-oxyaniline and 1 drop 2 *N* NaOH in 30 ml MeOH plus 3 ml MeCN was added dropwise 10 ml 30% H_2O_2. This soln was heated to 50° while maintaining the pH near 9.5 by adding either 2 *N* NaOH or H_2O_2. Stirring was continued for ~15 min after the addition was completed and then the soln cooled in an ice bath. The precipitate was collected by filtration, washed with H_2O, and dried to give 2.59g (84.1%) of a brown solid. This material was dissolved in $CHCl_3$, treated with decolorizing carbon and filtered through Celite® on glass fiber filter paper. Concentration of the filtrate *in vacuo* gave a yellow solid which was recrystallized twice from abs EtOH to give 1.67g (54.2%) of the desired compound **2**; IR ($CHCl_3$) 2230, 2120 (med d, C-D) and 1600 cm^{-1} (str with wk sh at 1560).

4-*n*-Octyl-d_{17}-oxybenzoic Acid Methyl Ester, 10 (n = 8)

A soln of 2.96g (19.5 mmoles) of 4-hydroxybenzoic acid methyl ester and 776 mg NaOH in 70 ml of a 1:1 mixture of ϕH and DMF was refluxed using a Dean-Stark trap until the distillate was clear. Octyl-d_{17}-iodide (5.0g = 19.5 mmoles) was added dropwise in ca. 5 min and refluxing continued for 4.5 hr. The reaction mixture was cooled to RT, the insoluble material removed by filtration and the filtrate concentrated to dryness *in vacuo*. The remaining solid was dissolved in Et_2O, extracted with 5% aq KOH, H_2O, dried over anhyd Na_2SO_4 and filtered. Concentration of the filtrate to dryness *in vacuo* gave 4.32g = 79.0% of the crude ester, **10**. Two recrystallizations from abs EtOH gave 2.04g (37.3%) of the purified ester **10**: mp 35-37 and IR ($CHCl_3$) 2230, 2120 (med d, C-D), 1720 (str s, ester C=O), 1600 cm^{-1} (str s, Ar) and no OH absorption.

4-*n*-Octyl-d_{17}-oxybenzoic Acid, 2 (n = 8)

A soln of 2.4g (8.7 mmoles) of 4-*n*-octyl-d_{17}-oxybenzoic acid methyl ester and 1.4g NaOH in 14.2 ml H_2O + 4.4 ml EtOH was refluxed 2 hr, cautiously acidified with conced HCl while still hot and cooled in an ice bath. The resulting precipitate was removed by vacuum filtration, washed with H_2O and dried *in vacuo* to give 2.28g (98.3%) of the desired acid **2** (n = 8); TLC ($CHCl_3$) R_f = 0.04 (R_f for starting material = 0.68); IR 2230, 2120 (med d, C-D), 1680 (str s, acid C=O), 1600 (str s, Ar) and 1560 cm^{-1} (wk s, Ar) and NMR showed no C_8H_{17} protons.

4-*n*-Octyl-d_{17}-oxybenzoyl Chloride

A mixture of 2.17g (8.13 mmoles) of the above acid and 1.69g (8.13 mmoles) PCl_5 was stirred at RT until liquid. The $POCl_3$ was removed by distillation *in vacuo* and the residue distilled at 161° (1.2mm) to give 1.92g (82.8%) of the desired acid chloride: IR (film) 2230, 2120 (med d, C-D); 1770, 1740† (str d, COCl) and 1600 (str s, Ar) and 1570 cm^{-1} (str s, Ar) and NMR (CT) δ7.93 (2,d,J = 9.0 Hz, ArH ortho to COCl), 6.80 (2,d,J = 9.0 Hz, ArH ortho to RO) and no aliphatic protons.

4-*n*-Pentylbenzenethio-4′-octyl-d_{17}-oxybenzoate IVb

To a soln of 955 mg (5.30 mmoles) of 4-*n*-pentylbenzene thiol‡ and 0.76ml Et_3N in 5ml CH_2Cl_2 was added dropwise a soln of 1.60g (5.30 mmoles) of 4-*n*-octyl-d_{17}-oxybenzoyl chloride. This rxn mixture was stirred for 30 min at RT; extracted with 10ml H_2O, 5% aq KOH soln and H_2O, dried and filtered. Concentration of the filtrate *in vacuo* gave 2.12g (90.2%) of the crude thio ester. This material was recrystallized twice from abs EtOH to give 1.75g (74.5%) of the purified thio ester IVb; IR ($CHCl_3$) 2230, 2120 (med d, C-D), 1670 (str s, COS) and 1600 with a shoulder at 1580cm^{-1} (Ar) and NMR showed no C_8H_{17} protons.

4-*n*-Heptyl-d_{15}-oxybenzoic Acid-d_1 (II)

A mixture of 2.71g of 4-*n*-heptyl-d_{15}-oxybenzoyl chloride in 4ml of 30% NaOD in D_2O + 18 ml D_2O was refluxed 4 hr, cautiously acidified with 38% DCl in D_2O while still hot§ and cooled to RT. The precipitate was removed by filtration, washed with D_2O and dried to give 3.0g of the crude acid. This material was recrystallized twice from abs EtOD to give 1.52g (60.1%) of the acid II. ^{2}H-NMR showed the presence of the acid deuteron.

4-*n*-Octyl-d_{17}-oxybenzoic Acid-d_1 (III)

a. *By hydrolysis of the methyl ester*

A soln of 3.52g (12.5 mmoles) of 4-*n*-octyl-d_{17}-oxybenzoic acid methyl ester in 4.5 ml 40% NaOD in D_2O + 18 ml D_2O was refluxed

†These benzoyl chlorides show a doublet due to Fermi resonance as do the 4-alkybenzoyl chlorides (ref. 32).

‡Prepared by the method described in ref. 41.

§Cooling the rxn mixture before acidification tended to give a mixture of the acid and the salt.

1 hr, cautiously acidified while still hot with 30% DCl in D_2O and cooled in an ice bath. The precipitate was removed by filtration on glass fiber filter paper, washed with D_2O, and dried over P_2O_5 *in vacuo* to give 3.26g (97.0%) of the crude product. This material was recrystallized from abs EtOD to give the desired acid III.

b. *By deuterium exchange in base*

A soln of 4-*n*-octyl-d_{17}-oxybenzoic acid in the same concentration of NaOD used to hydrolyze the ester was heated until all the solid dissolved, cautiously acidified while still hot and then cooled in an ice bath. The precipitate was treated as above to give the desired acid III.

^{2}H-NMR showed the presence of the acid deuteron in both samples.

4-*n*-Heptyl-d_{15}-oxybenzaldehyde (12)

A soln of 2.30g (19.1 mmoles) of 4-hydroxybenzaldehyde and 763mg (19.1 mmoles) of NaOH in 28ml of a 1:1 mixture of ϕH and DMF containing 4.1g of Linde molecular sieves no. 4A was refluxed using a Dean-Stark trap until the distillate was clear, n-heptyl-d_{15}-bromide (3.70g = 19.1 mmoles) added dropwise in 5 min and refluxing continued for 4.5 hr. This mixture was cooled to RT, filtered through glass fiber filter paper and the filtrate concentrated to dryness *in vacuo* to give 4.8g of the crude aldehyde **3**. This liquid was dissolved in Et_2O), extracted with 5% aq KOH soln and H_2O, dried and filtered. Concentration of the filtrate to dryness *in vacuo* gave a liquid which was distilled at 172° (5.5 mm) to give 3.19g (71.2%) of the purified aldehyde **3**: IR 2820, 2740 (med d, CHO), 2230 and 2110 (str d C-D), 1690 (str s, C=O), 1600, 1580 cm^{-1} (str d, Ar) and no aliphatic protons and NMR showed no C_7H_{15} protons.

4-Bromophenol-2,6-d_2

A soln of 10g (57.8 mmoles) of bromophenol in 34.4ml 40% D_2SO_4-D_2O was refluxed 24 hr, cooled to RT and extracted twice with Et_2O. The Et_2O layer was washed with H_2O, dried and filtered. The filtrate was concentrated to dryness *in vacuo* to give a black liquid. This was treated again in the same manner to give 9.5g (94%) of the crude product. Distillation of this material at 104° (7mm) gave 7.3g (72.3%) of 4-bromophenol-2,6-d_2: TLC ($CHCl_3$), R_f = 0.19 same as R_f for 4-bromophenol and NMR (CD, F) 7.32 (s,2,ArH ortho to Br), 6.71 (d, estd 13% ArH ortho to OH, doublet occurs at 6.70 in non-deuterated material) and 5.20 (s, estd 26% non-exchanged OH).

Acetanilide-d_5, 13

A soln of 10.0g (0.102 mole) of aniline-d_5 and 14ml Et_3N in 100ml of CH_2Cl_2 was added dropwise to a soln of 8.81g (0.112 mole) of acetyl chloride in 100ml of CH_2Cl_2 at RT. This rxn mixture was stirred at RT for 2 hr; extracted with H_2O, 5% aq KOH and H_2O; dried and filtered. Concentration of the filtrate to dryness *in vacuo* gave 13.5g (94.4%) of an off-white solid. Recrystallization of this material from EtOH-H_2O gave 11.2g (78.3%) of the anilide **13**: mp 117-119° (lit. mp 114-115°[46a]).

4-*n*-Heptanoylacetanilide-d_4, 16 (R′ = C_6H_{13})

To a mixture of 11.2g (80.0 mmoles) of acetanilide-d_5 and 28.5g (0.19 mole) of heptanoyl chloride in 64ml of CS_2 was added 42.6 (0.32 mole) of $AlCl_3$ in small portions and the mixture refluxed for 4 hr. The CS_2 was removed by distillation, the residue poured onto crushed ice and the precipitated oil extracted into $CHCl_3$. The organic layer was extracted with 5% aq KOH, washed with H_2O, dried and filtered. Concentration of the filtrate to dryness *in vacuo* gave a brown solid. This material was recrystallized from EtOAc using a treatment with discolorizing carbon to give 8.0g of the desired ketone. A second crop (1.7g) was obtained from the filtrate by concentrating it to half its volume and diluting with ligroine to give a total crude yield of 9.7g (49.5%). These 2 crops were combined and recrystallized from EtOAc to give 7.0g (34.6%) of a colorless solid: mp 122-125°, mixture mp with acetanilide-d_5 86-93° (lit. mp for non-deuterated material 122-123.5°[46b]) and IR ($CHCl_3$) 3300 (wk br s, NH), 1670 (str s, amide C=O) and 1575 cm^{-1} (str s, Ar).

4-*n*-Heptylaniline-d_4, 15 (R′ = C_6H_{13})

A soln of 9.79g (39.0 mmoles) of 4-*n*-heptanoylacetanilide-d_4 and 8.1g KOH in 6.6ml 95% NH_2NH_2 in 119ml triethylene glycol was heated to 120° using a Dean-Stark trap until all the H_2O was removed. Heating was continued at 178° for another 3 hr and then the rxn mixture cooled to 25°. The contents of the trap were added to this mixture which was then extracted 3 times with 200ml Et_2O. The Et_2O layer was washed with H_2O, dried over anhyd Na_2SO_4 and filtered. Removal of the solvent from the filtrate *in vacuo* gave 6.9g of a yellow oil which was distilled at 118-120° (1.2mm) to give 3.78g (49.7%) of the desired aniline **15**: IR 3350 (med br s, NH) and 1620, 1590 cm^{-1} (med d, Ar) and NMR showed ca. 9.25% protons at 6.81δ and 11.1% at 6.41δ.

Catalytic Reduction of 4-*n*-Heptanoylacetanilide, 16

A soln of 1,0g (4.05 mmoles) of 4-*n*-heptanoylacetanilide in 75ml abs EtOH was prepared by heating this mixture until all the material dissolved and then cooling to RT. This soln was hydrogenated at ~50 psi for 4 hr using 181mg of 5% Pd/C. The catalyst was removed by filtration over Celite® on hard filter paper and washed thoroughly with abs EtOH. Removal of the solvent from the filtrate *in vacuo* gave 1.1g of a grey solid. TLC (EtOAc) of this material showed 3 spots at R_f = 3.2 (alcohol **32**), 4.1 (same R_f as for starting material) and 4.9 (same R_f as for an alkyl acetanilide). Recrystallization of this mixture from a mixture of EtOAc and ligroine gave the purified alcohol **32**: mp 83-86°; TLC (EtOAc) showed one spot with R_f = 0.50 (starting ketone R_f = 0.59, alkyl acetanilide R_f = 0.61) and IR ($CHCl_3$) 3200-3400 (br, NH_2), 1675 (srt s C=O) and 1600 cm^{-1} (str s, Ar).

This reduction was repeated in the same manner but using HOAc as the solvent and a reduction time of 21 hr to give a crude yield of 888mg (94.2%) of 4-*n*-heptylacetanilide which was recrystallized twice from EtOAc to give 226mg (24.0%) of the purified amide **14** (R = C_6H_{13}): mp 92-93.5°, mixture mp with 4-*n*-heptanoylacetanilide 81-88° and IR ($CHCl_3$) 3300 (wk br s NH), 1670 (str s, amide C=O) and 1600 cm^{-1} (med s, Ar).

Aceto-d_3-phenone, 17 (R′ = CD_3, Y=H)

Acetyl-d_3 chloride was prepared by adding 35.7g (0.26 mole) PCl_3 dropwise to 50g (0.78 mol) CD_3CO_2D† and heating this mixture until the liquid began to reflux and two layers formed. Distillation at 51° gave 39.3 (61.8%) of acetyl-d_3 chloride. This material (18.5g, 0.23 mole) was added dropwise to a suspension of 42.2g (0.32 mole) of $AlCl_3$ in 225ml anhyd ϕH at RT (maintained using an ice bath) and stirring continued for 1 hr at RT. This was then poured onto ice and the organic layer separated, washed with H_2O; 10% aq KOH, H_2O, dried and filtered. Concentration of the filtrate to dryness *in vacuo* gave 31.4g of the crude product. Distillation of this liquid at 68° (~5mm) gave 23.0g (82.4%) of the desired ketone, **17**: TLC showed one spot with R_f = 0.60 (same R_f as shown by butyrophenone), IR (film): 2600-1900 (br wk m, m, C-D), 1670 (str s, COCl) and 1600, 1580 cm^{-1} (str d, Ar) and NMR showed no protons at 7.90δ.

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†The acid deuteron was not necessary but the perdeuterated acid was less expensive than the d_3 one.

n-Butyrophenone-d_5, 17 (R′ = C_3H_7, Y = D)

To a soln of 6.00g (71.4 mmoles) of benzene-d_6 and 15.2g (0.14 mole) of propionyl chloride in 50ml CH_2Cl_2 was added in small portions 9.5g (71.4 mmole $AlCl_3$). This mixture was refluxed 1 hr, poured into ice cold D_2O and the CH_2Cl_2 layer separated, extracted with Na_2SO_4 and filtered. Concentration of the filtrate to dryness *in vacuo* gave a liquid which was distilled at 89° (3.5mm) to give 8.50g (78.0%) of the desired ketone: IR (film) 2230, 2120 (med d, C-D), 1680 (str s, C=O) and 1570 cm^{-1} with shoulder (str, Ar) and NMR showed no Ar protons.

4-n-Butyl-α,α-d_2-benzene, 18 (R′ = C_3H_7, X = D, Y = H)

A soln of 50g (0.34 mole) of butyrophenone in 100 ml abs EtOD containing 20g Strem 10% Pd/C was deuterated with D_2 at ~50 psi at RT for 18 hr. The catalyst was removed by filtration of this mixture through Celite® on hard filter paper. Concentration of the filtrate to dryness *in vacuo* gave 33.7g (73.4%) of the crude alkylbenzene which showed one spot with R_f = 0.78 (R_f for starting ketone = 0.48, nondeuterated butylbenzene 0.78) on TLC ($CHCl_3$). This liquid was distilled at 177-179° to give 30.9g (69.3%) of the purified alkylbenzene, **18**. NMR showed ~5.3% protons at 2.5δ.

4-Ethyl-d_2-benzene, 18 (*R′ = CD_3, X = D, Y = H*) was prepared in the same manner in an 81.1% purified yield using aceto-d_3-phenone, D_2 and THF. NMR showed no aliphatic protons.

4-n-Butylbenzene-d_5, 18 (*R′ = C_3H_7, X = H, Y = D*) was prepared in the same manner using butyryl chloride-d_5, H_2 and abs EtOH to give a purified yield of 69.1%. NMR showed no AR protons.

4-n-Octylbenzene-d_5, 18 (*R′ = C_7H_{15}, X = H, Y = D*) was prepared in the same manner using *n*-octanoyl benzene-d_5, H_2 and abs EtOH to give a purified yield of 76.2%. NMR showed no Ar protons.

4-n-Butylbenzoic Acid-d_4, 20 (R′ = C_3H_7, X = H, Y = D)

To a suspension of 4.80g (36.0 mmoles) $AlCl_3$ in 25ml CH_2Cl_2 at RT was added dropwise in 5 min, 9.14g (71.9 mmole) oxalyl chloride followed immediately by the dropwise addition of a soln of 5.00g (36.0 mmoles) of butylbenzene-d_5 in 37ml CH_2Cl_2 in 30 min. Half the CH_2Cl_2 was removed by distillation and the remaining mixture cooled in an ice bath and poured into 25ml cold (~5°) D_2O containing 5.5g $CaCl_2$. The organic layer was separated, washed with H_2O, dried and filtered. Concentration of the filtrate to dryness *in vacuo* gave a liquid which showed an acid chloride doublet in the IR spectrum at

1770 and 1740 cm^{-1}. This material was hydrolyzed by refluxing for 2 hr in a soln of 6.5g NaOH in 38ml H_2O and 35ml EtOH. Cautious addition of concd HCl to this hot soln followed by cooling to RT gave a precipitate which was extracted into Et_2O. The Et_2O layer was washed with H_2O and extracted twice with 10% aq KOH. The basic layer was washed with Et_2O, cooled in an ice bath, acidified with concd HCl and extracted with Et_2O. This Et_2O extract was washed with H_2O, dried and filtered. Concentration of the filtrate to dryness *in vacuo* gave 5.03g (77.4%) of the crude acid: IR ($CHCl_3$) 3400-2400 (br acid OH and aliphatic CH), 1690 (str s, acid C=O), 1580 (med s Ar) and 1545 cm^{-1} (weak s, Ar) and NMR showed no Ar protons. Compounds in which Y=H were prepared in the same manner but using H_2O to decompose the Friedel-Crafts complex.

4-*n*-Octyl-d_{17}-aniline-d_4, 19 (R′ = C_7D_{15}, X=D, Y=D)

To a stirred soln of 2.6g (10.2 mmoles) of crude 4-*n*-octyl-d_{17}-benzoic acid-d_4 in 15ml concd D_2SO_4 in a 50ml Erlenmeyer flask at 50-55° was added in small protions 982mg NaN_3. Heating was continued for 4.5 hr and then the soln cooled in an ice bath and made basic with a dilute soln of NH_4OH. Additional H_2O was added if any solid was present and this soln extracted with Et_2O. The Et_2O layer was washed with H_2O, dried and filtered. Concentration of the filtrate to dryness *in vacuo* gave 1.9g (82.6%) of the crude aniline; TLC ($CHCl_3$) R_f = 0.40 (same R_f as butylaniline), IR (film) showed no carbonyl at 1700 cm^{-1} and NMR showed no Ar protons.

4-*n*-Butyaniline-2,6-d_2, 22 (R = C_4H_9)

A soln of 25g (0.13 mole) of freshly distilled 4-*n*-butylaniline in 36ml of a 1:1 (by volume) soln of concd D_2SO_4 in 18ml D_2O was refluxed 17 hr, cooled in an ice bath and made basic with dil NH_4OH. Additional H_2O was added when necessary to dissolve any solid present. The resulting oil was extracted into Et_2O, washed with H_2O, dried and filtered. Concentration of the filtrate to dryness *in vacuo* gave 23.4g (92.6%) of the crude aniline. Distillation of this liquid at 135° (2.3mm) gave 19.0g (75.2%) of the purified material. NMR (CT) showed ~21.7% protons at 6.47δ (78.3% D incorporation).

General Procedure for Preparing Deuterated Anils (V-IX)

A soln of equimolar amounts of the aldehyde **4** and the aniline **5** containing 10g Linde no. 4A molecular sieves/0.1 mole in 260ml abs

EtOH was stirred and refluxed for 2.5 hr. The sieves were removed by vacuum filtration through glass fiber filter paper and the filtrate concentrated to dryness *in vacuo* to give the crude anil. Anils with RT nematic phases were purified by vacuum distillation whereas those with RT smectic phases were recrystallized from abs EtOH by cooling in either an ice-H_2O or a dry-ice acetone bath until crystals formed. These crystals were quickly removed by filtration on a sintered glass funnel, washed with cold abs EtOH, quickly transferred to a tared container while still wet and immediately dried using a high vacuum. Chloroform had to be used to keep the deuterated 90.2, 90.4 and TBBA in soln during hot filtrations to remove dirt. In these cases, the filtrates were concentrated to a small volume to remove the $CHCl_3$ and abs EtOH added before being cooled for crystallization. The deuterated 40.7 was recrystallized from MeOH instead of EtOH. In some instances the aniline was distilled before being used. In these cases, the anil was usually sufficiently pure after 2 recrystallizations for broadline H^1-NMR studies. However, in most instances, the crude aniline was used which usually required 3 recrystallizations of the anils. Typical purified yields were 40-66%.

Acknowledgments

This work would not have been possible without the generous support of the National Science Foundation in grant numbers DMR74-13173, 76-21365, 79-04393, 82-04342 and 44468 awarded to J. W. Doane and 81-15544, 83-09739 LCI group synthesis grant. The contributions of D. L. Fishel for his preliminary results on the Schmidt reaction, R. R. Biggers for obtaining the HPLC data, R. E. Kline, Jr. for the PE283 spectra, T. Longo and D. L. Fishel for mass spectral data, K. Y. Leung for her help on the acid catalyzed exchange and the synthesis of 70.4 (R'2,6-d_2) and 70.7 (R'2,6-d_2) and the Chemistry Department for providing A-60 and FT-80 data are also greatly appeciated.

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