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**Synthesis and mesomorphic properties of deuteriated
4,4'-di-*n*-alkyloxyazoxybenzenes- $d_{2(2n+1)}$ †**

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Symmetrically deuteriated liquid crystals, 4,4'-di-*n*-alkyloxyazoxybenzenes- $d_{2(2n+1)}$ with $n = 2, 3, 4, 5, 6$, i.e. 2OAOB- d_{10} , 3OAOB- d_{14} , 4OAOB- d_{18} , 5OAOB- d_{22} and 6OAOB- d_{26} were synthesized by oxidation of the corresponding deuteriated alkyloxyanilines. The catalytic deuterium exchange on levulinic acid was used as the first step in the synthesis of the perdeuteriated alkyl bromides. The mesomorphic properties of the deuteriated 4,4'-di-*n*-alkyloxyazoxybenzenes were determined by DSC. Phase transition temperatures as well as their enthalpy and entropy values were lower than the respective values for the undeuteriated analogues.

1. Introduction

Symmetrically substituted alkyloxyazoxybenzenes are liquid crystal homologues which have been long investigated with various experimental methods. Among those, quasi-elastic neutron scattering plays an important role in the studies of molecular dynamics (see, for example [1, 2]). This technique is particularly useful for the comparison of the properties of undeuteriated versus selectively deuteriated molecules. It has also been applied in systematic investigations of seven members of the 4,4'-di-*n*-alkyloxyazoxybenzene homologous series by Janik and his group namely 4,4'-dimethoxyazoxybenzene [3-5] an 4,4'-di-*n*-heptyloxyazoxybenzene [5, 6] with normal and with deuteriated chains. In addition, in the investigations of further homologues: 2OAOB- d_{10} and - d_0 [7], 3OAOB- d_{14} and - d_0 [7], 4OAOB- d_{18} and - d_0 [8, 9], 5OAOB- d_{22} and - d_0 [9, 10] and 6OAOB- d_{26} and - d_0 [11] which were synthesized by us.

Among the various methods for the synthesis of symmetrically substituted azoxybenzenes [12, 13] the method based on the oxidation of substituted aniline with hydrogen peroxide [14, 15] seems the most suitable. It fulfils the general requirements for the minimum number of steps in the synthesis, gives maximum yields of the selected products and ensures minimum probability of the reverse isotope exchange [16]. Recently, Neubert reported the synthesis of the C_7 - d_{30} homologue of PAA using this method [17]. Earlier, Hayamizu and Yamamoto reported other ways of synthesizing

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PAA- d_6 and PAA- d_8 [18]. In this paper, the synthesis of symmetrically deuterated 4,4'-di- n -alkyloxyazoxybenzenes- $d_{2(2n+1)}$, $2 < n < 6$, is described.

The main problem in this synthesis is the complete deuteration of the alkyl bromides. Usually, the first stage in these methods consists of hydrogen-deuterium exchange for the long chain fatty acids [16], in the presence of catalysts, under normal or elevated pressure [19–21]. However, this method involves specialized equipment whereas ours does not. The method presented is suitable for the production of perdeuterated alkyl bromides with a small n ($4 \leq n \leq 6$).

The phase behaviour of the 4,4'-di- n -alkyloxyazoxybenzenes has been studied widely [22–25]. Here a comparison is made between the transition temperatures, enthalpies and entropies of symmetrically deuterated compounds and their undeuterated analogues. Similar comparisons, regarding the differences between the transition temperatures of other liquid crystals, have been published by Gray and Mosley [26] and Neubert [17].

2. Synthesis of perdeuterated alkyl bromides ($C_nD_{2n+1}Br$, $n = 3, 4, 5, 6$)

The perdeuterated levulinic acid $CD_3COCD_2CD_2COOD$ was used as the starting material for the perdeuterated bromides with $n = 4, 5, 6$ (see figure 2). This acid was prepared by catalytic deuterium exchange with D_2O (isotopic purity 99.8 per cent). The efficiency of the α - CH_2 exchange is better than that for the methyl group after 20 hours. The high passivity of the hydrogen atoms in the β methylene group is worthy of special attention. It can be supposed that the differences in the deuteration rate for particular sites in levulinic acid result from the different influence of the carbonyl and carboxyl groups on the delocalization of electrons in the molecule, and consequently, from the different acidities of the hydrogen atoms involved.

Although the maximum enrichment in deuterium occurred at $pH = 13.5$, the optimum condition for the overall exchange was at $pH = 11.7$. At the latter pH the recovery of levulinic acid was higher (74 per cent versus 62 per cent after 20 hours). The catalytical exchange reaction was repeated three more times with new portions of D_2O until perdeuterated γ -ketovaleric acid (isotopic purity 96 per cent) was obtained. The deuterium content, determined by MS [16, 17, 27–29] and 1H NMR [16, 19, 30] spectra was 99 per cent for the α methylene and the methyl group and 91 per cent for the β methylene group. Deuterated levulinic acid- d_8 was used as a starting compound for the synthesis of deuterated alkyl bromides: butyl- d_9 bromide, pentyl- d_{11} bromide and hexyl- d_{13} bromide. These substances were prepared using the appropriately deuterated intermediates by standard methods available in the literature for preparing the analogue undeuterated materials as shown in figure 1 [31]. Valeric- d_{10} acid was obtained by the reduction of the carbonyl group by the Clemmensen method [32]. n -Butyl- d_9 bromide, the intermediate for the synthesis of 4OAOB- d_{18} , was obtained by bromination-decarboxylation of pentanoic- d_{10} acid following the modified method of Hunsdiecker [33], using a 1 : 1.2 mixture of valeric- d_{10} acid and red mercuric oxide in CCl_4 . The intermediate for the synthesis of 5OAOB- d_{22} , n -pentyl- d_{11} bromide, was obtained by the reduction of pentanoic- d_{10} acid to n -pentanol- d_{12} using lithium aluminium deuteride (99.5 per cent D). $C_5D_{11}Br$ was formed by nucleophilic substitution in the reaction of the alcohol with bromodeuterium acid in the presence of concentrated D_2SO_4 . The intermediate for the synthesis of 6OAOB- d_{26} , n -hexyl- d_{13} bromide, was obtained by the $C_5 \rightarrow C_6$ extension of the aliphatic chain via

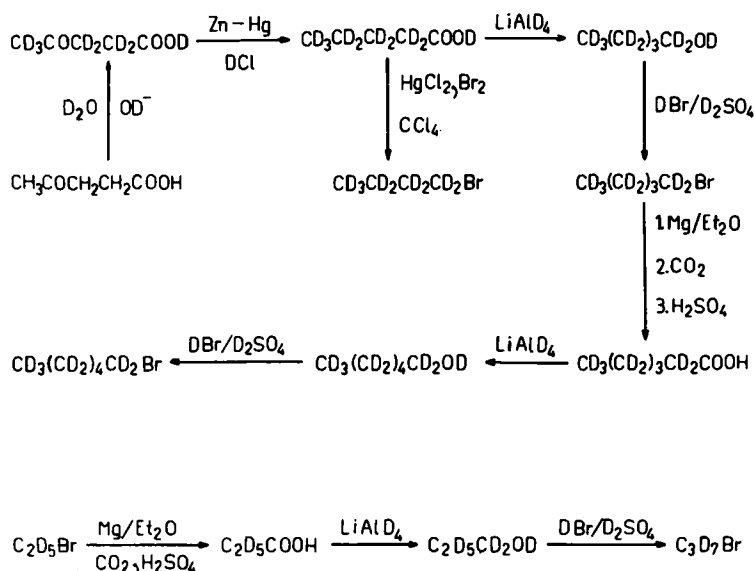


Figure 1. Synthetic methods for the preparation of perdeuteriated alkyl bromides $\text{C}_n\text{D}_{2n+1}\text{Br}$, $n = 3, 4, 5, 6$.

carbonization of the pentyl- d_{11} magnesium bromide, reduction of the resultant hexanoic- d_{11} acid to hexanol- d_{14} and transformation into $\text{C}_6\text{D}_{13}\text{Br}$. Propyl- d_7 bromide was obtained by carbonization of ethyl- d_5 magnesium bromide, reduction of propanoic- d_5 acid and substitution of the OD group with bromine. The compound $\text{C}_3\text{D}_7\text{Br}$ was the intermediate for the synthesis of 3OAOB- d_{14} . Ethyl- d_5 bromide, the intermediate for the synthesis of 2OAOB- d_{10} , was obtained from Doane (Liquid Crystal Institute, Kent, Ohio, U.S.A.).

3. Synthesis of 4,4'-di-*n*-alkyloxyazoxybenzenes- $d_{2(2n+1)}$

From various methods of synthesis of symmetrically substituted azoxybenzenes the method chosen was that of oxidation of substituted aniline with hydrogen peroxide [14, 15, 17]. Figure 2 shows the scheme for the synthesis of symmetrically deuteriated 4,4'-di-*n*-dialkyloxyazoxybenzenes- $d_{2(2n+1)}$ from the appropriate alkyl bromides [34]. It was observed that the reaction yields depends not only on the pH (the value suggested earlier was 8.5–9.0 [14, 15]) but also on the temperature. By comparing the melting points of deuteriated and undeuteriated 4,4'-di-*n*-alkyloxyazoxybenzenes with the optimum temperatures of the reaction it was concluded the higher the melting point of the compound, the higher was the temperature of its formation. The optimum time for the reaction was 90–120 min. The 4,4'-di-*n*-alkyloxyazoxybenzenes- $d_{2(2n+1)}$ obtained were purified from trace amounts of the corresponding di-*n*-alkyloxyazoxybenzenes by means of column chromatography, using silica gel type 60 as the column bed and benzene as both the developing phase and the eluent. Based on MS, ^1H NMR, ^{13}C NMR and IR spectra of the homologues of the alkyloxyazoxy compounds, the possibility of the secondary D–H exchange in the alkyl chains was ruled out for the reaction conditions. The isotopic purities were 99 per cent for 2OAOB- d_{10} and 3OAOB- d_{14} , and 96 per cent for 4OAOB- d_{18} , 5OAOB- d_{22} and 6OAOB- d_{26} .

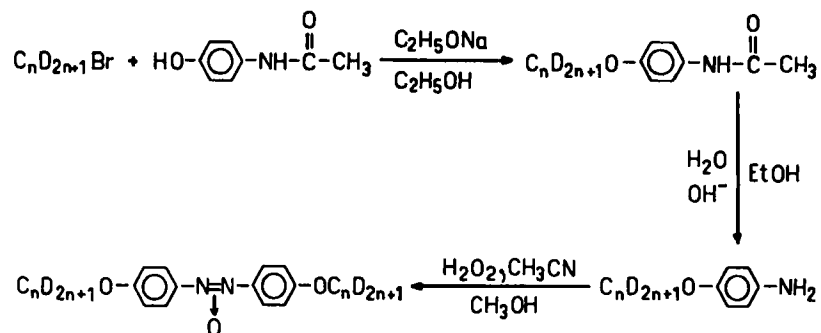


Figure 2. Synthetic methods for the preparation of deuteriated 4,4'-disubstituted alkyloxyazoxybenzenes.

4. Phase behaviour of 4,4'-di-*n*-alkyloxyazoxybenzenes- $d_{2(2n+1)}$

The phase behaviour of the deuteriated 4,4'-di-*n*-alkyloxyazoxybenzenes- $d_{2(2n+1)}$ and, for comparison, of their hydrogen analogues was investigated by means of DSC, using a differential scanning calorimeter DSC-2 (Perkin-Elmer). The measurements were carried out at the Institute of Chemistry of the Martin Luther University Halle-Saale, G.D.R. The heating and cooling rates were always 5 K/min, and the other parameters of the apparatus were also kept constant. The masses of the samples were in the range of 2.50–2.55 mg [35].

The DSC thermograms recorded in the temperature range of 290–500 K indicate that only 2OAOB- d_{10} and 5OAOB- d_{22} have identical phase behaviour for heating and cooling, although phase transitions take place in different temperature ranges. For 2OAOB- d_{10} only one stable solid phase, CI, is observed, whereas for 5OAOB- d_{22} there are two stable crystalline phases, CI and CII. These enantiotropic phases are reproduced in the subsequent cycles of heating and cooling (see the table).

For 3OAOB- d_{14} and 4OAOB- d_{18} , the phase behaviour during the sample heating is different from that when the isotropic sample is cooled back to room temperature. When a fresh sample of 3OAOB- d_{14} is heated the following phases are observed: low temperature CI, high temperature CII, nematic N, and isotropic I. When the sample is cooled, only three condensed phases are observed: isotropic, nematic and crystalline. When the sample is reheated, only CI-N and N-I transitions are observed, and the CII-CI transition is missing. During the heating of a fresh sample of 4OAOB- d_{18} three solid phases appear: CIII, CII, and CI. When the sample is reheated, the CII-CI transition is observed at the same temperature as before.

During the heating of 6OAOB- d_{26} four phases: CII, monotropic crystalline CI appear in a narrow temperature range (3°C), nematic and isotropic. On cooling the sample, four phases: isotropic, nematic, monotropic smectic C and crystal appear. As the reheating of the sample leads to the same phase sequence: CII-CI-N-I, the crystalline phase observed during the cooling should be CII.

Melting and clearing temperatures as well as the range for the existence of the crystalline phases during the heating of 4,4'-di-*n*-alkyloxyazoxybenzenes- $d_{2(2n+1)}$ are shown in figure 3. The temperatures, enthalpies and entropies of the phase transitions are compared in the table. The temperatures of the CI-N and N-I transitions are identical only for 2OAOB- d_{10} and 2OAOB- d_0 . For other homologues, the transition temperatures are lower for deuteriated than for undeuteriated compounds. The

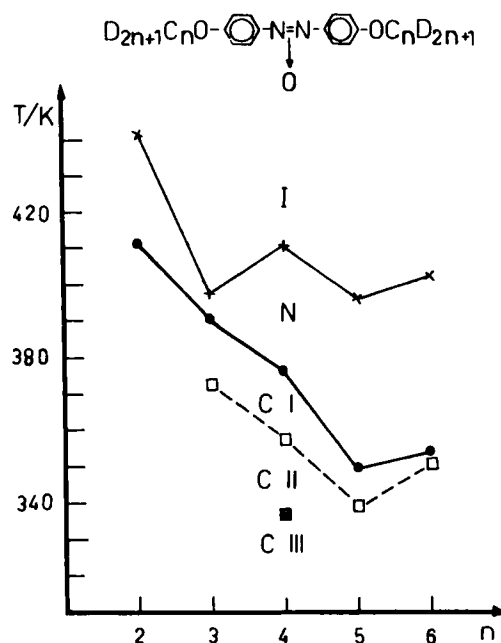


Figure 3. Phase diagram for the homologous series of 4,4'-di-*n*-alkoxyazoxybenzenes- $d_{2(2n+1)}$, $n = 2, 3, 4, 5, 6$.

temperature gaps increase with the per cent contribution of deuterium in the molar mass, and for the sixth homologue the difference is as much as 1.5°C .

All the compounds were purified by repeated crystallization until constant transition temperatures were obtained. The values of ΔT are very small and it could be argued that such small changes could be due to the presence of impurities. However, the corresponding deuteriated and undeuteriated compounds were prepared by identical synthetic routes and both compounds had identical chromatographic purities. All of the compounds, deuteriated and undeuteriated, had extremely narrow ranges (0.2°C) for the CI-N and (0.1°C) for N-I transitions. These factors lead us to believe that the effects illustrated in the table, are genuine, particularly the values of ΔT which are greater than 0.5°C .

The differences in the transition temperatures are probably due to the difference in polarizability of the C-D and C-H bonds [26] and possibly to structural or packing differences between the normal and deuterium substituted molecules.

The transitional enthalpies and entropies are also lower for the deuteriated compounds (see the table). The character of the variations of ΔH and ΔS as well as the sequence of the condensed phases are similar for normal and chain deuteriated nematogens.

5. Conclusions

(a) A method for H-D isotope exchange on γ -ketovaleric acid has been developed. It resulted in the production of a deuteriated analogue of the acid and then in the production of deuteriated alkyl bromides with $n = 4, 5, 6$.

(b) By oxidation of the corresponding 4-alkoxyanilines- d_{2n+1} with hydrogen peroxide in the presence of acetonitrile, symmetrically deuteriated 4,4'-di-*n*-alkoxybenzenes- $d_{2(2n+1)}$ of high isotopic purity were obtained with good chemical yields.

Table 1. Comparison of the transition temperature, enthalpies and entropies of transition for the 4,4'-di-*n*-alkyloxyoxybenzenes- d_{2n+1} and $-d_0$ obtained from DSC. (ΔT = transition temperature of deuterated mesogen-transition temperature of undeuterated mesogen; $\Delta(\Delta H)$ = enthalpy change of deuterated mesogen-enthalpy change of undeuterated mesogen; $\Delta(\Delta S)$ = entropy change of deuterated mesogen-entropy change of undeuterated mesogen.)

Substance	Phase transition	T_d/K	T/K	$\Delta T/K$	$\Delta H_d/kJ mol^{-1}$	$\Delta H/kJ mol^{-1}$	$\Delta(\Delta H)/kJ mol^{-1}$	$\Delta S_d/JK^{-1} mol^{-1}$	$\Delta S/JK^{-1} mol^{-1}$	$\Delta(\Delta S)/JK^{-1} mol^{-1}$
2OAOB	CI-N	411.4	411.4	0	24.60	25.80	-1.20	59.80	<	62.70
	N-I	441.4	441.4	0	1.64	1.75	-0.11	3.71	<	3.96
3OAOB	CII-CI	372.5	372.5	0	20.20	20.60	-0.40	54.20	<	55.30
	CI-N	390.2	390.7	-0.5	26.50	27.40	-0.90	67.90	<	70.10
	N-I	397.2	397.8	-0.6	0.82	0.92	-0.10	2.07	<	2.31
4OAOB	CIII-CII	337.0	338.0	-1.0	4.80	5.20	-0.40	14.20	<	15.40
	CII-CI	358.6	360.6	-2.0	1.02	1.37	-0.35	2.84	<	3.80
	CI-N	376.5	377.5	-1.0	18.50	19.50	-1.00	49.10	<	51.70
	N-I	410.7	411.9	-1.2	1.15	1.25	-0.10	2.80	<	3.03
5OAOB	CII-CI	339.0	342.0	-3.0	19.80	22.00	-2.20	58.40	<	64.30
	CI-N	349.5	350.5	-1.0	14.20	15.80	-1.60	40.60	<	45.10
	N-I	395.8	397.2	-1.4	0.90	1.50	-0.60	2.27	<	3.77
6OAOB	CII-CI	351.0	352.0	-1.0	3.50	3.90	-0.40	9.97	<	11.10
	CI-N	354.0	355.5	-1.5	35.10	37.50	-2.40	99.20	<	105.50
	N-I	402.0	403.5	-1.5	1.25	1.35	-0.10	3.11	<	3.35

(c) The phase behaviour of 2OAOB- d_{10} , 3OAOB- d_{14} , 4OAOB- d_{18} , 5OAOB- d_{22} and 6OAOB- d_{26} was studied in the temperature range 290–500 K. It was shown that the difference in the transition temperatures of the CI-N and N-I transitions of deuteriated and undeuteriated compounds increases from 0 to 1.5°C, proportional to the per cent contribution of deuterium to molar mass.

6. Experimental procedures

Alu-Fol. silica gel 60 5×20 cm (obtained from Merck) was used for TLC. Melting points were determined using a calibrated polarizing microscope (VEB Analytic Dresden). A Perkin-Elmer model 577 was used to obtain routine IR spectra. NMR spectra were recorded using a Varian CFT-20 and a Jeol MH-100 with TMS as an internal standard using CDCl_3 as the solvent. Mass spectral (MS) data were collected using a LKB-2091 instrument at 70 eV.

Levulinic- d_8 acid: 30.3 ml (0.3 mol) of γ -ketovaleric- d_0 acid and 173.4 ml of D_2O (isotopic purity 99.8 per cent) was placed in a thoroughly dried conical wide-necked flask (300 ml volume) with a magnetic stirrer. After the solution had been thoroughly stirred, an electrode connected with a numerical pH meter was immersed in the solution. While the solution was being mixed, 51.6 ml of 20 per cent NaOD solution (isotopic purity 99.8 per cent) was added from a micropipette to make the pH of the solution equal to 11.4. Then the total volume of the solution was transferred to a well-dried round-bottomed flask (500 ml volume). The flask was equipped with 1 m reflux condenser with a double cooling jacket ending with a tube filled with CaCl_2 . The solution was heated for 20 hours. Then it was cooled and while the solution was stirred, 51.6 ml of 20 per cent DCl was added. The solution pH was observed to make it equal to 2.5. Water was distilled at a reduced pressure and then levulinic acid was distilled when the boiling fraction was collected at 140°C with 9–10 mm Hg. The acid isolated was dried in a vacuum desiccator in the presence of P_2O_5 and then it was exposed to isotopic exchange again. The exchange was repeated three times to obtain 21 g (61 per cent) of levulinic- d_8 acid (isotopic purity 96 per cent). ^{13}C NMR: δ_{C} 177.35 (COOD), δ_{C} 37.11 (CD_2COOD), δ_{C} 27.63 (COCD_2), δ_{C} 208.39 (CO), δ_{C} 29.83 (CD_3); MS: m/e 124 (M^+), m/e 104 ($M^+ - \text{D}_2\text{O}$), m/e 78 ($\text{CD}_2\text{CD}_2\text{COOD}$), m/e 58 (CD_2CDCO), m/e 60 ($\text{CD}_2\text{CD}_2\text{CO}$), m/e 46 (CD_3CO).

4,4'-diethoxyazoxybenzene- d_{10} (2OAOB- d_{10}). A three-necked round-bottomed flask (500 ml volume) equipped with a thermometer, mechanical stirrer and a reflux condenser was filled with 94 ml of methanol, 12 ml (9.4 g, 0.23 mol) of acetonitrile and 6 g (0.04 mol) of 4-ethoxyaniline- d_5 . The whole solution was thoroughly mixed and 11 ml (0.115 mol) of 30 per cent hydrogen dioxide was added. While the solution was stirred, two drops of 2N of NaOH solution were added and the pH of the mixture was 9. The automatic temperature rise was stopped at 55–60°C by cooling the flask with cold water. This temperature was maintained at the same level for 2 hours by, first, cooling and then heating the flask. The pH of the mixture was 9–8.5 during the reaction. Next the contents of the flask were cooled in a mixture of water and ice, the yellow deposit obtained in the reaction was filtered off on a Büchner funnel and cooled with cold methanol to rinse out the post-reaction liquor and finally the deposit was dried.

The crude product was dissolved in benzene (c. 5–7 ml) and put into a chromatographic column packed with type 60 silica gel (the packing was 80 cm long and its diameter was 2 cm); benzene was used as the mobile phase. Particular fractions

containing one product (checked by TLC) were put together, benzene was distilled in a vacuum evaporator and the residue was crystallized from ethanol. 4.13 g 4,4'-diethoxyazoxybenzene-*d*₁₀ in the form of yellow crystals was obtained. Transition temperatures were: 138.2°C (melting point), 168.2°C (clearing point). Isotopic purity was 99 per cent.

IR: 2240 cm⁻¹ (CD₃), 2120 cm⁻¹ (CD₂), 1600, 1500, 1460 cm⁻¹ (C₆H₄), 1310 cm⁻¹ (N(O)=N); ¹H NMR: δ 8.10–8.23 (*q*, 4, *J* = 4 Hz, *ortho H Ar*), δ 6.74–6.86 (*q*, 4, *J* = 4 Hz *meta H Ar*); ¹³C NMR: δ_c 141.52 (C–N(O)=N), δ_c 127.82 (Ar C *ortho* –N(O)=N–), δ_c 114.21 (Ar C *meta* –N(O)=N–), δ_c 161.51 (Ar C *para* –N(O)=N–), δ_c 137.89 (–N(O)=N–C–φ), δ_c 123.72 (–N(O)=N– *ortho C Ar*), δ_c 114.01 (–N(O)=N– *meta C Ar*), δ_c 159.66 (–N(O)=N– *para C Ar*); MS: *m/e* 296 (*M*⁺), *m/e* 260 (*M*⁺ – 16), *m/e* 108 (DO–φ–N), *m/e* 126 (C₂D₃O–φ).

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