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Synthesis and Properties of Thermotropic Liquid Crystals Bis[4-(5-Alkyl-1,3-Dioxan-2-yl)Phenyl]Terephthalate

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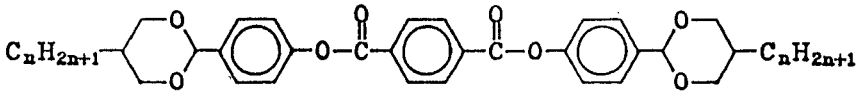
The homologues of bis[4-(5-alkyl-1,3-dioxan-2-yl)-phenyl]terephthalate were synthesized. Wide mesophase temperature ranges, nematic for butyl to dodecyl and smectic C for octyl to tetradecyl derivatives, were observed. The trans-cis isomerization of the heterocyclic rings and dissociations of the ester linkages after heating the sample to high temperatures were studied by NMR spectroscopy.

Keywords: 2,5-disubstituted-1,3-dioxane

INTRODUCTION

Ferroelectric liquid crystals have attracted a great deal of attention due to the potential applications. The tilted orientation of molecular long axis with respect to molecular layer and the existence of chiral center are necessary properties for the mesogens to be ferroelectric.[1] There are reports of various families exhibiting ferroelectric properties,[2–8] one of them is the 2,5-disubstituted 1,3-dioxane system.[7,8] In this system, the reported compounds consist of one such heterocyclic ring. We have synthesized new liquid crystals of symmetrical structure in geometry and consisting of two such rings, bis[4-(5-alkyl-1,3-dioxan-2-yl)-phenyl]terephthalate(1). The results are reported here.



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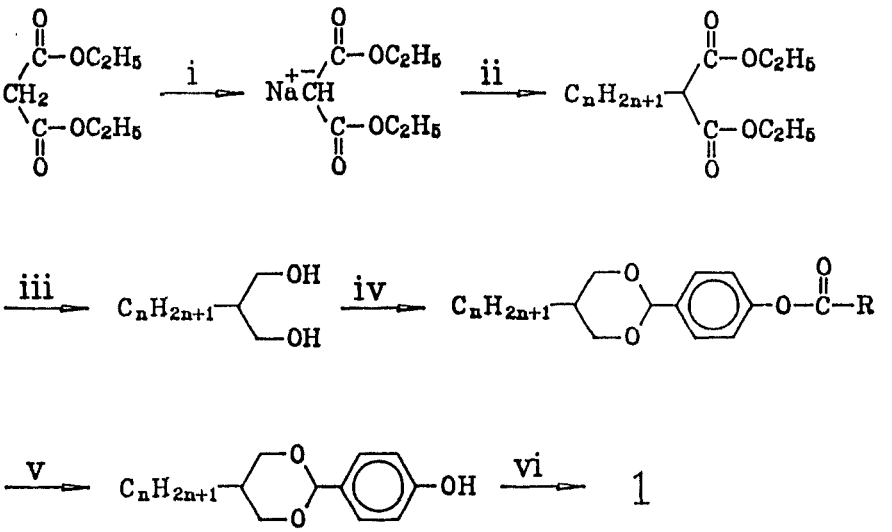
EXPERIMENTAL

The final products[1] were obtained according to the known procedures as shown in Scheme I. The 2-alkyl diethyl malonate was obtained by dropwise addition of alkyl



i : Na/EtOH ; ii : $C_nH_{2n+1}Br$; iii : $LiAlH_4$/ether

iv : H–C(=O)–Ph–O–C(=O)–R/TsOH/Benzene ,
R = $-CH_3$, $-OCH_3$, $-OC_2H_5$;

v : NaOH/EtOH/H_2O ;

vi : Cl–C(=O)–Ph–C(=O)–Cl/Pyridine

SCHEME I

bromide liquid into the ethanolic sodium diethyl malonate solution in ice bath. The reduction of this product by $LiAlH_4$ was carried out in dry ether. The cyclization of 2-alkyl-1,3-propanediols with protected *p*-hydroxybenzaldehyde was catalyzed by *p*-toluenesulfonic acid (TsOH) in benzene with a Dean-Stark trap. Three different protecting agents, acetic acid, ethyl- and methyl-chloroformate were employed and better yield was obtained with the last one. The cis- and trans-isomers were separated by recrystallization from *n*-hexane. The corresponding phenols obtained after deprotection of the trans-isomer were stirred with terephthaloyl chloride in dry pyridine at room temperature to give the final products.

The results of elemental analysis and NMR (Bruker WP100SY FTNMR) spectra gave consistent structures with those desired for all the intermediates and final products. Liquid crystal textures were characterized with a polarizing microscope (Nikon OPTIPHOT-POL) equipped with a home made heating stage. The phase transition temperatures were determined by a Perkin-Elmer differential scanning calorimeter (DSC-2).

RESULTS AND DISCUSSION

The product obtained from cyclization of 2-alkyl-1,3-propanediol with benzaldehyde consists of trans- and cis-isomers. The proton NMR spectrum of a typical product is shown in Figure 1 along with the corresponding configurational isomers. The equatorial proton of C-2 shows 0.1 ppm down field shift as compared to the axial proton. This is ascribed to the deshielding effect of the oxygen atoms at 1 and 3 positions of the ring system, Figure 1A and 1B. Similar results were observed

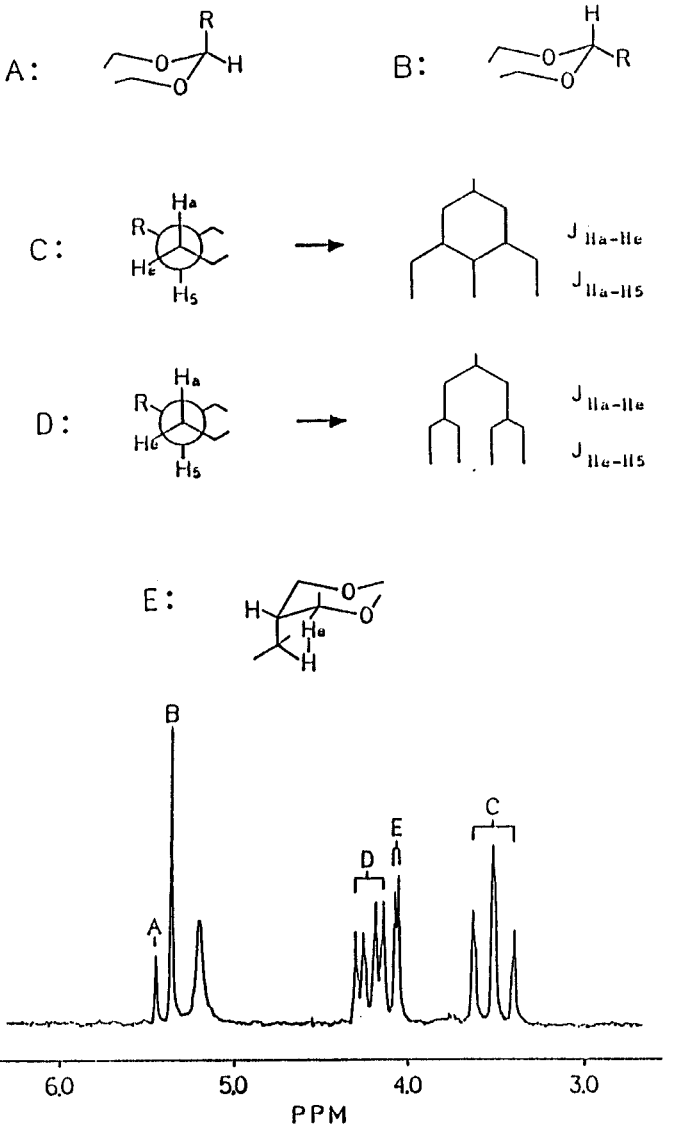


FIGURE 1 A portion of the proton NMR spectrum for the products obtained from cyclization of 2-alkyl-1,3-propanediols with para-substituted benzaldehyde.

by Haramoto *et al.*,[7,8] and Hsu, *et al.*[9] The axial proton of C-4 (and C-6) experiences comparable coupling strengths with the equatorial proton of C-4 (and C-6) and axial proton of C-5, hence a triplet is observed, Figure 1C. The doublet-doublet observed for C-4 and C-6 (of trans-isomer) equatorial protons is due to the couplings with the axial proton of the same carbon atom (J = 11.7 Hz) and the axial proton of C-5 (J = 4.7 Hz), Figure 1D. The sharp doublet located at slightly higher field than this doublet-doublet is ascribed to the coupling of equatorial protons of C-4 and C-6 (of cis-isomer) with the methylene protons of the axially oriented alkyl chain, Figure 1E. This is confirmed by a decoupling test on the methylene protons, which results in a singlet peak.

The mesophases observed for the present homologues are shown in Figure 2. These phases persist to relatively high temperature (~290°C). Considering a rod like structure with five rings and two ester linkages as the central core, a relatively large and high temperature range is expected. Only nematic phase is observed for the lower members of the homologues. Smectic phase starts to exist for the octyl derivative and nematic phase no longer exists for tetradecyl derivative. The smectic phase observed is of type C schlieren texture and with temperature ranges of about 100°C for dodecyl and tetradecyl derivatives. The present molecule is symmetrical with an inversion center located at the central phenyl ring. All the dipole moments are associated with the central core and tilted with respect to the molecular long axis. While the components of these dipoles along the long axis might cancel out each other, the lateral components are pointing in the opposite directions. For molecules to be packed in layers, the preferred orientations are the tilted arrangements. Hence, only the C type smectic phase exists. The tilted arrangement and wide temperature range render these homologues to be good precursors for ferroelectric liquid crystals.

During the studies of phase transitions for these compounds under microscope, the nematic-isotropic transition spanned a relatively wide range (10°C). Similar results were obtained from the DSC studies. It was suspected that the present homologues might decompose at high temperatures. The following experiment was therefore carried out. A NMR containing a pure dodecyl derivative without solvent

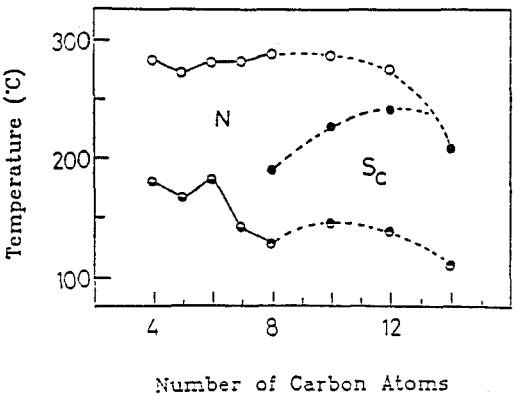


FIGURE 2 The mesophases of bis[4-(5-alkyl-1,3-dioxan-2-yl)-phenyl]terephthalate homologues. Lines are drawn as guides for eyes.

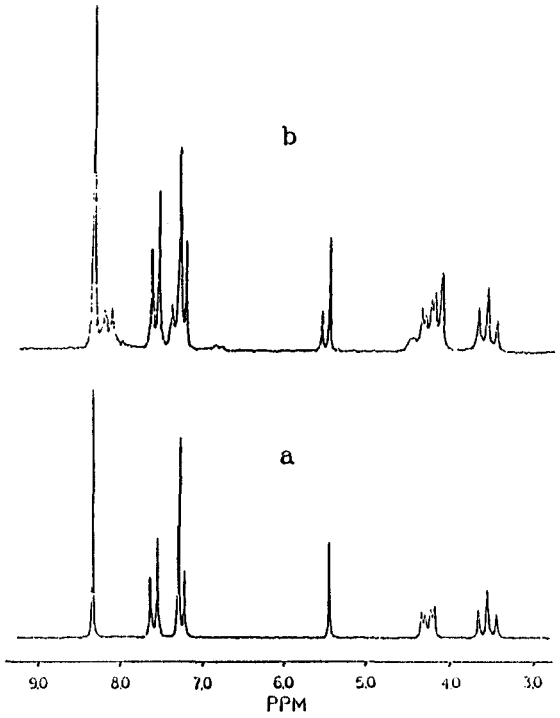


FIGURE 3 The proton NMR spectra of pure(a) and heat treated(b) bis[4-(5-dodecyl-1,3-dioxan-2-yl)phenyl]terephthalate in $CDCl_3$.

was immersed in an oil bath and warmed up to 280°C with a heating rate of 3°C/min. The sample turned to a slightly yellow liquid gradually at high temperature. After cooling the sample to room temperature, the deuterated chloroform was added and spectrum taken. The result is shown in Figure 3 along with that of a pure sample. As can be seen from Figure 3b, the existence of cis-isomer is clearly indicated by the sharp doublet at 4.2 ppm and small singlet at 5.5 ppm. This trans-cis isomerization of 2,5-disubstituted 1,3-dioxane, possibly involving a free radical formation mechanism, has been reported by Hsu, *et al.*[9] In the lower field region, aside the peaks from pure trans-isomer, extra peaks are observed at 6.8 and 8.4 ppm. These are identified to be those of the products after breaking the ester linkages, i.e., the unsymmetrically substituted phenyl ring.

In conclusion, rod like molecules of symmetrical structure consisting of two 2,5-disubstituted 1,3-dioxane heterocyclic rings have been synthesized. These homologues exhibit large temperature range of smectic C phase. The trans-cis isomerization of the heterocyclic rings and dissociations of the ester linkages were observed.

Acknowledgment

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