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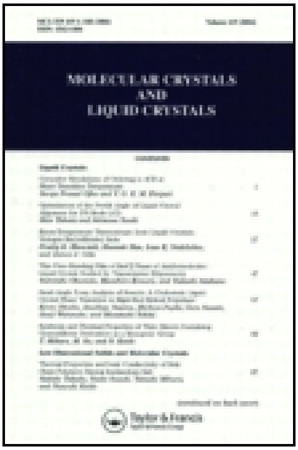

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Liquid Crystalline Behavior of Some Bipolar Quaternary Ammonium Salts and Phosphate Amphiphiles

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LIQUID CRYSTALLINE BEHAVIOR OF SOME BIPOLAR QUATERNARY AMMONIUM SALTS AND PHOSPHATE AMPHIPHILES

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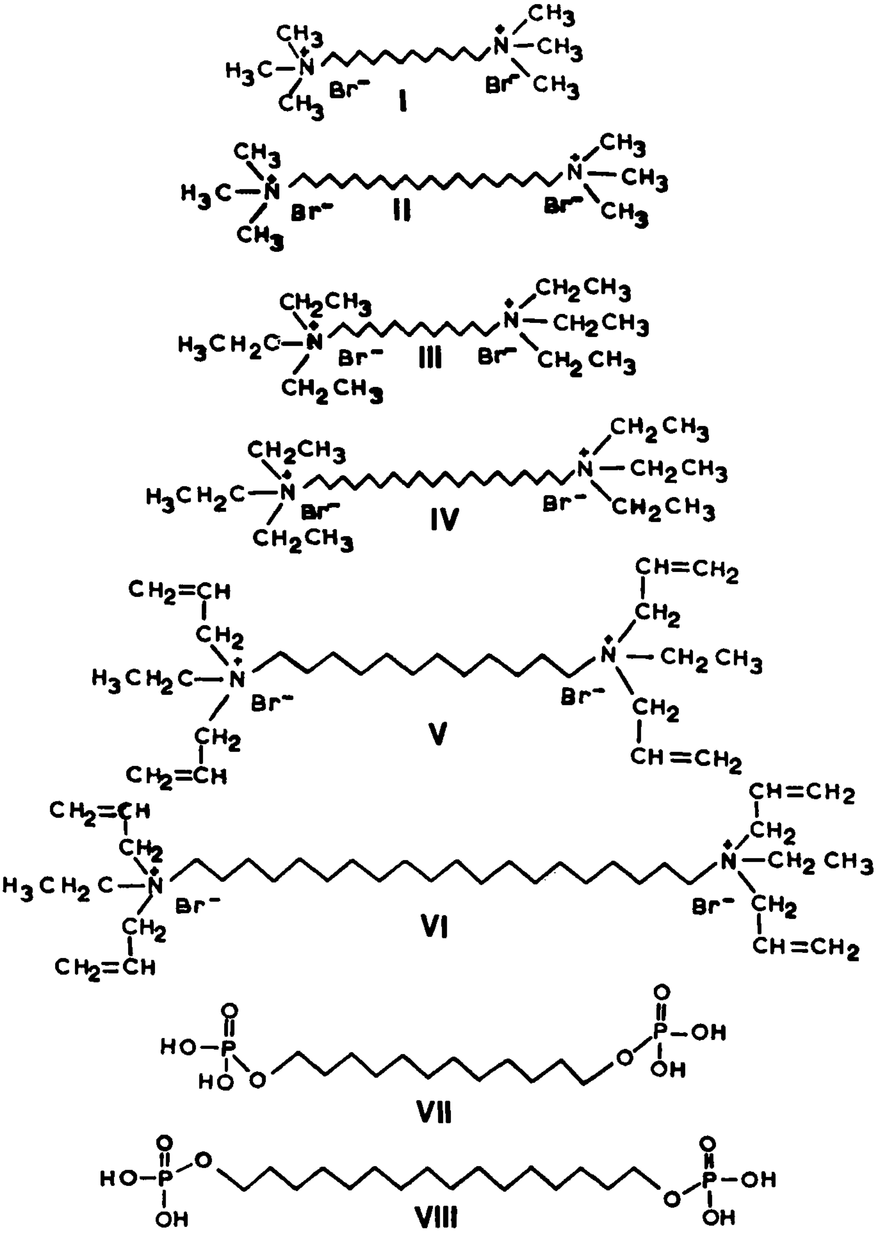
Abstract In this study we investigate the structural features that induce, modify or even inhibit the exhibition of liquid crystallinity in a series of aliphatic α-ω diquaternary and α-ω diphosphate amphiphiles. It was found that the appearance of thermally stable liquid crystalline phases is favored by increasing chain length and employing triethylammonium and phosphate groups as heads of the amphiphiles. On the contrary, the bulky diallylethylammonium group has a rather destructive effect on the existence of the mesophase.

INTRODUCTION

Mesomorphic behavior of amphiphilic molecules, discovered several years ago[1], was ignored and the emphasis was placed on the preparation and characterizaton of a vast number of compounds based on the rigid-rod moeity concept[1]. Recently, however, systematic studies[2-27] on simple, one-polar head amphiphiles, have established the smectic character of these aliphatic compounds. These liquid crystals, which we may characterize as of "amphiphilic type" consist of alternating lipophilic and polar layers which are formed respectively from the long aliphatic chains and the polar heads. In amphiphilic compounds the presence of distinct molecular portions of differing polarity is the driving force for the formation of lamellar structures both in the solid phase and in the melt. It seems that this segregation of polar and lipophilic groups is of such general applicability that even half-fluorinated hydrocarbons[28] form smectic phases in the melt due the formation of separate layers by hydrocarbon and fluorinated portions. Bipolar amphiphiles, also known as bolaamphiphiles[27], now employed for the formation of monolayer membranes or for spanning and stabilizing bilayer membranes[28], conform in general with the structural feature of exhibiting distinct molecular portions of differing



Scheme 1

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polarity. Therefore they could, in principle, show liquid crystalline behavior in the melt.

In the present study a series of aliphatic α-ω diquaternary and α-ω diphosphate amphiphiles, Scheme 1, has been prepared and it is investigated whether the structural modifications imposed on the basic structure, I, induce, modify, or even inhibit the exhibition of liquid crystalline behavior.

EXPERIMENTAL

Materials

1,20 dibromoeicosane was prepared electrolytically by the method employed by Woolford[29] and diallylethylamine according to the procedure of Harada and Arai[30]. The rest of the materials were commercially available.

Synthesis of diquaternaries

Diquaternaries I[31], II[31], III[31], IV[31], V and VI (VI) were prepared by quaternizing the appropriate amines with α-ω dibromides and their structure was established by elemental analysis and proton NMR spectroscopy.

Synthesis of Diphosphates

Dodecane-1,12 Diphosphate,(VII) and Hexadecane-1,16 Diphosphate, (VIII) were prepared by adding 0.005 mole of the respective α-ω diol to 0.02 mole of $POCL_3$ dissolved in dry benzene and refluxed for three hours. Benzene was distilled off and, to the remaining material, water was added and refluxed for one hour. The hydrolyzed compounds were centrifuged and dried over phosphorous pentoxide. Their structure was established by elemental analysis and NMR spectra.

Proton NMR spectra were obtained on a Varian XL-200 spectrometer operating at 200 MHz and at room temperature. Chemical shifts were measured relative to TMS in organic solvents, whereas the spectra of compounds in D_2O were unreferenced.

Optical microscopy studies were performed with a Reichert Thermopan polarizing microscope.

DSC studies were done in a DSC-4 Perkin Elmer Differential Scanning Calorimeter coupled with a System-4 programmer.

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RESULTS AND DISCUSSION

Dodecane-1,12-Bis(trimethylammonium bromide (I) was considered as the basic structure of diquaternaries. Its structure can be modified by changing aliphatic chain length or by functionalizing its polar heads. In this way we can determine the structural criteria for the exhibition of liquid crystallinity by this type of compound . Quaternization was performed by reacting the corresponding dibromides with appropriate tertiary amines, preferably in polar but aprotic solvents[32]. The solubility of dibromides was the limiting factor for choosing the appropriate quaternization solvent since lipophilic dibromides do not dissolve in strongly polar solvents as required by the reaction conditions[32]. By raising the temperature however it was possible to use acetonitrile, a strongly polar and aprotic solvent, for conducting quaternization.

Introduction of a diallyl moiety at the end of the lipophilic chain coupled with an ethyl group does not result only in the formation of another head group in this series of diquaternaries. The bulkiness and /or lipophilicity of head groups determine, in part, the exhibition of liquid crystallinity by these compounds. Indeed diallyl group polymerizes easily and therefore it will be of great significance for these compounds when incorporated in membranous structures or polymerized in the bulk.

The synthesis of monomeric α-ω diphosphates devoid of polymeric phosphate esters was accomplished by using a great excess of phosphorous oxychloride. It is the molar ratio of diols to phosphorous oxychloride, that determines which of the materials,i.e. monomeric or polymeric phosphate esters,will be the major product.

As mentioned,the structure of the bolaamphiphiles was established by proton NMR experiments. The peak assignment was facilitated through homodecoupling and integration experiments. The chemical shifts of the various resonances for compounds I-VIII are summarized in Table I. For compounds III and IV the peaks of the methyl protons of the ethyl substituents at ca. 1 ppm are somewhat overlapped by the envelope of the unresolved internal methylene protons of the aliphatic chain.

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TABLE I. Proton NMR chemical shifts of α-ω diquaternaries and α-ω diphosphates.

Compound	α-CH_2	β-CH_2	γ-CH_2	$(CH_2)_x$	CH_2	CH_3	CH_2=CH-	CH_2-C=
I[a]	3.05	1.49		1.05		2.81		
II[a]	3.15	1.53	1.12	1.05		2.81		
III[a]	3.21	1.60		1.07	2.98	1.00		
IV[a]	3.22	1.61	1.39	1.07	3.00	1.00		
V[b]	3.21	1.62		1.25		1.25	5.91-5.50	3.92
VI[b]	3.24	1.52		1.26		1.24	5.78-5.56	3.85
VII	4.09	1.79		1.26				
VIII	3.95	1.64		1.25				

a. Unreferenced peaks in D_2O.

b. Relative to TMS in DMSO

The liquid crystalline character of bolaamphiphiles I-VIII was investigated by optical microscopy and differential scanning calorimetry. Thus compounds I and II melt at 215°C and 200°C respectively to anisotropic phases which progressively decompose as the temperature increases. Clearing points were not observable. In Fig. 1 and Fig. 2 are shown the DSC traces which, in addition to melting point transitions, also show peaks at lower temperature attributed to solid-solid transitions. The introduction of a longer aliphatic chain in II, although it resulted in a loweing of the melting point, it did not reduce it significantly enough so that thermally stable mesomorphic phases could be obtained.

The lowering of the melting point of this type of compound was attempted by somewhat enhancing the lipophilic character of the head groups through the replacement of the methyl groups at the quaternary nitrogens with ethyl groups. This modification was more effective in lowering the melting point as evidenced by optical microscopy and DSC studies. Thus in optical microscopy experiments, compound III melts, by pressing the cover slip at about 50°C, to an isotropic melt whose viscosity decreases at about 85 °C. The bulkiness of the head groups, coupled with the relatively short polymethylene chain, either does not permit the organization to occur in such an extent that

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mesomorphic phases are observed, or it favors the formation of a homeomorphic phase. The latter possibility seems more probable, especially if one considers DSC diagram of compound III, Fig. 3, and the peak at approximately 115°C, which apparently corresponds to the clearing point transition. For compound IV, it seems that the introduction of ethyl groups at the head groups in conjuction with C_{20} polymethylene moiety results in significant lowering of melting and clearing points. In Fig. 4 a smectic texture is observed on cooling, which is rather stable, as judjed from two consecutive heating-cooling runs. The clearing point remains almost constant. DSC diagram, Fig. 5, is also in agreement with optical microscopy experiments. For the diallyl biquaternary with a C_{12} aliphatic chain a mesomorphic phase was not observed as judjed by optical microscopy and DSC. Apparently the relatively short polymethylene chain coupled with bulky heads do not permit the existence of mesomorphic phases. For the biquaternary with C_{20} aliphatic chain, the first transition was observed at about -15°C. It was transformed to an isotropic melt at about 50 °C as shown in its DSC diagram in Fig.6. Compound VI when melted showed rather homeomorphic textures.

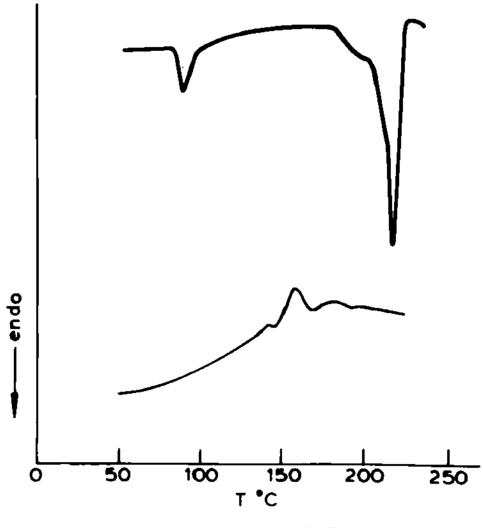

FIGURE 1 DSC trace of compound I

Diphosphates with less polar heads possess lower clearing points and therefore thermally stable liquid crystalline mesophases are obtained. In Fig.7 and Fig.8 the DSC traces of the bolaamphiphiles VII

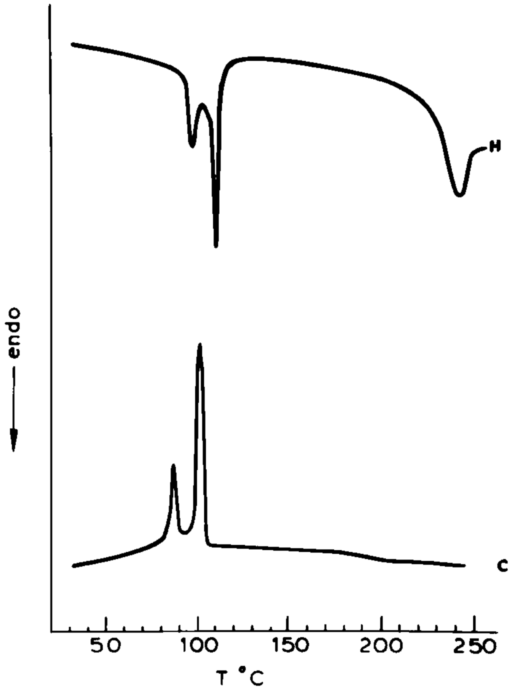

FIGURE 2 DSC trace of compound II.

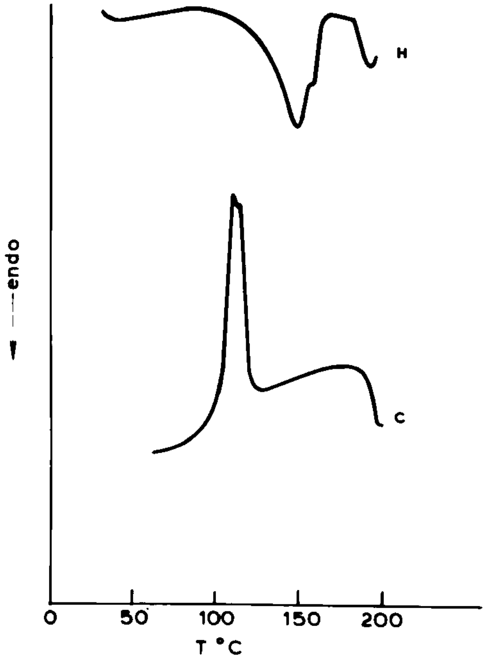

FIGURE 3 DCS trace of compound III.

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FIGURE 4 Mesomorphic texture of compound IV.

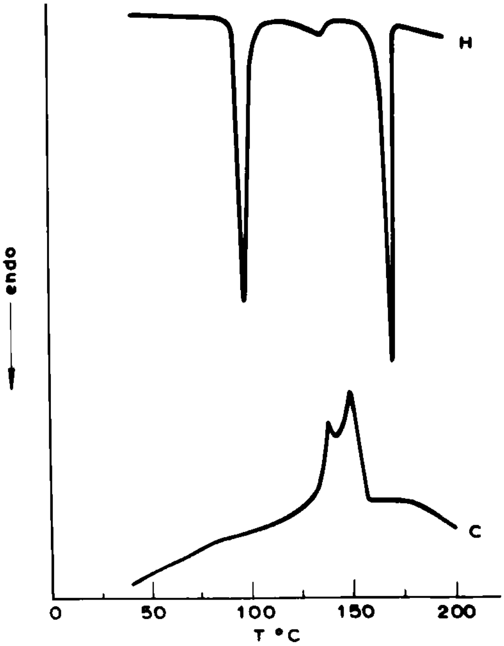

FIGURE 5 DSC diagram of compound IV.

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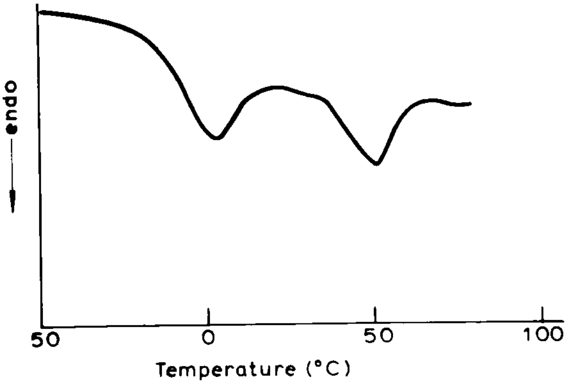

FIGURE 6 DSC diagram of compound VI.

and VIII are shown. For VII it is interesting to note that on cooling its mesomorphic phase is in a transient state and soon reverts to a crystalline phase. The texture shown in Fig.9 is characteristic for this material in which both mesomorphic and crystalline phases co-exist. Diphosphate VIII melts to a mesomorphic phase, Fig. 10, which on cooling from the isotropic melt is transformed directly to the solid phase.

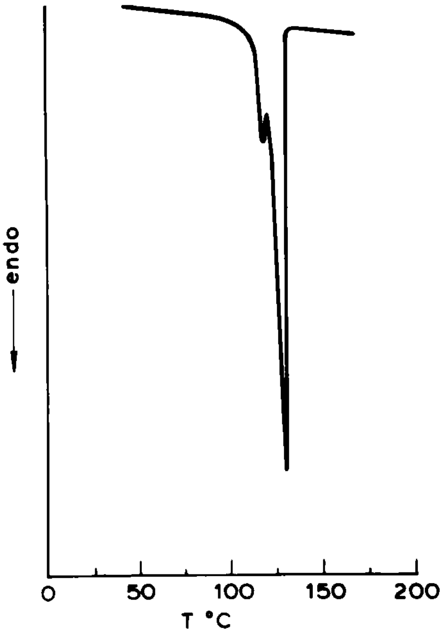

FIGURE 7 DSC trace of compound VII.

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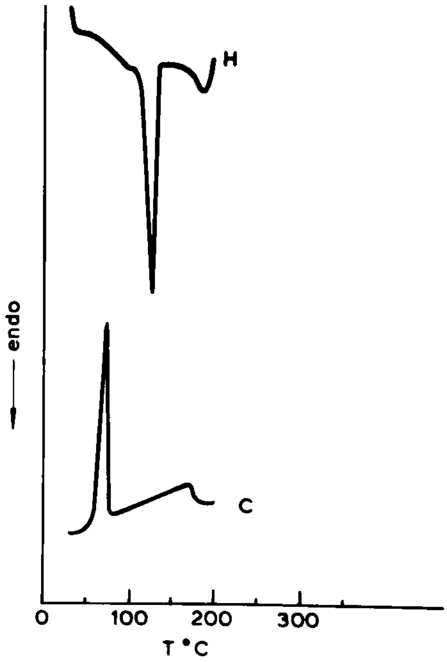

FIGURE 8 DSC trace of compound VIII.

FIGURE 9 Coexistence of mesomorphic and crystalline phases of compound VII.

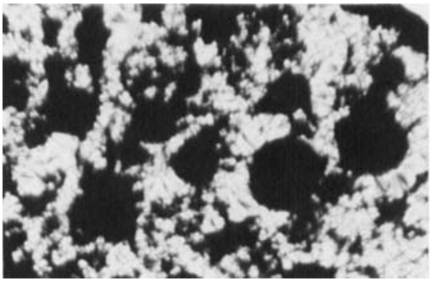

FIGURE 10 Mesomorphic texture of compound VIII

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CONCLUDING REMARKS

The separation of the polar heads by longer aliphatic chains favors the occurence and thermal stability of liquid crystalline phases. Specifically, by increasing chain length, melting and clearing points were lowered and also broader and relatively more thermally stable phases were obtained. Concerning head groups, triethylammonium or phosphate groups seem to favor the appearance of mesophases. On the contrary, the bulky diallylethylammonium group has a rather destructive effect on the existence of mesophases as it is the case with C_{12} diquaternary derivative.

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