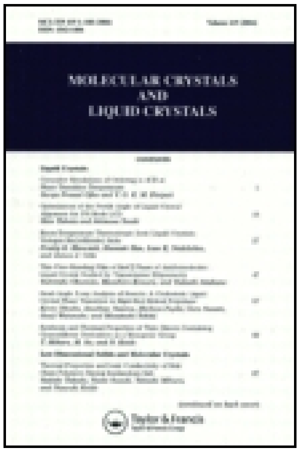

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LC Low Molecular Weight Compounds,Dimers,Vinyl Monomers and Polymers Based on Anilides of Formylbenzoylmethanes. Intra- and Intermolecular Hydrogen Bonds and CIS - Trans Isomerism

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LC LOW MOLECULAR WEIGHT COMPOUNDS,DIMERS,VINYL MONOMERS AND POLYMERS BASED ON ANILIDES OF FORMYLBENZOYLMETHANES. INTRA- AND INTERMOLECULAR HYDROGEN BONDS AND CIS - TRANS ISOMERISM.

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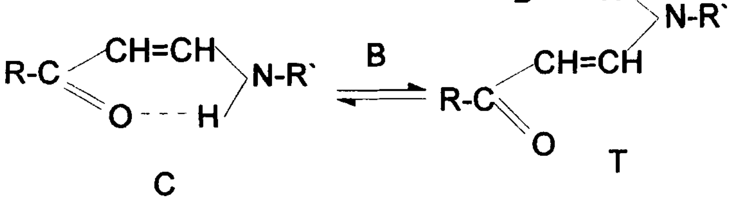
Abstract Low molecular weight compounds, dimers, and side chain polymers the mesogenic fragments of which contains the enamino ketone fragment were synthesised.These compounds the mesogen of which can exist as a mixture of isomers differet in shape and are stabilized by intra- and intermolecular hydrogen bonds and the factors which determined the appearance of the LC state were studied.

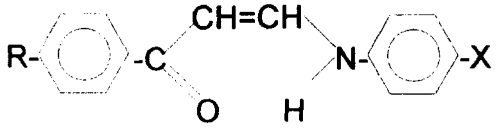
INTRODUCTION

The formation of the LC order in both low molecular weight compounds and polymers is due to a tandem of intra- and intermolecular interactions. The contribution of these specific interactions to this order is a topical problem.LC compounds are convenient for this study. The LC state in these compounds is formed as a result of inter- and intramolecular H-bonds,for instance,in the compounds containing the enamino ketone fragment. This structure can exist in the form of two isomers: a cis-isomer (C) stabilized by an intramolecular H-bond, and a trans-isomer(T) stabilized by an intermolecular H-bond with a proton acceptor center B .Another molecule of the same compound in the condensed state can play the role of this center[1]:



In solution, compounds with this fragment exist in the form of a mixture of C and T ,the proportion of the latter increasing with the concentration of proton acceptor centers B. LC low molecular weight compounds[2-6], dimers[7], and main chain polymers[2,7,8] containing the enamino ketone fragment in the mesogen have already been obtained. However,these works do not deal with the possibility of C-T isomerism and the possible effect of intra- and intermolecular H-bonds on phase behaviour.

Ketovinylidene anilines I substituted into the nucleus were chosen for this investigation:



I

Insertion of substituents of different electronic natures, into the nucleus changes the relative stability of isomers and makes it possible to vary the existence range of the mesophase in the desirable direction. An advantage of these compounds is the possibility of an easy,reliable, and quantitative C-T determination from their NMR spectra[9] .This is due to the difference in the NMR parameters of these isomers and also by the fact isomerisation rate is sufficient for attaining equilibrium in reasonable time but is not sufficient for the undesirable broadening and merging of the NMR signals of isomers.

RESULTS AND DISSCUSION

Low molecular weight compounds

A set of compounds II(R= C_6H_{13}) with different electron acceptor and electron donor substituents was synthesized(Table 1). Isomer C(in $CHCl_3$ solution) is characterized by the following spectral characteristics. ^{1}H NMR(δ) NH~12 ppm,J~12Hz. This is typical of the -NH-CH= fragment in trans conformation with an intramolecular H-bond C=O...HN . The low spin-spin coupling constant between vinyl and azometine protons(7.5-8Hz) in the C-CH=CH-NH fragment indicates the cis arrangement. Other characteristic signals from which isomers were determined were ^{1}H NMR(δ) C=CH-C (5.90-6.30 ppm), and ^{13}C NMR -C=O (190-191ppm) and =CH-C(91-93 ppm).The T isomer has the following spectral characteristics:^{1}H NMR(δ) NH~10 ppm,-C=CH-C(6.30-6.60 ppm); ^{13}C NMR -C=O (187-188 ppm) and =CH-C(95-10 ppm).

It was shown that in a relatively inert solvent($CHCl_3$) which is not capable of acting as a proton acceptor medium ,compounds II are present in the form of only one isomer C.In a proton acceptor solvent ,DMSO, a strong intermolecular H-bond formed between the NH group and DMSO stabilizes the T isomer,and, hence, C and T isomers coexist in solution.The C-T equilibrium in a DMSO solution was investigated(Table1).The displacement of this equilibrium towards the formation of the T isomer with increasing electron negative character of the substituent X can be due to increasing proton donor ability of the NH group and to stronger intermolecular bond with DMSO.This is manifested in a strong displacement of the NH ^{1}H NMR signal in spectra towards a weak field (12-12.30 ppm). The corresponding effect for intramolecular H-bond in the C isomer is weakened by decreasing proton acceptor ability of the carbonyl group as a result of its interaction with substituent X. In fact, for the Hammett dependence of C-T tautomeric equilibrium of compounds II we have ρ=0.36 ,whereas the Hammett dependence of (C=CH-C) chemical shift in the T form is ρ=0.20 ,which indicates the existence of the electron effect of substituent X on the carbonyl group. At the same time this effect is weaker by the factor 0.5 than that for the NH group,which is typical when an additional double bond is present[10].As has been shown previously,with increasing temperature the C-T equilibrium is displaced towards the C isomer,which indicates the energetic advantage of the existence of intermolecular H-bond[9].

TABLE 1. Properties of compounds II

Substituent X	T_m °C	T_i °C	T-C ratio in DMSO at 22°C
$N(CH_3)_2$	116	162	30-70
OCH_3	101	166	38-62
CH_3	95	140	40-60
H	103	no LC	43-57
Br	165	no LC	49-51
$COOC_4H_9$	169	no LC	53-47
$COCH_3$	171	no LC	55-45
NO_2	125	no LC	63-37

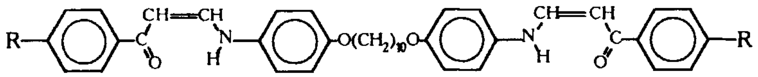
The Hammett dependence of the C-T tautomeric equilibrium in compounds II shows that the substituents plays an important role in the selection of isomers,and one can hope to change the shape of compounds II by an appropriate choice of the substituent (straight or bent rod). Examples of choice according to shape are known for some dinuclear Schiff bases (cyclic or linear form)[11]. However, the CP/MAS ^{13}C NMR investigation in crystal showed that all compounds II are present only in the form of the C isomer. However, for compounds I (R=H) in a crystal only C isomer exists for X= H, NO_2 and $N(CH_3)_2$, whereas for X = Cl, Br and CH_3 compounds I(R=H) crystallize in the T form. Hence, in the generation of a crystal, the choice of an appropriate isomer is a problem with many parameters,in which probably the shape effect predominates.Therefore,the choice of of certain isomer cannot be uniquely related to energetic preferences in solutions.

The following behaviour can be observed in the melting of compounds II (Table 1). Compounds II with electron donor substituents X form the nematic mesophase, whereas compounds II with electron acceptor substituents pass into isotropic melt. Moreover, as IR investigation have shown, the transitions crystal-liquid crystal-isotropic melt involves no essential conformational changes ,and the C isomer dominates in all phases as other authors have indicated previously apriori[6]. The formation of the nematic mesophase indicates the intermolecular H-bonds are absent.

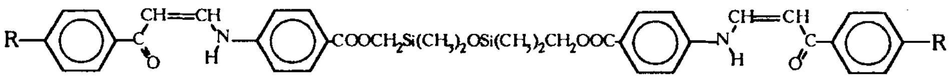
In contrast ,the presence of a T isomer and,hence,of intermolecular H-bonds (according to ^{1}H NMR data in the melt in an amount not exceeding 2-3%) makes the formation of the LC state impossible for compounds II with proton acceptor substituents X.Consequently,the form effect plays the predominate role in the possibility of forming the LC state for low molecular weight compounds and the presense of intermolecular H-bonds in combination with bent isomers prevents the formation of the LC order.

Dimers

The transition to the investigation of main chain polymers containing fragment I as mesogen is complicated ba the fact that main chain polymers ussualy have very high phase transition temperature. Hence, dimers, the conformational behaviour of which simulated that of main chain polymers were choisen for investigation[12]. Dimers III and IV containing substituents of different electron natures were synthesized:



III



IV

Dimer III containing a polymethylene spacer has a substituent of the same electronic nature as the compounds II(X= OCH_3). In fact, the C-T isomers ratio in DMSO solution at 22°C is the same (62/38). Therefore,the LC behaviour of the nematic type could be expected for dimer III. However, this compound is relativly highly fusible (T_m= 210°C), and, passes at once into the isotropic melt.

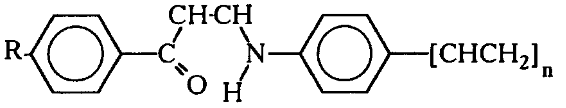
Dimer IV contains an electron negative substituent $COOCH_2$. The C-T isomers ratio in a DMSO solution is even more displaced towards to the T isomer (41/59) than that for low molecular weight analog(47/53). Neverthless, on melting (T_m=148°C) dimer IV passes into the smectic C phase with T_i = 165°C. This seems surprising because dimer IV crystallises in the form of the T isomer. Acctually,as the IR study has shown, melting is accompanied by dramatic conformational changes, particularly in the siloxane fragment. As a result, the C isomer dominates in the LC melt. However, a small fraction of the T isomer (1-2%) is present, and, hence, the existence of intermolecular H-bonds leads to the appearance of the smectic mesophase. As has been shown previously [13] the active role of the spacer in the LC state formation is a due to steric interaction between the ortho-protons of phenyl rings of the mesogen and methyl groups of the spacer. As a result, the linear arrangement of the mesogens fragment in the mesophase and the absence of the conformational flexibility are ensured. Hence, the dimer has a rigid-rod shape. Therefore, in spite of unfavorible electron factors, dimer IV forms the LC state. Moreover, in the mesophase only that isomer(C), which favours the stabilisation of the LC state is chosen. In other words, this is similar to the choice of only trans isomer of the 1,4-cyclohaxanedicarboxylic acid in the LC state[14].The rigid rod-like shape of dimer IV is confirmed by the fact that because of the absence of the conformational freedom the phenyl and carbonyl groups in the LC melt are conjugated.

This is manifestad in increasing intensity of the band of the C=O group over that the crystal. With increasing temperature the intensity of the C=O band usually decreases, which is actually observed on passing into the isotropic melt.

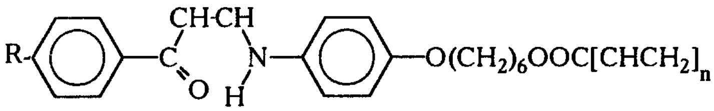
Hence,in dimers which are analogs of main chain polymers ,the formation of the LC state is ensured by a complex interaction of electronic and conformational factors, which confirms the active role of the polymer effect in the formation of the LC state.

Side chain polymers

Polymers V and VI with and without a spacer between the main chain and mesogen were also synthesised:



V



VI

Polymer V($[\eta]$ = 0.42 dl/g in $CHCl_3$ at 25°C) is crystallized in the C form just as compounds II, and exist in this form in the $CHCl_3$ solution(polymer is poorly soluble in DMSO). This polymer does not melt up to 300°C.

Polymer VI($[\eta]$= 0.11dl/g in $CHCl_3$ at 25°C) is glassy and noncrystallisable. Therefore, although the coresponding monomer forms the mesophase of the namatic type (T_m = 45°C, T_i = 110°C), polymer VI is not liquid crystalline, and passes from glass into the isotropic melt. The electron factors influence the C-T ratio of isomers in polymer VI, monomer, and the low molecular weight analog identically. The C-Tratio in DMSO solution at 22°C is 62/38 for all of them. This can probably be related to the fact that in a noncrystallisable polymer VI in the glassy state such a factor of isomer selection as crystallization does not exist. As a result, the isomer ratio in glass is similar to that in a solution in a proton acceptor solvent and is retained after T_g is exceeded. The high percentage of the T isomer leads to the impossibility of LC state formation.
Consequently, the factors of selection according to the rod-like shape determine the possibility of the LC state formation both in low molecular weight compounds and in polymers the mesogenic fragment of which can exist in the form of a mixture of isomers with different shape.

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