^{13}C NMR STUDY OF THE MIXTURE MBBA/EBBA/DECANE: THE INFLUENCE OF DECANE ON THE MOLECULAR ORDERING IN THE NEMATIC PHASE

Josef ŠEBEK[a]* and Raivo TEEAAR[b]

[a] *Polymer Institute, The Centre of Chemical Research,*
Slovak Academy of Sciences, 842 36 Bratislava, Czechoslovakia and
[b] *Institute of Chemical Physics and Biophysics,*
Estonian Academy of Sciences, Tallinn 200001, U.S.S.R.

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Influence of various amounts of decane dissolved in the eutectic nematic mixture in methoxybenzylidenebutylaniline and ethoxybenzylidenebutylaniline (MBBA/EBBA) on the ordering and structure of mesomorphic molecules has been determined employing high-resolution proton enhanced ^{13}C NMR spectroscopy. The obtained results are compared with temperature behaviour of the ordering and structure of EBBA studied by means of the same technique. Slight differences in the ordering of the phenyl parts of molecules in the dependence on temperature and on decane concentration have been observed. This contrasts with great differences observed in the behaviour of the butyl parts of mesogenic molecules. Two possible explanations of the behaviour of butyl chain atoms in the dependence on decane concentration are presented. According to one approach, conformational order parameters of the first butyl carbons increase with the increasing decane concentration. Another possibility is that decane increases the correlation between the whole molecule rotation and the internal rotation around the first butyl bond.

During recent years a raising interest in the study of the behaviour of aliphatic parts of the rod- and disc-like molecules which form liquid crystals is quoted. The chains anchored at the ends of hard rods and/or symmetrically on hard discs influence phase transition temperatures, temperature interval of the appearance of liquid crystal phases, as well as the variety of these phases. Two experimental techniques enabling an insight into the structure and dynamics of the chain parts are used preferentially at present: (i) ^{2}H NMR spectroscopy of selectively deuterated mesogenic molecules[1-9] an (ii) ^{13}C NMR spectroscopy[10-13].

Both the quadrupole splitting δ_i and the chemical shift difference $(\sigma^i - \sigma^i_{iso})$ represent a direct quantitative measure of the ordering of indiviual carbons in the molecule. From the experimental results the statistical probability of chain conformations can be calculated[4-6,9]. Providing information on the behaviour and influence of aliphatic molecular parts on the liquid crystalline structure.

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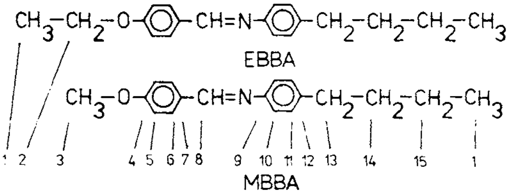
* To whom the correspondence should be addressed.

In the present paper we report on ^{13}C NMR measurements of the eutectic mixture MBBA/EBBA in which different amounts of n-decane have been dissolved. In this manner we attempt to study the influence of alkanes on the behaviour of both aromatic cores and butyl chains of MBBA and EBBA. The existing NMR studies on similar systems, i.e. chain molecules dissolved in thermotropic[14–16] and lyotropic[17,18] liquid crystals, are concerned with the influence of the orienting medium on the conformational structure of solute molecules.



The obtained results on the structure of mesogenic molecules are compared with the behaviour of molecules in pure liquid crystals in dependence on the temperature.

EXPERIMENTAL

The experiments were performed on a Bruker CXP-200 spectrometer with the home-built solid-state probehead[19]. Cross-polarization[20] and high-power proton decoupling were used for the ^{13}C signal enhancement and for the achievement of high resolution.

The sample was thermostated by an intensive air stream through the air channel in the probehead. The heating of the air was regulated by a B-VT-1 000 variable temperature unit. Due to the probehead construction, the upper temperature limit was 65°C. The air temperature was measured two centimetres before the sample. The actual sample temperature was by approximately 2°C higher than the air temperature because of the decoupling power absorption. The mean output of the decoupler averaged over the whole pulse sequence was about 1 W. As we were not interested in the exact temperature value but only in relative temperature changes, the obtained temperature scale was not recalibrated.

Approximately 300 scans per spectrum were accumulated to obtain sufficient signal-to noise ratio.

The samples were prepared from the commercially available eutectic mixture MBBA/EBBA (melting point −10°C, clearing point 55°C, Reachim, U.S.S.R.) by addition of the corresponding amount of $C_{10}H_{22}$ and heating well above the clearing point of the mixture. Pure EBBA was purchased from Reachim (melting point 37°C, clearing point 80°C) and was used without further purification.

RESULTS

Fig. 1 shows the measured spectra obtained for the pure eutectic mixture MBBA/EBBA and for five different concentrations of decane in this mixture: 2, 4, 6, 8 and

10%. Solutions with 0 to 8% gave a signal typical for liquid crystals. 10% mixture was nematic at room temperature, however, the temperature increase due to high-power decoupling induced phase transition of the sample to the isotropic state. The values σ^{i}_{iso} for individual carbons are taken from the spectrum of the isotropic solution (10%). Fig. 2 shows the measured spectra of pure EBBA at different temperatures.

The assignment of the lines to the individual carbons was carried out according to Teeaar et al.[21]. All the lines in the spectra are well resolved with the exception of the low-field region. This region should consist of five lines corresponding to carbons: C_4, C_7, C_8, C_9 and C_{12}. Nevertheless, the spectrum of the best resolved 2% solution clearly consists of at least eight lines, i.e. three additional lines are present. Several explanations exist of this effect. One of the possible reasons can be the differences in the orientation ordering of molecules MBBA and EBBA. These differences are then reflected in chemical shifts of carbons C_4, C_7, C_8, C_9 and C_{12}, since their main axes are parallel with the long molecular ones. Hence, they are most sensitive to the differences in orientation. Nevertheless, such great differences in the orientation of

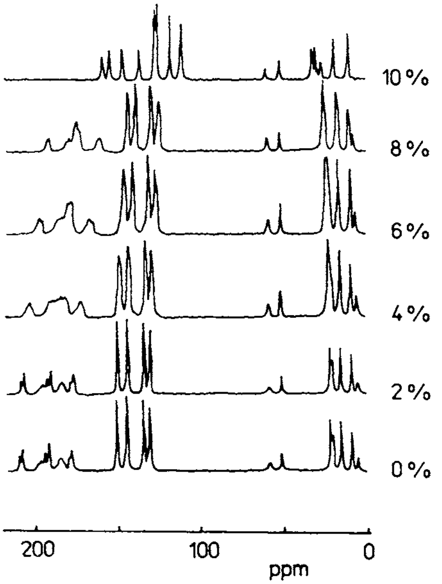


FIG. 1

High resolution ^{13}C NMR spectra of the mixture MBBA/EBBA/decane for different concentrations of decane. Chemical shifts are given in ppm units relative to TMS

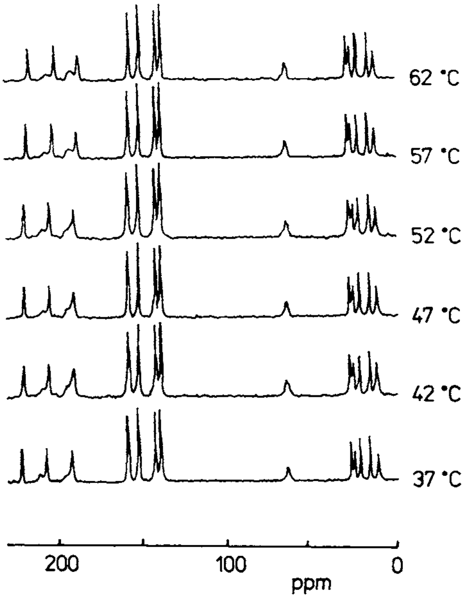


FIG. 2

High resolution ^{13}C NMR spectra of pure EBBA by different temperatures two similarly structured molecules, as MBBA and EBBA are, is not probable. The other possible explanation is that the line splitting is caused by dissimilar averaged conformational structures of MBBA and EBBA molecules. The differences in internal rotation around the bonds O—C_4, C_7—C_8 and N—C_9 can lead to different positions of the lines of carbons C_4, C_7 and C_9. Although the latter explanation seems to be more probable to us, neither can be verified on the basis of the present experiment.

Tables I and II present chemical shifts σ^i of hard rod and alkyl chain carbons as a function of decane concentration. The obtained results are similar to the tempera-

TABLE I

Chemical shifts of hard-core carbons of MBBA and EBBA in dependence on the concentration *c* of decane in the mixture MBBA/EBBA/decane

c %	σ^i								
	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
0	211·5	135·3	155·0	181·9	188·4	197·4	138·9	148·9	195·5
2	210·0	134·6	154·3	180·2	187·3	195·8	138·4	148·3	193·8
4	205·5	133·3	152·4	175·4	185·7	193·7	137·2	146·9	187·0
6	198·6	130·4	149·3	169·0	182·6	188·6	134·9	144·3	180·9
8	193·7	128·2	146·6	163·8	181·1	182·0	132·8	142·0	177·6
10	161·9	114·0	130·5	129·6	157·6	149·8	121·1	129·0	139·9
σ^i_{cf}	—	58·0	68·0	—	—	—	56·0	55·0	—

TABLE II

Chemical shifts of the butyl chain carbons of MBBA and EBBA in dependence on the concentration *c* of decane in the mixture MBBA/EBBA/decane

c %	σ^i						
	C_1	C_2	$C_{2'}$	C_3	C_{13}	C_{14}	C_{15}
0	54·9	13·5	9·7	61·9	24·6	26·0	19·9
2	54·9	13·5	9·7	62·1	24·9	26·3	20·0
4	54·9	13·6	10·2	62·1	26·4	26·4	20·3
6	54·9	13·6	10·7	62·2	27·9	27·1	20·7
8	54·8	13·6	11·3	62·4	28·8	27·5	21·0
10	54·8	14·1	14·1	63·2	35·4	33·8	22·7
σ_{cf}					27·0	27·0	18·45

ture dependence of chemical shifts in liquid crystals, i.e. with increasing concentration the value $(\sigma^i - \sigma^i_{iso})$ decreases[10-13].

The tensors of chemical shifts σ consist of three different components σ_{11}, σ_{22} and σ_{33}. Even if one assumes the molecules to rotate rapidly around the axes parallel with the phenyl ring long-axes, for complete characterization of phenyl ordering it is necessary to use at least two order parameters S_{zz} and $(S_{xx} - S_{yy})$ for each ring[22]. Nevertheless, from the obtained experimental data it is not possible to determine both these order parameters. Therefore, we shall apply a frequently used semiquantitative description of the ordering of the whole rod part of the molecule with an one order parameter $S_A = S_{zz}$ (ref.[10-12]).

The order parameter S^i_{zz} for aromatic carbons can be calculated from the equation[10]

$$S^i_{zz} = 3/2\,(\sigma^i - \sigma_{iso})/\delta_{ef}\,, \tag{1}$$

where $\delta_{ef} = \langle\sigma_{\parallel}^{i,0}\rangle - \langle\sigma_{\perp}^{i,0}\rangle$ and $\langle\sigma_{\parallel}^{i,0}\rangle$, $\langle\sigma_{\perp}^{i,0}\rangle$ are the parallel and perpendicular components of chemical shifts relative to the long axis of the *all-trans* butyl chains.

The value of the hard rod part order parameter S_A is expressed as a mean value of S^i_{zz} for carbons C_5, C_6, C_{10}, C_{11}, the lines of which are well resolved. The values δ_{ef} are taken from ref.[21] and their values for the individual carbons are in the bottom row of Table I.

Fig. 3 shows the dependence of S_A on the decane concentration. For comparison, Fig. 4 shows the temperature dependence of S_A for pure EBBA. As can be seen, the increase of the decane concentration influences S_A in the same way as the temperature increase, i.e. it leads to a more disordered structure.

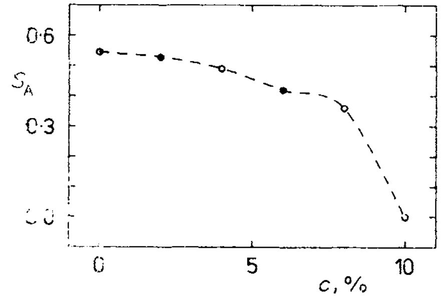


FIG. 3

The course of aromatic core order parameter S_A in the mixture MBBA/EBBA/decane in dependence on the decane concentration

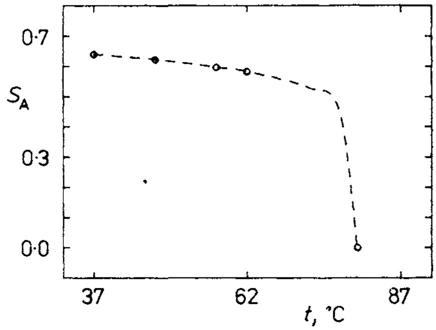


FIG. 4

The dependence of aromatic core order parameter S_A on temperature in pure EBBA. The course above the probe-head upper limit 65°C is taken from the tabulated values

More complicated is the analysis of the ordering of butyl chain carbons. In this case, the measured chemical shifts result from an uncomplete whole-molecule rotational averaging, described by the order parameter S_A, as well as from the averaging by the conformational rotation of chains.

The values of the measured chemical shifts are proportional to[12]

$$\sigma^i = \sigma^i_{iso} + \tfrac{2}{3} S_A(\langle \sigma^i_{\parallel} \rangle_{conf,para} - \langle \sigma^i_{\perp} \rangle_{conf,para}) \qquad (2)$$

For a given carbon, the expression

$$(\langle \sigma^i_{\parallel} \rangle_{conf,para} - \langle \sigma^i_{\perp} \rangle_{conf,para}) = \varphi^i = 3/2\,(\sigma^i - \sigma^i_{iso})/S_A \qquad (3)$$

is a measure of conformational order averaged by the whole molecule rotation. S_A is the order parameter of the long axis phenyl ring part. Figs 5 and 6 show the values of φ^i in the dependence on decane concentration in the system MBBA/EBBA and in the dependence on temperature in pure EBBA, respectively. The values φ^i decrease with the increasing temperature in EBBA, and oscillate along the chain in an agreement with the known even-odd effect. On the other hand, the results for the

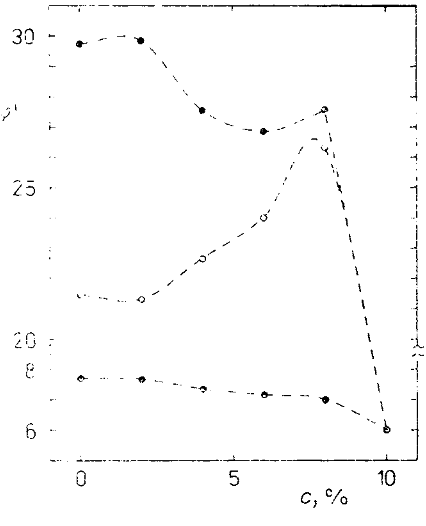


FIG. 5

The dependence of the values β^i for carbons i = 13 (◓), 14 (○), 15 (●) on decane concentration in the mixture MBBA/EBBA/decane

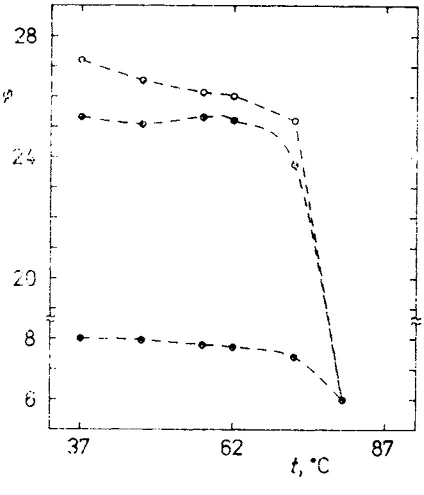


FIG. 6

The course of β^i as a function of temperature in EBBA mixture MBBA/EBBA/decane are quite different. In this case, the values φ^i do not periodically oscillate along the chain. However, most surprising is that values φ^i, $i = 13, 14$, increase with the increasing concentration of decane in the mixture. It means that an increasing amount of decane increases the rotation-conformational ordering of these first segments of the butyl chain. It is an unexpected behaviour which, according to our knowledge, has not been reported up to now.

Following the work of Rutar et al.[12] we can obtain the conformationally averaged chemical shifts from equations

$$\langle\sigma^i_{\parallel}\rangle_{conf} = \sigma^i_{iso} + \tfrac{1}{3}S^i_{conf}(\langle\sigma^{i,0}\rangle - \langle\sigma^{i,0}_{\perp}\rangle) \tag{4}$$
$$\langle\sigma^i_{\perp}\rangle_{conf} = \sigma^i_{iso} - \tfrac{2}{3}S^i_{conf}(\langle\sigma^{i,0}\rangle - \langle\sigma^{i,0}_{\perp}\rangle)\,.$$

The orientation of the long axis of the *all-trans* butyl chain with respect to the long axis of the phenyl ring part is characterized by angles Ω and Φ, Fig. 7. The angle Ω determines the angle between the two axes. The angle Φ is the angle between the plane of phenyl ring and the plane of angle Ω. Thus, the angle Φ is the dihedral angle of the internal rotation around the first bond C_{12}—C_{13} φ_1. Angle ω describes the whole-molecule rotation.

Characteristic times of conformational rotations are considerably shorter than the period of the whole molecule rotation. These two rotations can be therefore viewed as independent[12]. The parallel and perpendicular components of chemical shifts averaged over the conformational and the whole molecule rotations have then, in the laboratory coordinate system, the form

$$\langle\sigma^i_{\parallel}\rangle_{conf,para} = \langle\sigma^i_{\parallel}\rangle_{conf}\cos\Omega + \langle\sigma^i_{\perp}\rangle_{conf}\sin\Omega \tag{5}$$
$$\langle\sigma^i_{\perp}\rangle_{conf,para} = \tfrac{1}{2}\langle\sigma^i_{\parallel}\rangle_{conf}\sin\Omega + \tfrac{1}{2}\langle\sigma^i_{\perp}\rangle_{conf}(1 + \cos\Omega)\,.$$

After substitution of Eqs (*5*) and (*4*) into Eq. (*2*), the measured value of chemical shift is equal to

$$\sigma^i = \sigma^i_{iso} + \tfrac{1}{3}S_A\sigma^i_{iso}(\cos\Omega + \sin\Omega - 1) +$$
$$+ \tfrac{1}{9}S_A S^i_{conf}\delta^i_{ef}(\cos\Omega - 4\sin\Omega + 1)\,. \tag{6}$$

The conformational order parameters of butyl carbons have then the form

$$S^i_{conf} = 9(\sigma^i - \sigma^i_{iso} - \tfrac{1}{3}S_A\sigma^i_{iso}(\cos\Omega + \sin\Omega - 1))/$$
$$/(S_A\delta^i_{ef}(5\cos\Omega - 4\sin\Omega + 1))\,. \tag{7}$$

Fig. 8 shows the dependence of S^i_{conf} on the concentration of decane in the mixture MBBA/EBBA/decane. In Fig. 9 are the corresponding dependences of S^i_{conf} on temperature in pure EBBA. When compared with Figs 5 and 6, it is clear that the unexpected behaviour of φ^i, $i = 13, 14$, is conditioned by the conformational structure of molecules.

Nevertheless, there exists another possible explanation of this effect. As it was mentioned previously the conformational rotation around the/bond C_{12}—C_{13} for butyl carbons is undistinguishable from the whole molecule rotation around the long axis of the phenyl ring part in the laboratory coordinate system (angle ω). If these two rotations are not independent, the increase in φ^i of carbons C_{13} and C_{14} need not be inevitably connected with the increase in their conformational order parameters, S^i_{conf}. From Figs 3, 4, 5 and 6 it is evident that φ^i increases with the increasing decane concentration when the averaged orientation of the long axis

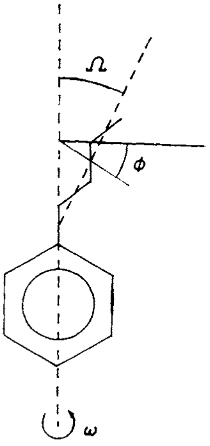


FIG. 7

Schematic representation of the structure of the butyl-aniline part of MBBA and/or EBBA. Angles Ω and Φ characterize the relative orientation of the long axis of phenyl ring part and the long axis of the *all-trans* butyl chain. Angle ω describes the whole molecule rotation

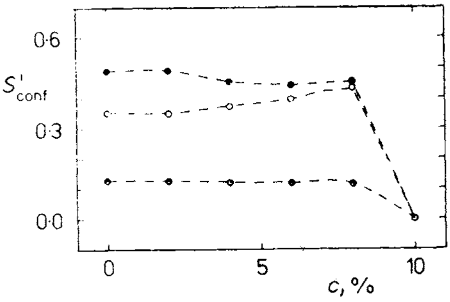


FIG. 8

The course of conformational order parameters of butyl carbons C_{13} (●), C_{14} (○), C_{15} (●) in the dependence on decane concentration

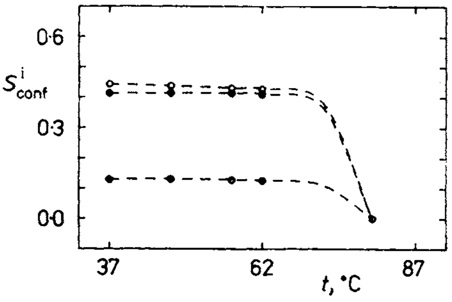


FIG. 9

The dependence of S^i_{conf} on temperature for first three butyl chain carbons $i = 13, 14, 15$

of the phenyl part

$$\vartheta_0 = \arccos \tfrac{2}{3}(S_A + \tfrac{1}{2}) \qquad (8)$$

approaches the angle Ω.

If the rotations are correlated, i.e. the angular velocities are equal and of opposite direction, the position of the first two carbons in the chain (and also the direction of the long axis of the *all-trans* chain) is stabilized in the laboratory coordinate system. The increased positional order of carbons C_{13} and C_{14} can be the reason of the increase in values of φ^i. All the following chain carbons are not influenced by this correlation, since their conformational averaging is, in addition to the first bond, given by internal rotations around all bonds between them and the phenyl ring.

In the case where the whole molecule rotation and conformational motions of molecule are independent (usual temperature experiments on nematics), the orientation of the long axis of the phenyl ring part is parallel with the averaged orientation of the long axis of the butyl chain. Hence, the orientation ordering of the molecule as a whole is determined by the orientation ordering of the phenyl part long axis.

The situation is different in the mixture MBBA/EBBA/decane. It can be said that in the laboratory coordinate system the averaged orientation of the long butyl axis is fixed. The long axis of the whole molecule is not parallel with the para axis of the phenyl ring. This explains why in the MBBA/EBBA/decane mixture the order parameters S_A can be lower than those which have been observed in usual nematic phases.

CONCLUSIONS

In the present work the influence of aliphatic chains on the structure of mesogenic molecules in nematic phase is studied. The obtained results can be summarized as follows:

1) The ordering of hard phenyl parts of molecules decreases with the increasing decane concentration in the mixture. The measured order parameters S_A are bellow the values typically observed in nematic liquid crystals.

2) The behaviour of butyl chains of molecules MBBA/EBBA in the dependence on decane concentration differs from the effects which have been observed in nematics up to now. The even-odd effect is not present, and the rotation-conformational ordering of the first two carbons even increases with the increasing decane concentration.

Following the usual approach[12], considering the whole molecule and conformational rotations independent, the increasing decane concentration increases the conformational order parameters of carbons C_{13} and C_{14}.

However, analysis of the geometrical structure of the studied molecules suggests a more probable explanation of the observed effects. The increasing rotation-conformational ordering of the first two carbons can result from increasing correlation between the whole molecule and the internal rotation around the first butyl bond. The orientation of the long axis of the butyl chain is then fixed in the laboratory coordinate system and is no more parallel with the long axis of phenyl rings. As a result, the molecular long axis is not parallel with the long axis of the phenyl ring part. The order parameter S_A does not represent the ordering of the molecule as the whole. Thus, the parameter S_A can be lower than the order parameters of the molecules in the nematic phase. Hence, the second hypothesis can also explain the experimentally observed lower values of S_A.

Correlations in motions of hard-core and alkyl chain parts of molecules could explain the phase transition SmA–SmC liquid crystals. In these systems, the "effect of decane" is caused by the alkyl chains of neighbour molecules which are satisfactorily long (from eight to eighteen segments).

In order to understand and explain the effect of chains on the structure of mesogenic molecules in detail, further experiments on similar systems are needed.

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