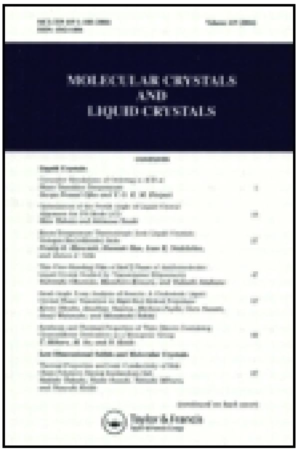

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Liquid Crystalline Compounds Based on 1,4-Disubstituted But-1-Yne

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LIQUID CRYSTALLINE COMPOUNDS BASED ON 1,4-DISUBSTITUTED BUT-1-YNE

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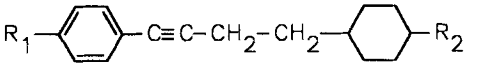
Abstract Liquid crystalline compounds containing the $-CH_2CH_2-C\equiv C-$ inter-ring linkage between cyclohexane and benzene rings belonging to four homologous series have been prepared. Their mesogenic, viscous, dielectric, optical, and dielectrooptical properties were investigated and compared with the properties of analogous compounds with the $-CH_2CH_2-$ or $-C\equiv C-$ bridge groups. The mesogenic and physical properties of the compounds with the $-CH_2CH_2-C\equiv C-$ linkage group are intermediate between properties of the compounds with $-C\equiv C-$ and the properties of the compounds with $-CH_2CH_2-$ group, except that their clearing points are lower and viscosity is higher.

INTRODUCTION

Liquid crystalline molecules containing the $-CH_2-CH_2-$ or $-C\equiv C-$ bridging groups between rings are important for display applications[1-7] because of their advantageous physical properties. The compounds with the flexible inter-ring $-CH_2-CH_2-$ linkage are especially attractive when this group is situated between cyclohexane and benzene rings[8,9] (for example PECH) because they have low viscosity and small melting enthalpy and the thermal stability is as high as for the compounds with a direct bond between cyclohexane and benzene rings (e.g. PCH). This is also true for multiring compounds.[1] For these reasons they are used as convenient components for preparing mixtures with a broad range of the nematic phase. The compounds containing the rigid triple bond -C≡C- linkage have large birefringence, especially when this linkage is between aromatic rings.[10] Compared to the compounds with $-CH_2-CH_2-$ bridging group, the acetylene compounds have the highest nematic phase thermal stability especially when the -C≡C- bridge group is placed between benzene rings.

We therefore expected that the compounds with a $-CH_2-CH_2-C\equiv C-$ linkage group might have similar properties to those of the compounds with the -C≡C- group and of the compounds with the $-CH_2-CH_2-$ group. We synthesized the following 1,4-disubstituted but-1-yne derivatives to check this idea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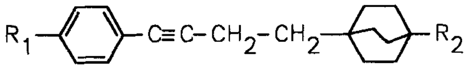
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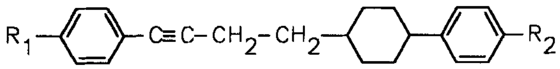
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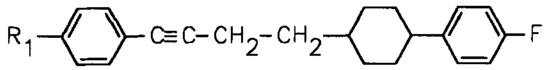
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wherein R_1 and R_2 are unbranched alkyl or alkoxy chains.

The compounds with the $-CH_2-CH_2-C\equiv C-$ bridge group have not been investigated yet.

RESULTS AND DISCUSSION

Mesogenic properties

In Table I the phase transition temperatures of compounds 1 and 2 are compared with those of compounds of a similar structure but containing either the $-CH_2-CH_2-$ or -C≡C-

TABLE I Comparison of phase transition temperatures (°C) of compounds 1 and 2 with similar ones containing the -C≡C- or $-CH_2-CH_2-$ bridge group

No	R_1	R_2	$-C\equiv C-CH_2-CH_2-$				$-C\equiv C-$			$-CH_2-CH_2-$			
			Cr	S_B	N	I	Cr	N	I	Cr	S_B	N	I
							Compound 1						
a	C_5H_{11}	C_3H_7	* 36.4			*							
b	C_5H_{11}	C_5H_{11}	* 31.2	*	* (4.5)^b	*	* 30.1	* (25.0)^a	*	* 9.5	* 30.0^a		*
c	C_6H_{13}	C_3H_7	* 30.1			*							
d	C_6H_{13}	C_5H_{11}	* 24.9			*							
e	C_2H_5O	C_4H_9	* 54.6			*							
f	C_2H_5O	C_5H_{11}	* 50.0			*	* 70.4	* 75.3^a	*	* 27	* (8)	* 47^a	*
g	C_3H_7O	C_5H_{11}	* 42.3		* (22.9)	*	* 65.1	* (60.8)^a	*	* 24.5	* 32.5	* 33.5	*
h	C_4H_9O	C_3H_7	* 50.5		* (17.8)	*							
i	C_4H_9O	C_5H_{11}	* 47.9		* (34.9)	*	* 44.3	* 70.0^a	*	* 25.5	* 44	* 45^a	*
j	$C_5H_{11}O$	C_5H_{11}	* 30.9		* (24.9)	*							
							Compound 2						
a	C_2H_5O	C_6H_{13}								* 42.5		* 95.2	*
b	C_4H_9O	C_3H_7	* 92.4		* (73.8)	*							

a - Ref. [11]; b - the S_B-N transition temperature is below 0°C

linkage. The 1-(alkylphenyl)-4-(trans-4-alkylcyclohexyl)but-1-ynes (1) are solids without an enantiotropic or monotropic liquid crystal phase, excepted for the dipentyl derivative which is the monotropic nematic. There is a smectic phase below the nematic one, probably the smectic B phase. This was concluded from the phase diagram with 1,2-bis-(trans-4-pentylcyclohexyl)ethane. Comparison of compound 1b with its analogues shows that it has lower stability of the nematic phase than the compounds with the -C≡C- group (clearing point is lower by 20 degrees) but it shows a higher tendency to form the nematic phase than compound with the $-CH_2-CH_2-$ bridge, which exhibits only the smectic B phase.

All (1-(alkoxyphenyl)-4-(trans-4-alkylcyclohexyl)but-1-ynes) investigated by us are only monotropic nematics, their clearing points are lower by about forty degrees than their acetylene and by about 10 degrees lower than their ethane analogues. Their phase properties: melting points, clearing points and the temperature of the S-N phase transition change in the following way:

T_m $-C{\equiv}C- > -C{\equiv}C\text{-}CH_2\text{-}CH_2- > -CH_2\text{-}CH_2-$

$T_{N\text{-}I}$ $-C{\equiv}C- > -CH_2\text{-}CH_2- > -C{\equiv}C\text{-}CH_2\text{-}CH_2-$

$T_{S\text{-}N(I)}$ $-CH_2\text{-}CH_2- > -C{\equiv}C-, -C{\equiv}C\text{-}CH_2CH_2-$

The phase situation of the compounds with $-C{\equiv}C\text{-}CH_2\text{-}CH_2-$ is more similar to this of the compounds with the $-C{\equiv}C-$ group than to that of compounds with the $-CH_2\text{-}CH_2-$ group. The introduction of the triple bond between the $-CH_2\text{-}CH_2-$ group and benzene ring does not increase the clearing point as it was observed in nonpolar molecules[11] when this bond was placed in the alkyl tail connecting it to the benzene ring. The molecules with the $-C{\equiv}C\text{-}CH_2\text{-}CH_2-$ group are less linear than the molecules from the two other groups.

Exchanging the cyclohexane ring for the bicyclo[2,2,2]octane significantly increases the clearing point (compound 2a). The same is observed in the case of other compounds containing the bicyclo[2,2,2]octane ring.[8,9] Simultaneously the melting point of compound 2b increases strongly. Compound 2b has only the monotropic nematic phase while the ethane analogues show a broad enantiotropic nematic phase.

The phase transition temperatures of compounds 3 are shown in Table II and of compounds 4 in Table III. Three ring compound 3 with alkyl substituents in both terminal positions (3a) has only the smectic B phase, its virtual N-I transition was estimated by extrapolation from the nematic n-CHBT host to be equal to 40°C. When alkyl and alkoxy chains are short, compounds 3 are nematics, when the chains become longer, the smectic B phase appears. For pentyl and pentyloxy derivatives (3e), only the smectic B is observed. Compound 4 with a fluorine atom in one terminal position and the alkyl or alkoxy chain in the other are nematics but in most cases this phase is monotropic.

TABLE II Phase transition temperatures (°C) of compounds 3

No	R_1	R_2	Cr	S_B	N	I
a	C_5H_{11}	C_3H_7	* 48	* 73.5		*
b	C_2H_5O	C_3H_7	* 94.9		* 101.9	*
c	C_3H_7O	C_3H_7	* 92.7		* (89.5)	*
d	C_4H_9O	C_3H_7	* 75	* 81.5	* 94	*
e	$C_5H_{11}O$	C_5H_{11}	* 74	* 90		*

TABLE III Phase transition temperatures (°C) of compounds 4

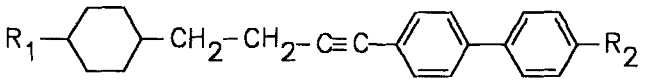
No	R_1	Cr	N	I
a	C_2H_5	* 79.5	-	*
b	C_3H_7	* 76.9	* 58.2	*
c	C_4H_9	* 44.6	* 49.7	*
d	C_5H_{11}	* 62.7	* (57.2)	*
e	C_2H_5O	* 102.7	* (95)	*
f	C_3H_7O	* 103.5	* (85)	*
g	C_4H_9O	* 83.0	* 94.5	*
h	$C_5H_{11}O$	* 69.0	* 84.2	*

Three-ring compounds 3 and 4 have low clearing points. It results mainly from the inconvenient ring sequence. In mesogens with the sequence of the rings:

benzene - cyclohexane - benzene

and when they follow one another or are separated by the $-CH_2-CH_2-$ or -COO- linkage the clearing points are much lower than for mesogens with the sequence cyclohexane - benzene - benzene[3,13]

The compounds



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should have the clearing point higher (about 70 degrees) than compound 3 and 4.

Viscous and electrooptical properties

The physical properties of the compounds but-1-ynes are compared to the properties of its acetylene and ethane analogues in Table IV.

The four-component mixture of 1e, 1f, 1i and 1j (in mole ratio 1:1:1:1) instead of individual compounds were investigated, because of their monotropic character. Alkyl, alkoxy substituted compound 1 have negative dielectric anisotropy as their ethane analogues but the value is smaller. The optical anisotropy of the investigated compounds is almost equal to the acetylene analogues but viscosity is probably higher.

It is difficult to say if for the greater value of viscosity the -CH_2-CH_2-$C\equiv C$- linkage is responsible or exclusively the -$C\equiv C$- linkage, because the values of viscosity for pure compound with -$C\equiv C$- linkage are not known, only the value extrapolated from mixture ZLI-3086 can be used for the comparison.

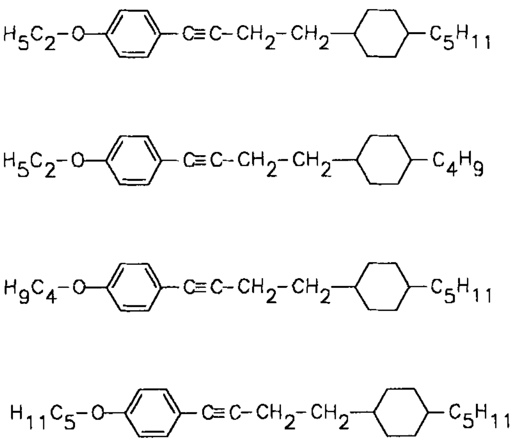
We can see from the Table V and VI that also in the case of compounds 1 the estimated values from the host mixture are much lower than those found for the mixture containing only compound 1.

In Table V the dielectric, optical and viscous properties of host mixture B composed of five Demus esters are compared to those of the same mixture doped with 10 wt.% of compound 1a, 1h or 2b. Only in the case of compounds 2b the viscosity of the host mixtures increases but for the other two compounds it does not change. In this mixture the non-additive behavior of viscosity is observed when the concentration of the -CH_2-CH_2-$C\equiv C$- component is not large. The compounds 1 increase the birefringence of host mixture B and does not change their small negative dielectric anisotropy significantly.

TABLE IV Comparison of the physical properties of the compounds with the acetylenoethylene, acetylene and ethylene bridge group

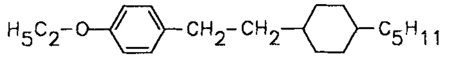
Materials	T_{N-I} °C	n_o	n_e	Δn	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$	η mm^2/s
Mixture A	29	1.4888	1.6182	0.1294	2.90	2.93	-0.03	43.2
Compounds 5	46	1.483	1.557	0.074	2.67	2.93	-0.26	12.9^a
Compounds 6		1.503	1.635	0.132	3.0	2.8	0.2	23^b

a - at -22°C[1], b - these values were extrapolated from 2LI-3086 mixture[10]



A

mole ratio 1:1:1:1



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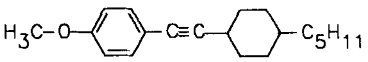

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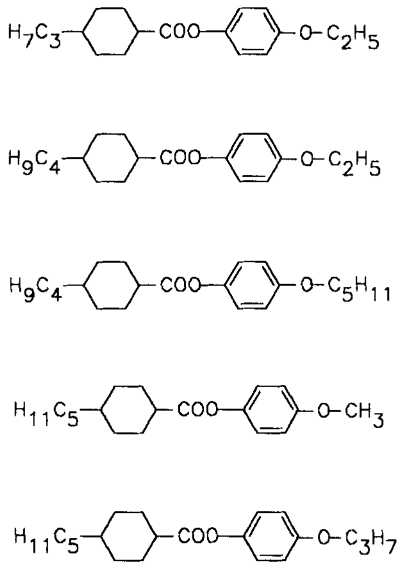
TABLE V Dielectric, optical and viscous properties of liquid crystal mixture B and B doped with 10 wt. % of compound 1 or 2

Mixtures	$T_{N\text{-}I}$ °C	n_o	n_e	Δn	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$	η mm^2/s
B	71	1.4780	1.5532	0.0752	3.00	4.05	-1.05	23.2
B and 1a	60.5	1.4791	1.5682	0.0891			-0.95	22.6
B and 1h	63.5	1.4782	1.5692	0.0910	2.95	3.90	-0.95	23.4
B and 2b	70.5	1.4797	1.5700	0.0903	3.00	4.10	-1.10	26.0



B

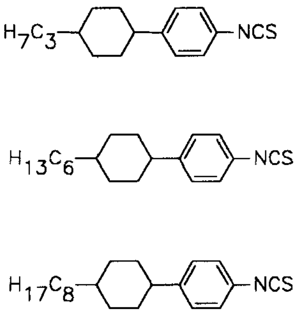
1:2:2:2:2 by weight

Table VI shows the viscosities and electrooptical properties of the 10 wt. % solution of but-1-ynes 1, 2, 3 and 4 in eutectic host mixture C composed of three isothiocyanates (n-CHBT; n=3, 6, 8; in wt.% ratio 40:42:18). After doping the viscosity of mixture C increases 10-20% for the two-ring compounds 1 and 2, and 20-30% for two-ring compounds 3 and 4. This allows estimation of the value of viscosity for pure two-ring compounds as 20-30 mm^2/s and for the three-ring compounds as 30-40 mm^2/s.

TABLE VI Dielectric, optical, viscous and electrooptical properties of liquid crystal mixture C and C doped with 10 wt. % of compounds 1, 2, 3 or 4.

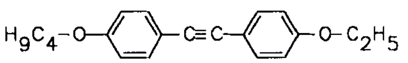
Mixtures	$T_{N\text{-}I}$ °C	Δn	$\Delta\varepsilon$	V_{10}	V_{90}	V_{90}/V_{10}	η mm^2/s
C	42	0.1680	8.1	1.55	2.25	0.45	12.9
C and 1a	33.8	0.1514	8.2	1.25	1.92	0.50	15.1
C and 1h	37.5	0.1585	6.9	1.5	2.10	0.40	14.8
C and 2b	44	0.1681	7.5	1.52	2.10	0.38	15.7
C and 1a,1h,2b*	35.5	0.1514	4.15	1.80	2.58	0.43	20.7
C and 7	42.5	0.1794					13.8
C and 3a	39	0.1639	6.8	1.62	2.20	0.36	15.4
C and 3d	43	0.1688	6.5	1.63	2.23	0.37	16.3
C and 4f	43	0.1696					15.9

* 10 wt. % of each



C

40:42:18 by weight



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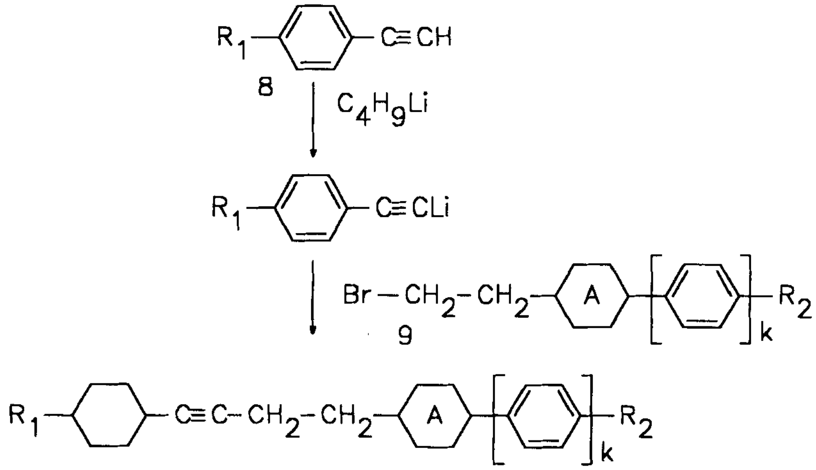
The steepness of electrooptical curves of mixture C and C after doping in some cases increases and in other decreases (compound 1h). But-1-ynes may by used to adjust the properties of TN and STN mixtures composed of isothiocyanates but their concentration should not be higher than 20% because they cause the increase of the viscosity.

EXPERIMENTAL

The 1-(4-alkylphenyl)- and 1-(4-alkoxyphenyl)-4-(trans-4-alkylcyclohexyl)but-1-yne, 1-(4-alkoxyphenyl)-4-(trans-4-alkylbicyclo[2,2,2]octyl)but-1-yne,1-(4-alkylphenyl)-and 1-(4-alkoxyphenyl)-4-[trans-4-(4-alkylphenyl)cyclohexyl]but-1-yne, 1-(4-alkylphenyl)- and 1-(4-alkoxyphenyl)-4-[trans-4-(4-fluorophenyl)cyclohexyl]but-1-yne were prepared in the same way by synthetic route I shown below:

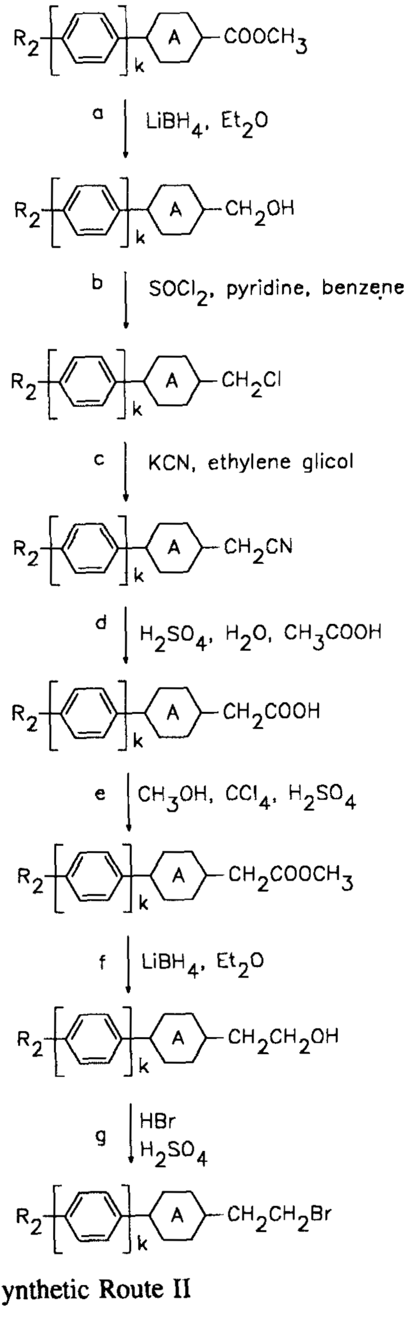


1−4

Synthetic Route I

R_1=alkyl, alkoxy and R_2=alkyl, fluorine atom, k=0 (compounds 1, 3), k=1 (compounds 3, 4), A=hexane ring (compounds 1, 3, 4) and bicyclo[2,2,2]octane ring (compound 2).

2-Substituted ethyl bromides (compound 9) was prepared by synthetic Route II



Synthetic Route II

The acetylenes were obtained from the laboratory of prof. P.Adomenas, Vilnius State University, Lithuania.

All the final products and where necessary, the intermediates in various steps in the synthesis, were tested to be pure by various technique (TLC, GLC) and confirmation of their structure was obtained by NMR, mass spectrometry and combustion data.

Preparation of 1-(4-butoxyphenyl)-4-(trans-4-pentylcyclohexyl)but-1-yne

The 4-butoxyphenyl acetylene (8) was dissolved in 45 cm^3 HMPT and butyllithium (0.036 mole) was dropped under nitrogen atmosphere at temperature 0°C and the mixture was stirred an hour. The 2-(trans-4-phenylcyclohexyl)ethyl bromide (0.036 mole) was dropped, the mixture was stirred for four hour and then was left to reach room temperature.

The mixture was poured onto water, and shaken three time with cyclohexane. The combined hexane extracts were dried ($MgSO_4$), filtrated by Fuller earth; the solvent was then removed.

The crude product was crystallized from ethanol, the yield was 38%. Phase transition Cr 47.9 N (34.9) I.

Analysis for $C_{25}H_{38}O$

calculated: 84.67%C, 10.82%H

found: 84.62%C, 10.92%H

PRM: $1H^1$, 0.89-1.8 (20H, $-CH_3$, $-CH_2-CH_2-$), 2.3 (2H, t, $-\underline{CH_2}-CH_2-O-$), 3.9 (2H, t, $-CH_2-\underline{CH_2}-O-$), 6.78 (2H, d, Ar), 7.29 (2H, d, Ar)

Preparation of 1-(4-butoxyphenyl)-4-[trans-4-(4-fluorophenyl)cyclohexyl] but-1-yne

The compound was prepared in the same way as 1-(4-butoxyphenyl)-4-(trans-4-pentylcyclohexyl)but-1-yne Analysis for $C_{31}H_{44}FO$:

calculated: 82.48%C, 8.27%H

found: 82.46%C, 8.47%H

PRM: $1H^1$, 0.96 (3H, t, $-CH_3$), 1-2 (15H, m), 2.3 (3H, m, $-\underline{CH_2}-CH_2-O-$ and =CH-Ar), 6.7 and 7.31 (2H, d, and 2H, d, $-O-C_6H_4-C\equiv C-$), 6.95-7.14 (4H, m, $-C_6H_4-F$, spectrum of this ring is the same as in $Br-CH_2-CH_2-C_6H_4-F$, see Figure 1)

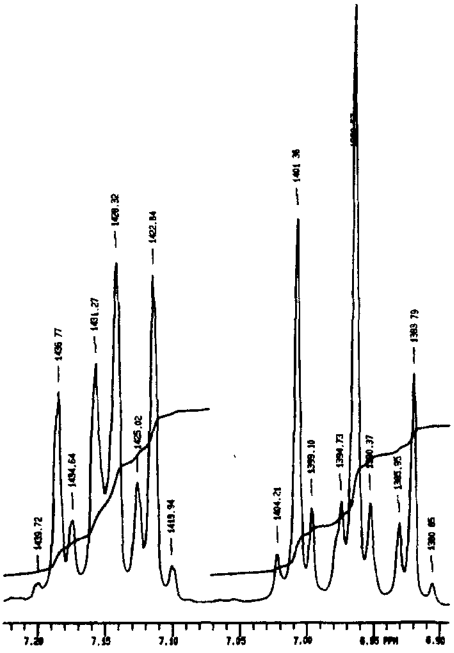


FIGURE 1 PRM spectrum of -C_6H_4-F ring in 2-[trans-4-(4-fluorophenyl)cyclohexyl]ethyl bromide

Preparation of 2-[trans-4-(4-fluorophenyl)cyclohexyl]ethyl bromide

The stages a, b, c, d are described in Ref. [13] for the cyclohexane derivatives

stage e

Methyl trans-4-(4-fluorophenyl)cyclohexylacetate

The trans-4-(4-fluorophenyl)cyclohexylacetic acid (0.5 mole), 180 cm^3 CCl_4, 60 cm^3 methanol and 1 cm^3 96% H_2SO_4 were refluxed 12 hour. The product was separated by the standard procedure and destilated, the fraction boiling at 125-132°C/0.1mm was collected, yield 76%.

stage f

2-[trans-4-(4-fluorophenyl)cyclohexyl]ethanol

This was prepared reducing of methyl trans-4-(4-fluorophenyl)cyclohexylacetate with $LiBH_4$ in diethylether solution by the standard procedure.

Product was crystallized from the mixture hexane-acetone 9:1 cooling to -20°C, yield 93%, m.p. 94-95°C.

stage g

2-[trans-4-(4-fluorophenyl)cyclohexyl]ethyl bromide

2-[trans-4-(4-fluorophenyl)cyclohexyl]ethanol (0.29 mole) was dropped to the mixture prepared from 150 cm^3 40 wt. % of HBr and 50 cm^3 of 96% H_2SO_4 and the mixture was then slowly heated to boil and refluxed until TLC did not showed the substrate. The product was separated by extraction with benzene and crystallized from methanol, yield 84 %, m.p. 62-63°C.

calculated: 59.14%C, 6.39%H, 27.78%Br
found: 59.05%C, 6.50%H, 28.56%Br
284 (and 2851.1) $(M-Br)^+$ - 135

Mass spectrum M^+ 284

PRM: $1H^1$, 1-2 (11H, m, $-CH_2-CH(CH_2)_2-$), 2.45 (CH-Ar) 6.9-7.20 (4H, m, $-C_6H_4-F$, see Figure 1)

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