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## NEW NEMATICS WITH HIGH BIREFRINGENCE #

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**ABSTRACT** We prepared new compounds with the hexen-  
diyne unit as central bridging group. The substances  
are nematic, with clearing temperatures much higher  
than those of other two ring compounds. They show the  
highest birefringence ever observed in liquid crys-  
tals, modest viscosities and medium dielectric aniso-  
tropy. Their stability in low polar mixtures allows  
their use in displays.

### INTRODUCTION

Liquid crystals have a broad spectrum of practical applica-  
tions<sup>1</sup>. In large quantities they are used in displays of  
different types. Each of these types needs substances with  
specific properties. Here we report on recent advances in  
substance research and development in Chisso Petrochemical  
Corporation, presenting compounds with high optical bire-  
fringence. We also make some considerations about the  
additivity of optical properties of mixtures.

### GENERAL

Nematic liquid crystals with high birefringence are useful

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Liquid Crystal Conference, Budapest 1994

as mixture components for all kinds of displays, and especially for application in displays using light scattering phenomena like the PDLC's and related techniques<sup>1</sup>.

Considering the relation 1 between dielectric constant and refractive index at high frequencies above the dipole relaxation region,

$$\varepsilon = n^2 \quad (1)$$

the Onsager theory for dielectric polarization, applied by Maier and Meier<sup>2</sup> to nematic liquid crystals, delivers by omitting the dipole term as usual at high frequencies.

$$\Delta\varepsilon = (NhF/\varepsilon_0)\Delta\alpha P_2 \quad (2)$$

$$= \varepsilon_1 - \varepsilon_2 = n_e^2 - n_o^2 = (n_e + n_o)(n_e - n_o)$$

Introducing  $n = 1/3(n_e + 2n_o)$  and assuming the approximation  $n_o = 1.5$ , we obtain :

$$\Delta n = NhF\Delta\alpha P_2/\varepsilon_0(3n - 1.5) \quad (2a)$$

$n_e, n_o$  = refractive indices of the nematics

$n$  = mean refractive index

$N$  = number density

$h, F$  are factors of the Onsager theory describing the reaction field, here both are considered to be constant, and to be approximately equal to 1.

$\varepsilon_0$  = dielectric constant of the vacuum

$\Delta\alpha$  = anisotropy of molecular polarizability

$P_2$  = order parameter of the liquid crystal

The birefringence of a given compound is mainly controlled by the polarizability anisotropy and the order parameter, because the expression in parentheses ( eq. 2a ) is only slightly dependent on the chemical structure. The order parameter can be somewhat enhanced by increasing the

length-to-breadth ratio of the molecules, but there are narrow limits. Much more potential lies in the increase of the polarizability anisotropy. We tried to obtain nematic compounds with high birefringence by introducing the hexendiyne bridge between two ring systems.

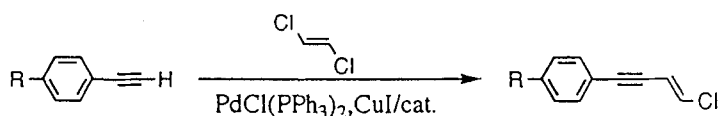
## SYNTHESIS

### General

The structure of the compounds was confirmed by  $^1\text{H}$ -NMR spectroscopy using a JEOL EX-90 and GC mass spectroscopy using a SHIMADZU GCMS-QP1000A at 70EV. Transition temperatures were determined using a RIGAKU DSC-8230 differential scanning calorimeter and by polarization microscopy using a Mettler FP52 hot stage. Bulk viscosities of these compounds were measured using a TOKIMEC ELD-R rotational viscometer and birefringence of the samples were measured using an ATAGO 4T & 2T Abbe refractometer.

Typical procedure for synthesis of hexendiyne derivatives.

Synthesis of (E)-chloro-4-(4-propylphenyl)buten-3-yne



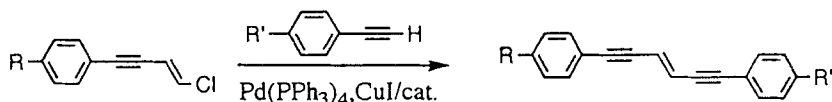
The diethylamine (1000ml) solution of dichlorobis(tri-phenylphosphine) palladium (7.0g), copper iodide (1.0g) and 1,2-dichloroethylene (50g) was added dropwise to a diethylamine (150ml) solution of 4-propylphenylacetylene (70.0g) under argon atmosphere. The mixture was stirred for 2 hours at room temperature and quenched with cold dil. HCl (500ml) and extracted with heptane (3 times with 300ml). The organic layer was dried over magnesium sulphate and concentrated under reduced pressure. The catalyst was removed by silica-gel (100g) short column chromatography, the resulting yellow oil of title compound (71g) was purified by distil-

lation (121-125 °C/3mm Hg, 55g).

$^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) $\delta$ 7.34(2H, d,  $J=8.2\text{Hz}$ ), 7.12(2H, d,  $J=8.2\text{Hz}$ ), 6.60(2H, d,  $J=13.7\text{Hz}$ ), 6.13(2H, d,  $J=13.7\text{Hz}$ ), 2.58(2H, t,  $J=7.0\text{Hz}$ ), 1.62(2H, brtq), 0.92(3H, t,  $J=7.3\text{Hz}$ )

MS; 175, 139, 28, 204 ( $\text{M}^+$ ), 190

Synthesis of 1-(4-ethylphenyl)-6-(propylphenyl)-3E-hexen-1,5-diyne.



The diethylamine (80ml) solution of tetrakis(triphenyl) phosphine palladium (1.0g), copper iodide (0.68g) and (E)-chloro-4-(4-propylphenyl)buten-3-yne (5.0g, 24mmol) was added dropwise to a diethylamine (20ml) solution of 4-ethylphenylacetylene (3.2g) under argon atmosphere. The mixture was stirred for 2 hours at room temperature, quenched with cold dil. HCl (50ml) and extracted with heptane (3 times with 50ml). The organic layer was dried over magnesium sulphate and concentrated under reduced pressure. The catalyst was removed by silicagel (50g) short column chromatography, the resulting brown oil (8.5g) was crystallized in heptane (7.8g). Recrystallization from heptane gave colorless crystals (5.2g, 16.8mmol) of title compound.

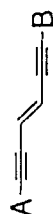
$^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) $\delta$ 7.38(2H, d,  $J=8.1\text{Hz}$ ), 7.16(2H, d,  $J=8.1\text{Hz}$ ), 6.26(2H, brs), 2.63(4H, m), 1.60(2H, brtq), 1.24(3H, t,  $J=8.1\text{Hz}$ ), 0.93(3H, brt)











MS; 298 ( $\text{M}^+$ ), 269, 127, 299, 247

## PROPERTIES

Table 1 presents the transition temperatures and transition enthalpies of different hexendiyne derivatives. All compounds are nematic. The clearing temperatures are much higher than those of other two ring compounds ( Table 2 )

TABLE I.  
Mesomorphic properties and transition enthalpies of hexendiyne compounds.

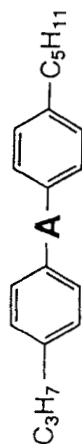


Compound	A	B	$T_m(^{\circ}\text{C})$	$\Delta H(\text{KJ/mol})$	$T_{\text{NI}}(^{\circ}\text{C})$	$\Delta H(\text{KJ/mol})$
1		 $\text{C}_2\text{H}_5$	81.2	22.6	150.0	1.2
2		 $\text{C}_3\text{H}_7$	95.3	22.0	162.3	1.6
3		 $\text{C}_4\text{H}_9$	56.3	15.4	143.8	1.8
4		 $\text{C}_5\text{H}_{11}$	64.1	19.4	146.0	1.5
5		 $\text{CH}_3\text{O}$	87.5	-	188.0	-
6		 $\text{C}_2\text{H}_5\text{O}$	111.0	-	200.0	-
7		 $\text{C}_3\text{H}_7$	94.2	23.6	147.6	1.3
8	 $\text{C}_3\text{H}_7$	 $\text{C}_3\text{H}_7$	89.4	25.7	149.4	1.5

and are rather comparable to those of typical three ring compounds<sup>3</sup>. This surprising fact should be due to the very high mean polarizability, because the intermolecular attraction in these low polar compounds is mainly based on dispersion energy, which is approximately proportional to  $\alpha^2$ . In the sense of the van der Waals molecular statistical theories of the nematic phase<sup>4</sup> the attraction is coupled with the shape anisotropy of the molecules. According to space filling models calculated by the semi-empirical

molecular orbital methods (MOPAC ver.6, AM1)<sup>6</sup> molecular shapes of compounds nos. 4,9-12 in table 2 are strongly linear. Only compound no. 13 resulted in a bent shape, which probably is the reason for the lack of liquid crystalline properties. In these calculations the alkyl groups are all-trans connected to the core to form a zigzag shape. According to a routine program of evaluation, some properties of mixtures containing the new compounds were deter-

TABLE 2.  
Comparison of clearing temperatures.



A	T <sub>m</sub>	T <sub>NI</sub>	$\bar{\alpha} [10^{-4} \text{J}^{-1} \text{C}^2 \text{m}^2]^\text{a}$
4	64.1	146.0	492.0
9	65.0	116.7	435.0
10	39.0	35.8	363.6
11	62.5	112.4	422.4
12	107.8	—	355.8
13	58.3	— <sup>b</sup>	418.6

a; Calculated with MOPAC ver. 6. Average polarizability  $\bar{\alpha} = (\alpha_X + \alpha_Y + \alpha_Z)/3$ , where  $\alpha_X, \alpha_Y$  and  $\alpha_Z$  are the principal axis of polarizability ellipsoid.

b; Isotropic melt supercooled to 15°C; not mesomorphic.

mined (Table 3). A highly polar (Mixture A), a low polar (Mixture B) and a medium polar (Mixture C) basic mixture were used. The obtained clearing temperatures follow approximately the linearity

TABLE 3.  
Clearing points(°C) of mixtures containing hexendiyne compounds.

Basic mixture	Basic mixture + 15 weight % of compound No.							
	none	1	2	3	4	5	6	7 8
Mixture A	72.4	83.2	83.4	82.3	83.1	87.0	88.5	81.8 80.4
Mixture B	55.3	67.8	70.2	67.3	68.7	75.2	79.0	66.6 64.4
Mixture C	74.6	84.1	85.7	83.7	84.7	90.6	92.0	82.7 80.5

Mixture A		Mixture B		Mixture C	
	24%		20%		28%
	36%		20%		21%
	25%		20%		21%
	15%		20%		17%
			20%		14%



$$T_{NI} = x_1T_{NI1} + x_2T_{NI2}$$

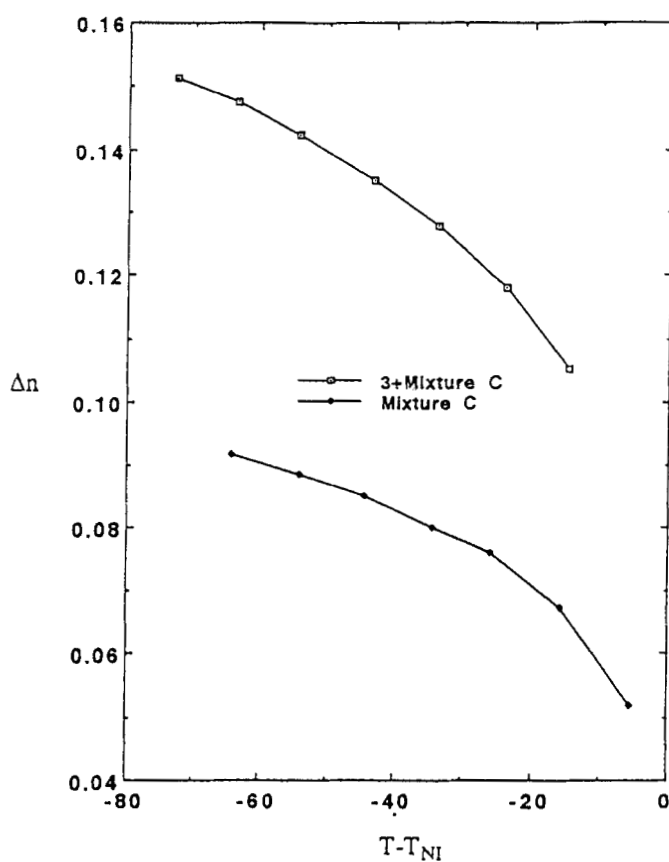
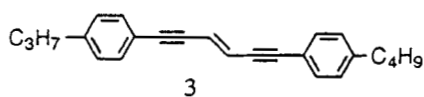
(3)

where  $x_1, x_2$  = weight fractions of the basic mixture (1) and the added component (2), respectively, and  $T_{NI}, T_{NI1}, T_{NI2}$  = clearing temperatures of the actual mixture, the basic mixture (1) and the added component (2), respectively.

TABLE 4.  
Birefringence ( $\Delta n$ ) of mixtures containing hexendiyne compounds<sup>a</sup>.

Basic mixture	none	Basic mixture + 15weight % of compound No.							
		1	2	3	4	5	6	7	8
Mixture A	0.1390	0.1797	0.1771	0.1741	0.1725	0.1840	0.1801	0.1558	0.1393
Mixture B	0.2908 <sup>b</sup>	0.2958	0.2961	0.2937	0.2988	0.3029	0.3031	0.2828	0.2720
Mixture C	0.0868	0.1446	0.1434	0.1403	0.1339	0.1475	0.1479	0.1191	0.0985

a. Temperature= $T_{NI-50}$ , unless otherwise indicated.  
b. Measured at  $T_{NI-45}$ .

FIGURE 1. Temperature dependence of  $\Delta n$ .

Temperature of basic mixture and the actual mixture= $T_{NI}-50$ .

Basic mixture	none	Compound No.							
		1	2	3	4	5	6	7	8
Mixture A	0.139	0.410	0.393	0.373	0.362	0.439	0.413	0.251	0.141
Mixture B	0.291 <sup>b</sup>	0.324	0.326	0.246	0.344	0.371	0.303	0.237	0.165
Mixture C	0.087	0.471	0.463	0.442	0.400	0.490	0.493	0.301	0.164

a; Concentration is 15weight%. b; Measured at T<sub>Nl</sub>-45.

a, Concentration is 15weight%. b, Measured at  $T_{NI}-45$ .

TABLE 5b. Birefringence( $\Delta n$ ), extrapolated from mixtures<sup>a</sup>.

Temperature of the actual mixture= $T_{NI}-50$ , temperature of the basic mixture is the same absolute temperature( $^{\circ}C$ ).

Basic mixture	Compound No.							
	1	2	3	4	5	6	7	8
Mixture A	0.450	0.433	0.407	0.402	0.492	0.473	0.284	0.171
Mixture B	0.422	0.439	0.401	0.445	0.511	0.549	0.338	0.209
Mixture C	0.487	0.482	0.457	0.415	0.527	0.531	0.313	0.170

a, Concentration is 15weight%.

Table 5a      Birefringence ( $\delta n$ ), extrapolated from mixtures<sup>a</sup>.

BIREFRINGENCE IN MIXTURES

Table 4 shows the measured birefringences of the mixtures. In all cases there is a distinct increase of the birefringence of the basic mixtures, which is more clearly seen in the example presented in Fig. 1.

Assuming the linear dependence of the birefringence on the composition

$$\Delta n = x_1 \Delta n_1 + x_2 \Delta n_2 \quad (4)$$

we extrapolated the birefringences for the pure compounds, using weight fractions instead of molar fractions (Table 5a and 5b). The data show that the same compound delivers different results, extrapolated from the different basic mixtures. We performed the extrapolation for the condition of equal reduced temperature of the basic mixture and the actual mixture (Table 5a). Partly the three sets of mixtures deliver very different results for the same compound (e. g. compound no. 1, 6). Generally, the low polar mixture (Mixture B) yields the smallest values, that with medium polarity (Mixture C) the highest. We also made the extrapolation using the same reduced temperature only for the actual mixtures, and taking as reference the basic mixture at the same absolute temperature as the actual mixture (Table 5b). Now the data show better coincidence. Comparing with Table 5a it becomes clear, that all extrapolated values now are higher. It is not easy to decide which method should be preferred.

Another point to be discussed is the validity of the empirical eq. 4. Referring to eq. 2, we define

$$R = n_e^2 - n_o^2 = NhF \Delta \alpha P_2 / \epsilon_0 \quad (5)$$

In mixtures the polarizabilities are accepted to be approximately additive. Then presuming small changes of  $n$  and  $P_2$ , in mixtures we may assume additivity also for  $R$  :

$$R = x_1 R_1 + x_2 R_2 \quad (6)$$

$x_1, x_2$  = molar fractions of the components

We extrapolated typical  $\Delta n_2$  using both formulas 4 and 6, and found that for small birefringes there is only a insignificant difference (Table 6). Because of convenience, then eq. 4 may be preferred.

TABLE 6  
Extrapolation of birefringence in mixtures

$$x_1 = 0.8, \quad x_2 = 0.2$$

$n_{e1}$	$n_{o1}$	$n_e$	$n_o$	$\Delta n$ from	
				eq. 6	eq. 4
1.6	1.5	1.68	1.5	0.468	0.500
1.6	1.5	1.63	1.5	0.245	0.250
1.6	1.5	1.59	1.5	0.049	0.050

In practice, in eq. 4 instead of mole fractions often the more convenient mass fractions are used. We can compare:

$$x_1 = n_1/(n_1 + n_2) = m_1 M/M_1(m_1 + m_2) = m_1/(m_1 + m_2) \quad (7)$$

$n_1, n_2$  = amounts of moles of the components

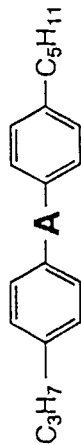
$M_1, M_2$  = molar masses of the components

$m_1, m_2$  = masses of the components

when  $M_1 = M$ . Using basic mixtures with average molar masses  $M$  similar to those of the compounds, we may expect only small errors from this source. The reasons for the large deviations found by use of three different basic mixtures should be based on the different intermolecular interactions.

The new compounds exhibit very high values of birefringence. There are several compounds with birefringences

TABLE 7.  
Polarizability data. [ $\times 10^{-41} \text{J}^{-1} \text{C}^2 \text{m}^2$ ], calculated with MOPAC ver. 6.



	A	$\alpha_X$	$\alpha_Y$	$\alpha_Z$	$\Delta\alpha$	$\Delta n$
4		976.3	348.5	151.3	726.4	0.421 <sup>a</sup>
9		847.5	315.9	141.5	618.8	0.402 <sup>b</sup>
10		643.7	309.0	138.0	420.3	0.272 <sup>b</sup>
11		782.2	331.9	153.2	539.6	0.366 <sup>b</sup>
13		741.8	341.6	172.5	484.7	0.243 <sup>b</sup>

a, Average from the three values of TABLE 5b.  
b, Extrapolated from Mixture C (15wt%) at  $T_{NI}=50$ .

TABLE 8. Viscosity(mPa•s) of mixtures<sup>a</sup> containing hexendiyne compounds.

Basic mixture	none	Basic mixture + 15 weight % of compound No.					
		1	2	3	4	5	6
Mixture A	27.0	21.9	17.1	22.3	21.8	24.2	<sup>b</sup>
Mixture B	16.8	17.2	17.6	17.9	17.9	<sup>b</sup>	<sup>b</sup>
Mixture C	19.4	9.8	19.2	19.0	19.3	20.9	<sup>b</sup>

a; Temperature=20°C. b; Crystallization.

TABLE 9. Extrapolated viscosity(mPa•s)<sup>a</sup> of hexendiyne compounds.

Basic mixture	1	Basic mixture + 15 weight % of compound No.					
		2	3	4	5	6	7
Mixture A	-7.0	-39.0	-4.3	-7.7	8.3	<sup>b</sup>	32.3
Mixture B	19.5	22.1	24.1	24.1	<sup>b</sup>	<sup>b</sup>	24.1
Mixture C	-44.6	18.1	16.7	18.7	4.4	<sup>b</sup>	18.7

a; Temperature=20°C. b; Crystallization.

above 0.5. Compound 6 in mixture B shows  $\Delta n = 0.549$ . This is higher than the maximum value reported until now in the literature,  $\Delta n = 0.43$  in reference 5. With respect to the large polarizability anisotropy calculated for a representative example of this substance class (Table 7) these high values are plausible.

### VISCOSITY

Table 8 presents the shear viscosities of the basic mixtures and actual mixtures and Table 9 contains the extrapolated data for the new compounds. It seems that most of these compounds have low viscosities. Of course, the negative values do not have physical reality, but are only calculation data. However, they point to the fact, that especially the viscosity of polar mixtures can be remarkably lowered by use of the new compounds.

In low polar mixtures the new compounds were proved to possess acceptable thermal, electrochemical and photochemical stability.

### CONCLUSIONS

The hexenediynes derivatives were proved to be compounds with

- high nematic clearing temperatures
- high birefringence
- low viscosity
- in low polar mixtures acceptable stability

They have a dielectric anisotropy of about +7. So they should be useful as components for mixtures with high birefringence, applied in displays.



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