Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 28 Mar 2007.

To cite this article: R. Dabrowski & E. [Zgrave]ytyńki (1982): Mesomorphic Properties of 4-n-Pentylbiphenyl Derivatives, Molecular Crystals and Liquid Crystals, 87:1-2, 109-135

To link to this article: http://dx.doi.org/10.1080/00268948208083777

Mol. Cryst. Liq. Cryst., 1982, Vol. 87, pp. 109–135
0026-8941/82/8701-0109$06.50/0

Printed in the United States of America

Mesomorphic Properties of 4-*n*-Pentylbiphenyl Derivatives

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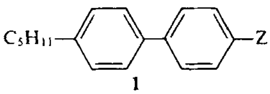
(Received April 21, 1981; in final form November 3, 1981)

In this work, 29 compounds having the general formula:



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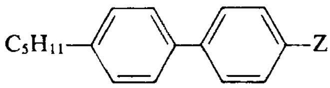
were prepared and their electron spectra, phase transition temperatures and mesomorphic properties determined. Compounds with Z = H, Br, I, NH_2, CN, CHO, NCS, NCO, N_3, COOH, CH_2COOH, CH_2Br, CH_2CN, $COCH_3$, $CH_2—CH_2Cl$, $CH_2—CH_2CN$, $CH_2CHClCN$, $CH^{=CH_2}$, $C\equiv CH$, $CH{=}CHCN$, $C(CH_3){=}NOH$, $CH{=}NOH$, $C(CH_3){=}NOC_2H_5$, C_5H_{11}, C_6H_{13}, C_7H_{15}, COC_4H_9, COC_5H_{11}, COC_6H_{13} were investigated. On the basis of compounds of formula **1**, differing only by the kind of the terminal substituent Z, the effects of geometry, coupling, direction and magnitude of the dipole moment on their mesomorphic properties are discussed. These relationships suggest that the nematogenic properties of biphenyl derivatives depend chiefly on the ability of the molecules to associate linearly.

INTRODUCTION

Mesogenic biphenyl compounds have been studied for some time[1-3] but it has only been since Gray *et al.*[4] obtained 4-*n*-alkyl-4′-cyanobiphenyls and 4-*n*-alkoxy-4′-cyanobiphenyls that they have become of importance in liquid-crystalline displays technology.[5,6] These cyanobiphenyls were the first known low-melting stable nematics with such a short molecular length which are non-planar and contain no central bridge. It seemed to us, therefore, worthwhile to prepare other 4-*n*-alkylbiphenyl derivatives in order to expand the number of known compounds with various terminal substituents. From these, we could obtain a better knowledge of the factors affecting stability and the types of liquid-crystalline phases as well as being able to study new mesogenes of practical interest. We studied compounds having the general formula 1



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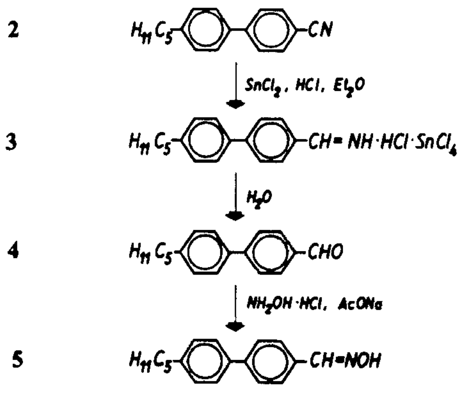
where *Z* represents various substituents as shown in Table I. The substituents *Z* are functional groups of different length and different dipole moment values and directions. Some of these contain π or lone-pair electrons which are conjugated with the π electrons of the neighboring benzene ring while others are deprived of such electrons. The substituent either lies in the plane of the neighboring benzene ring or protrudes above the benzene ring. Such a choice of substituents made it possible to determine the effect of the above mentioned factors on the mesogenic properties of the compounds obtained.

SYNTHESIS

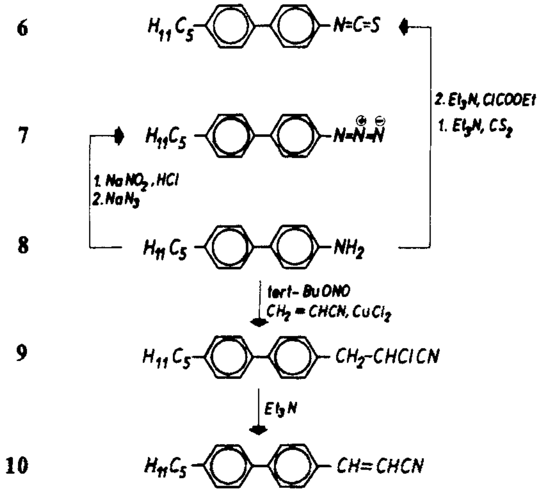
The aldehyde **4** was prepared from the nitrile **2** using the method shown in Scheme 1. This is based on the method described by Williams for 2-naphthaldehyde.[12] It is a simple and convenient method. The starting material **2** is commercially available or easily obtained in the laboratory.[9] Other, conventional methods were also tested, such as treating compound **24** with hexamine, compound **23** with dichloromethylbutyl ether (the Rieche reaction)[13] or with urotropin in trifluoroacetic acid,[14] but the results were unsatisfactory.



SCHEME 1 The reaction involving 4-cyano-4′-*n*-pentylbiphenyl (**2**)

The oximes **5** (Scheme 1) and **12** (Scheme 3) were prepared by treating the aldehyde **4** or ketone **13** with hydroxylamine hydrochloride in ethanol in a slightly alkaline medium (AcONa). Refluxing the latter compound with sodium ethoxide and ethyl iodide in ethanol solution yielded the ether **11** (Scheme 3).

4-Amino-4'-*n*-pentylbiphenyl (**8**) was used for obtaining compounds **6**, **7**, **9**, **10** as shown in Scheme 2.

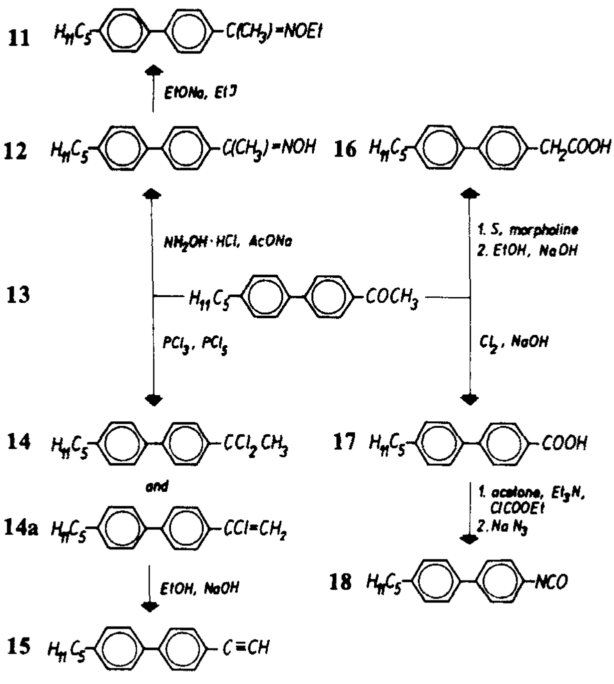


SCHEME 2 The reaction involving 4-amino-4'-*n*-pentylbiphenyl (**8**)

Compounds **9** and **10** were obtained by the preparative procedures described in Refs. 15 and 16. The amine **8** was diazotized in an organic solvent (acetonitrile), using tert-butyl nitrite, and subsequently treated with acrylonitrile in the presence of cupric chloride yielding an addition product **9**. This was converted to compound **10** by the elimination of HCl on heating with triethylamine.

Diazotization of the amine **8** via a conventional method in an aqueous solution and subsequent treatment with sodium azide, yielded 4'-azide-4-*n*-pentylbiphenyl **7**. 4-Isothiocyanato-4'-*n*-pentylbiphenyl **6** was obtained in a different way than that described in Ref. 17. Using the Hodgkins method,[18] we treated the amine **8** with carbon disulfide in the presence of triethylamine. The resulting triethylammonium biphenylthiocarbamate was transformed into the isothiocyanate **6** by treating with ethyl chloroformate in the presence of a base.

4-*n*-Acetyl-4'-pentylbiphenyl **13** was used to obtain compounds **11**, **12** and **14**–**18** by the procedure shown in Scheme 3.

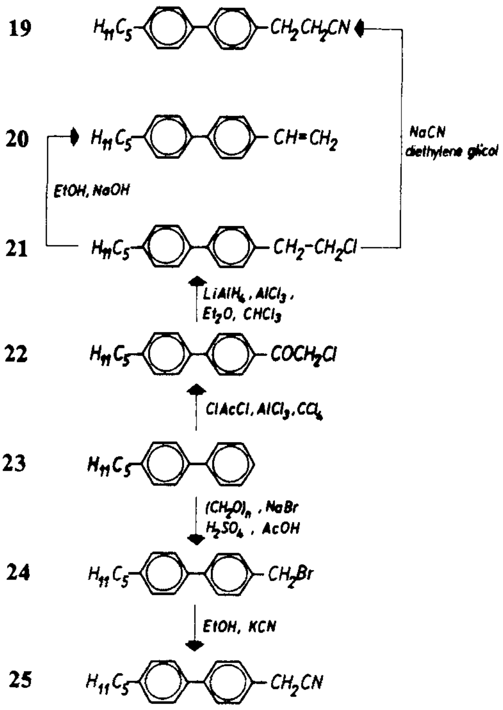


SCHEME 3 The reaction involving 4-*n*-pentylbiphenyl (**23**)

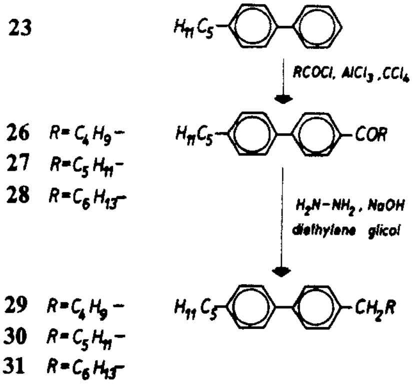
The ketone **13** was heated with PCl_3 and PCl_5 by a method based on Ref. 21. The resulting mixture of compounds **14** and **14a** (biphenyl chloroethenyl and dichloroethyl derivatives) was not separated but transformed into the acetylene derivative **15** by heating in a concentrated sodium hydroxide ethanol solution. Compound **21** treated likewise (Scheme 4) gave the vinyl derivative **20**. Compound **13** yielded the known 4-*n*-pentylbiphenyl-4′-carboxylic acid **17** on oxidation with sodium hypochlorite. When compound **17** was treated with ethylchloroformate and sodium azide by the procedure given in Ref. 22, it gave 4-*n*-pentylbiphenyl-4′-carboxylic acid azide. The latter when heated in dry toluene was rearranged to the isocyanate **18**.

Compound **13** was heated with sulfur in morpholine. The isolated product was hydrolyzed in a water-alcohol sodium hydroxide solution under conditions described in Ref. 23 yielding 4-*n*-pentylbiphenylacetic acid **16**.

p-*n*-Pentylbiphenyl **23** was used as the starting material for compounds **13**, **21**, **19**, **20**, **24** and **25** (Scheme 4) and compounds **26–31** (Scheme 5).



SCHEME 4 The reaction involving 4-*n*-pentylbiphenyl (**23**)



SCHEME 5 The reaction involving 4-acetyl-4′-*n*-pentylbiphenyl (**13**)

Acylation and chloroacylation of **23** was conducted at lowered temperature (0°C) in carbon tetrachloride according to the procedure described in Ref. 11 for compound **13**. Chloroketone **22** was reduced with $LiAlH_4 \cdot AlCl_3$ complex to **21** using Gray's method.[19] The remaining ketones **26–28** (Scheme 5) were reduced by the standard Huang-Minlon method in accordance with Ref. 9. Bromomethylation of **23**, conducted in accordance with Ref. 20, with using paraformaldehyde and solid NaBr in an acetic-sulfuric acid solution, yielded **24**. The bromomethyl **24** and chloroethyl **21** derivatives were easily transformed into the respective cyanocompounds **25** and **19** by heating with an aqueous-alcohol solution of potassium cyanide or with sodium cyanide in diethylene glycol. More details on the preparation of some of the above new compounds are given in the experimental part and also in an earlier work by the present authors.[24]

RESULTS AND DISCUSSION

Classification of the substituents:

Analysis of the data in Table I regarding the temperatures of phase transitions, electron spectra, dipole moments and geometric shapes of the 4-*n*-pentylbiphenyl derivatives of the general Formula **1** allows us to determine what effect the terminal substituents have on the ability of compounds to form liquid-crystalline phases. The character of the phase transitions of the compounds studied allows us to classify the terminal substituents *Z* into the four groups discussed below as A, B, C and D.

In group A, we have the substituents CN, CHO, CH=NOH, CH=CHCN, $C(CH_3)$=NOH, COOH which yield nematogenic compounds.

Group B includes substituents such as alkyls containing five or more carbon atoms in the chain (C_5H_{11}, C_6H_{13}, C_7H_{15}) or else alkyls combined with a functional group having a fairly high lateral dipole moment (COC_4H_9, COC_5H_{11}, COC_6H_{13}, $C(CH_3)=NOC_2H_5$), which favor smectic properties. In the case of $C(CH_3)=NOC_2H_5$ the alkyl substituent is shorter, nevertheless the total length of the molecules is considerable ($l \approx 22.8$ Å, $l/d = 3.8$). According to Ref. 7, alkoxy substituents on biphenyl compounds also form smectogens.

Group C includes such substituents as: H, CH_2Br, CH_2CN, CH_2—CH_2CN, CH_2—CH_2Cl, N_3 and Br. These terminal substituents give compounds with a virtual N → I phase transition distinguished by the fact that the clearing point (T_{N-I}) of their solutions in CPB **2** varies proportionally to concentration.

Group D includes the substituents C≡CH, $CH=CH_2$, NH_2, CH_2COOH, I, NCO, NCS and CH_3CO. These terminal groups give compounds with virtual N → I transition differing from those classified in group C in that the T_{N-I} of their solutions in CPB is not proportional to concentration or that the value of the N → I phase transition temperatures estimated in two different liquid-

TABLE I

Phase transition temperatures, positions and intensities of band p in the UV spectrum, the calculated dipole moments[a] (components parallel and perpendicular to the long axis of the molecule, $\mu_\parallel$ and $\mu_\perp$ respectively), length of molecules (l)[b], and the results of the combustion analysis compounds of the general formula **1**.

Compounds				spectral data		Dipole moments $[C \cdot m] \cdot 10^{-29}$		Combustion analysis					
								Cald.			Found		
No	Z	Phase trans. temp. (°C)	l Å	λ_{max} nm	log ε	$\mu_\parallel$	$\mu_\perp$	% C	% H	% N	% C	% H	% N
1	2	3	4	5	6	7	8	9	10	11	12	13	14
2	CN[c]	K 23 N 37 I	19.0	274	4.43	1.60[d]							
4	CHO	K 21.5 (N 19.5) I	18.5	290	4.28	1.02	0.559	85.66	8.00	—	85.20	7.95	—
5	CH=NOH	K 126 N 142 I	20.0	284	4.44	1.69	0.131	80.86	7.92	5.24	80.92	7.99	5.15
		dimer	40.0			0							
6	NCS	K 53 S_E 74.5 I	20.9	293	4.55	1.20		76.81	6.82	4.98	76.95	6.83	4.82
7	N_3	K 75 I	20.2	275	4.55	0.69		76.93	7.23	15.84	76.27	7.25	15.67
8	NH_2[h]	K 72 I	18.0	270	4.48	0.15	0.387						
9	$CH_2CHClCN$	K 45 I	21.7	257	4.35	1.28	0.765	77.02	7.12	4.49	76.60	7.07	4.42
10	CH=CHCN	K 53 N 112 I	21.7	307	4.48	1.43		87.21	7.70	5.09	86.74	7.63	5.55
11	$C(CH_3)=NOC_2H_5$	K 73 S_A 91 I	22.8	283	4.48	1.50	0.61	81.49	8.81	4.53	82.25	8.98	3.92
12	$C(CH_3)=NOH$	K 139 N 145 I	20.0	278	4.46	1.43	0.11	81.08	8.25	4.98	80.58	8.18	5.09
		dimer	40.0			0							
13	$COCH_3$[e]	K 83.5 I	19.2	284	4.27	0.86	0.74	85.65	8.34	—	85.69	8.19	—
15	C≡CH	K 80 I	19.5	273	4.48	0.45		91.87	8.13	—	91.47	8.08	—
16	CH_2COOH	K 168 I	20.3	258	4.36	0.29	0.34	80.80	7.88	—	80.60	7.88	—
˙17	COOH[e]	K 176 S_2 205 S_1 258 N 268 I	19.3	279	4.44								
		dimer	38.6			0							
18	NCO	K 132 I	20.1	290	4.49	0.99		81.46	7.23	5.28	80.76	7.15	
19	$CH_2—CH_2CN$	K 66.5 I	21.5	257	4.35	1.13		86.58	8.37	5.05	87.07	8.30	4.63
20	$CH=CH_2$[i]	K 107–122 I	20.0	284		0		91.13	8.97				
21	$CH_2—CH_2Cl$	K 49 I	20.7	255	4.39	0.60		79.54	8.10	—	79.12	8.03	—
23	H	K 11.5 I	16.3	250	4.32	0.13							
24	CH_2Br	K 76 I	19.2	257	4.42	0.14	0.57	68.13	6.68	—	67.92	6.64	—

TABLE I (*Continued*)

Compounds				spectral data		Dipole moments $[C \cdot m] \cdot 10^{-29}$		Combustion analysis					
								Cald.			Found		
No	Z	Phase trans. temp. (°C)	l Å	λ_{max} nm	log ϵ	$\mu_{\parallel}$	$\mu_{\perp}$	% C	% H	% N	% C	% H	% N
1	2	3	4	5	6	7	8	9	10	11	12	13	14
25	CH_2CN	K 84.5 I	19.0	255	4.18	0.29	1.15	86.63	8.05	5.32	86.64	8.08	5.33
26	COC_4H_9 [j]	K 106 S_B 110.5 I	23.2	285	4.43	0.86	0.74	85.65	9.17	—	85.32	9.11	—
27	COC_5H_{11} [j]	K 106 S_A 109.5 I	24.1	285	4.43	0.86	0.74	85.64	9.39	—	85.33	9.34	
28	COC_6H_{13}	K 96 S_A 111 I	25.6	285	4.43	0.86	0.74	85.64	9.60	—	85.47	9.57	—
29	C_5H_{11} [j]	S_E 47 S_B 52 I	23.0	256	4.39	0		89.71	10.29	—	89.33	10.20	—
30	C_6H_{13} [j]	S_E 42 S_B 53.5 I	24.0	254	4.39	0		89.53	10.47	—	89.94	10.39	—
31	C_7H_{15} [j]	S_E 36 S_B 63 I	25.4	257	4.38	0		89.35	10.65	—	88.97	10.54	—
32	Br [f]	K 94.5 I	18.9	260	4.41	0.75							
33	I [c]	K 112.5 I	19.3	263	4.47	0.68							

[a] The dipole moments have been calculated basing on the assumed geometry of the molecules and summating the group moments as given by Minkin.[25]

[b] The length have been calculated basing on the assumed geometry of the molecules and summating atomic radius. These compounds were synthesized after Refs.: 9-[c]; 11-[e]; 4-[f]; 10-[h].

[d] The experimental value of the dipole moment in cyclohexane is 1.62×10^{-29} [C · m].[26]

[i] The compound is contaminated with the polymer.

[j] These six compounds are similar to those described by Demus and Richter[7,8] and differ the kind of alkyl substituent.

crystalline matrices (CPB and 4-pentyl-4′-ethylazoxybenzene) vary considerably (Table II and Figure 1).

The terminal group NCS has been classified in D despite the fact that van der Veen reports that one modification of compound **6** has smectic A phase (K 51 S_A 73 I) whereas another one has a S_E phase (Ref. 17). We have obtained, very pure compound **6** with phase transitions K 53 S 74.5 I. Its behavior is strange; mixtures with CPB as well as with 4-cyano-4′-octyloxybiphenyl, which also has a S_A smectic phase,[4] are nematics, whereas mixtures with ethylphenyl 4-pentylbiphenyl-4′-carboxylate, a compound with phase transitions resembling those of 4-cyano-4′-octyloxybiphenyl, show smectic A phases.

THE STRUCTURE OF TERMINAL GROUPS AND ASSOCIATION OF THE PENTYLBIPHENYL DERIVATIVES

Features of the particular groups of substituents are characterized below and the kinds of intermolecular reactions they allow are discussed. All the terminal substituents Z classified in group A can lie in the plane of the nearest phenyl ring in the direction coinciding with the long axis of the molecule and have a large dipole moment fulfilling the condition $\mu_{\parallel} \gg \mu_{\perp}$ or may give strong intermolecular hydrogen bonds. In the latter case, the dimers formed have a resultant dipole moment equal to zero. It seems therefore that the value of the dipole moment alone is not important, but rather that the presence of such a group favors a definite intermolecular association. In the considered deriva-

TABLE II

Temperatures of the virtual N → I phase transition of compounds of the general formula **1**: a–in he 4-cyano-4′-*n*-pentylbiphenyl, b–in 4-ethyl-4′-pentylazoxybenzene

Compound		N → I transition temperature (°C)	
No	Z	a	b
6	$-NCS$	50	S_A phase induction
7	$-N_3$	20	—
8	$-NH_2$	strong specific interaction	−37
13	$-COCH_3$	50	S_A phase induction
15	$-C{\equiv}CH$	strong specific interaction	22
16	$-CH_2COOH$	specific interaction?	10
17	$-CH_2CN$	8	—
18	$-NCO$	53	30
19	$-CH_2-CH_2CN$	16	—
20	$-CH{=}CH_2$	specific interaction?	51.5
21	$-CH_2-CH_2Cl$	14	—
23	$-H$	−34	—
24	$-CH_2Br$	1.5	−12
32	$-Br$	29.5	—
33	$-I$	37.2	−12

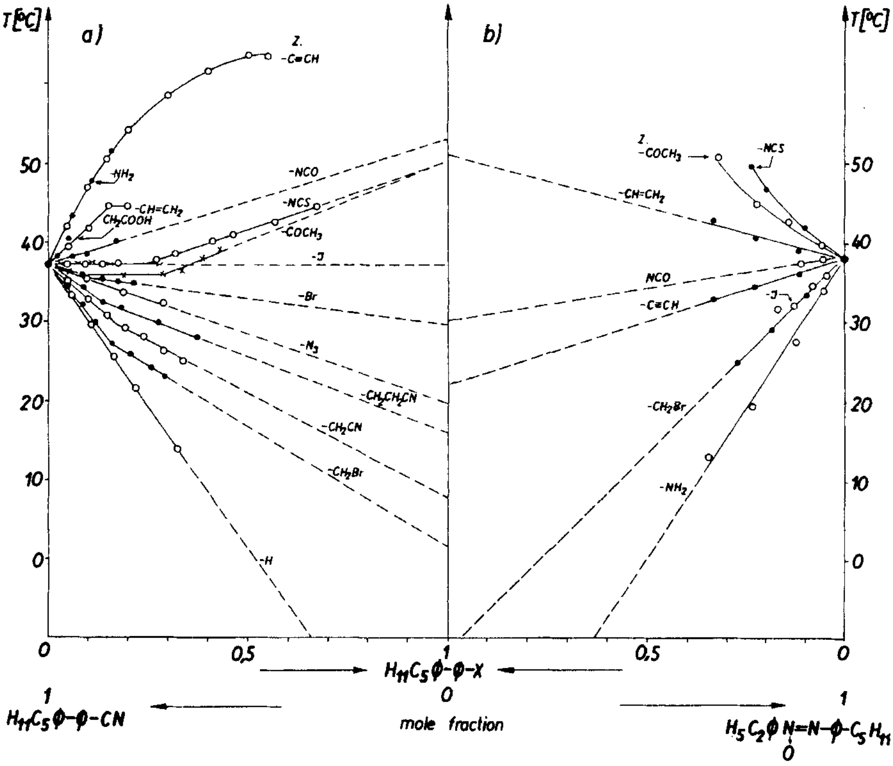


FIGURE 1 Phase transition temperatures of two-component mixtures composed of a compound of the general formula **1** and 4-cyano-4′-*n*-pentylbiphenyl (a) or 4-ethyl-4′-*n*-pentylazoxybenzene (b).

tives of 4-*n*-pentylbiphenyl, primarily two kinds of linear association of the molecules are possible.

The first one involves the orienting dipole-dipole and dipole-induced dipole interaction† supported, perhaps, by the donor-acceptor interaction, as the groups CN or CHO have electron-acceptor properties. Association of this kind is particularly favored in compounds with such terminal groups as CN, CH=CHCN, CHO, NO_2. It can be assumed that the energy of molecular interaction is probably small here, so equilibrium is established between the associated and monomeric forms (Figure 2).

Leadbetter *et al.*[27,28] found association to occur in 4-cyano-4′-*n*-pentylbiphenyl (CPB) and in 4-cyano-4′-*n*-heptylbiphenyl. They detected by X-ray

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† According to private information obtained from Dr. Baran, the dipole-induced dipole molecular interaction is decisive, as shown by quantum-mechanical calculations.

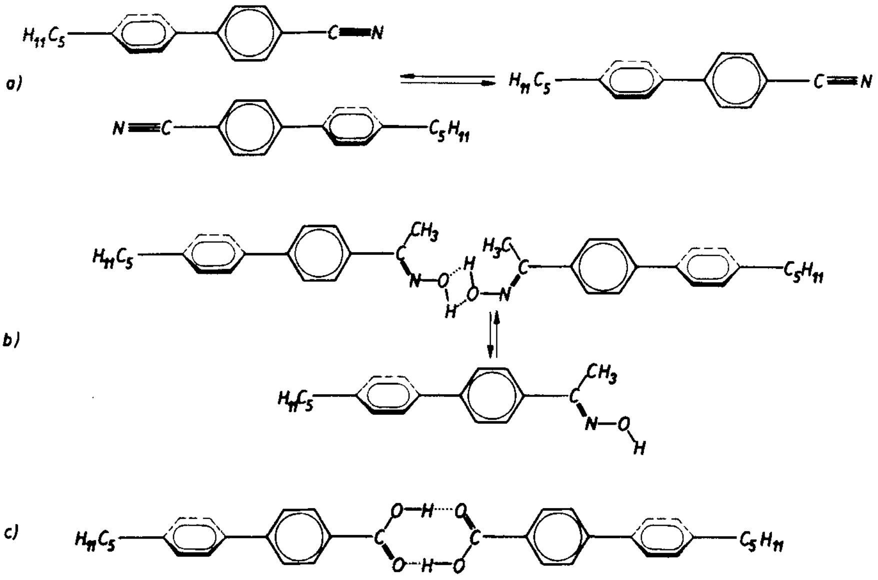


FIGURE 2 Expected structures of the dimers in 4′-substituted 4-*n*-pentylbiphenyls.

methods the presence of a structural element in the nematic phase with a length 1.4 times greater than that of a single molecule.

According to Lydon and Coakley,[29] the thickness of a layer in the 4-cyano-4′-*n*-octylbiphenyl smectic phase is 29 ± 0.3 Å, so it is also greater than the length of a single molecule (23 Å). The calculations of Baran,[30] who studied the distribution of charge and energy in the molecular interaction by the CNDO-2 and PCiLO methods, have shown that in CPB, favorable conditions exist for the formation of dimers. Baran suggests that dimers with both parallel and antiparallel arrangement of their dipole moments may exist. In our opinion, the low melting temperatures of compounds **2** and **4** are due to the fact that their crystal lattice consists of dimers which cause saturation of the stronger intermolecular bonds. Such a lattice is easily destroyed by thermal action which allows observation of the enantiotropic nematic phase. In compounds with the terminal groups N_3, NCO and NCS, which also have a considerable value of $\mu_{\parallel}$, we do not observe low melting points. This is probably due to the different electronic structure of those groups. The charge distribution is more complicated here since they behave like multipoles: $-\underline{N}\overset{\leftarrow}{=}\overset{\oplus}{N}\overset{\rightarrow}{=}\overset{\ominus}{\underline{N}}|$, $-\underline{N}\overset{\leftarrow}{=}C\overset{\rightarrow}{=}\overline{\underline{O}}$, $-\underline{N}\overset{\leftarrow}{=}C\overset{\rightarrow}{=}\overline{\underline{S}}$. This perhaps hinders linear association (dimerization) and contributes largely to the crystal lattice energy. Also in cases of nonpolar terminal groups which lie in the plane of the molecule, C≡CH and

$CH{=}CH_2$, where linear association is impossible, the compounds have higher melting points.

The properties of solutions of compound **15** (Z = $C{\equiv}CH$) in CPB show that the interaction in this sort of dimer is not purely of an electrostatic nature (Figure 1). Compound **15** is only a virtual nematic with $T_{N-I} = 22°C$. However, when it is mixed with CPB, the thermal stability of its nematic phase is strongly increased to the point where the composition of the solution reaches a 1 : 1 mole ratio. This molecule has a small dipole moment but is a fairly strong π-electron donor. Thus, the observed reaction may be of donor-acceptor character. Intermolecular reactions of analogous strength, observed for the CPB and amine **8** (Z = NH_2) as well as for similar amines, were explained by donor-acceptor interactions.[31] However, neither in the case of compound **15** or **8** can one exclude interactions via hydrogen bonds. If compound **15** or **8** is a component of the dimer shown in Figure 2a, then an elongated geometry of the hydrogen-bonded like dimer that shown in Figure 2b should be more favorable. The observed growth of the N → I phase transition temperature in mixtures of CPB and compounds **15** and **8** could, perhaps, be explained by the change of length of the complex.

The second kind of association observed in compounds of Formula **1** is dimerization involving hydrogen bonds. Strong hydrogen bonds occur in acids, oximes, amides both in the solid and liquid states. The functional groups COOH, $CH{=}NOH$ and $C(CH_3){=}NOH$ in compounds **17**, **5**, **12** are responsible for association. Among the compounds investigated only the above three are mesomorphic and have high N → I transition temperatures since only these three compounds can form flat, rigid linear dimers. In compound **16** (Z = CH_2COOH), formation of a dimer with such properties is hindered, since the CH_2COOH group does not lie either in the plane nor along the axis of the benzene ring. A similar effect of lack of linearity of the rigid central bridge on the mesogenic properties of the carboxylic acid dimers was observed by Gray for phenylpropionic acid.[32]

The binding energy of molecules via hydrogen bonds in much stronger than that of dipole-dipole or dipole-induced dipole electrostatic interaction. Thus, the stability of complexes composed of molecules of compounds with the COOH or $CH{=}NOH$ groups is much greater than that of complexes consisting of molecules with CN or CHO groups. Also the dimers of the former are much longer (Figure 2a, 2b, 2c).

Greater average dimensions of the dimers may thus be one of the causes of the observed stability of the mesophase. Destruction of the structure of dimer **12** (Z = $C(CH_3){=}NOH$) due to the formation of its O-ether derivative **11** results in the lowering of the melting point and more important by in the disappearance of the nematic phase. In **11**, only the smectic phase of lower thermal stability is observed. In **8**, weak hydrogen bonds may also be formed in the liquid and solid phases, but linear association is not favored, so the mesophase is not observed. Liquid-crystalline compounds with an amine terminal group are seldom encountered.

Compounds containing the terminal substituents in group C are virtual nematics. When mixed with CPB, they lower the clearing point proportional to their concentration. The efficiency in lowering the clearing point of the various substituent, can be arranged in the following series:

$$\underset{\mathbf{23}}{\mathrm{H}} > \underset{\mathbf{24}}{\mathrm{CH_2Br}} > \underset{\mathbf{25}}{\mathrm{CH_2CN}} > \underset{\mathbf{21}}{\mathrm{CH_2{-}CH_2Cl}} > \underset{\mathbf{19}}{\mathrm{CH_2{-}CH_2CN}} > \underset{\mathbf{7}}{\mathrm{N_3}} > \underset{\mathbf{32}}{\mathrm{Br}}$$

The clearing point is lowered the most by pentylbiphenyl **23**. It is the shortest molecule in the series. It seems, therefore, that the length of the molecule has a greater effect than that of other properties of the molecule.

Plots presenting the clearing temperature (T_{N-I}) versus solution concentration change their inclination (have a bend) Figure 1 for all these compounds except compound **23**. At small concentrations, we observe a greater lowering of the clearing point than that observed at high concentrations. This behavior is particularly obvious for compounds with $Z = CH_2Br$ and CH_2CN possibly due to the associated structure of CPB. When a compound with a functional group producing a spatial hindrance was added, a rapid, complete decomposition of CPB autocomplexes in the range of small concentrations of about 0.15 mole fraction was observed. Above that concentration range, compound **2** behaves as if it had a monomeric structure, i.e. it shows a lower clearing point.

The terminal groups: CH_2CN, CH_2Br, CH_2COOH and $CH_2CHClCN$ protrude from the benzene ring plane presenting a considerable steric hindrance for close contact of the molecules in the liquid phase difficult. The fact that a steric hindrance exists was established on models of the compounds and confirmed by the features of the electronic spectrum, e.g. of compound **25** (Figure 3). The maximum of the absorption band of compound **25** ($Z = CH_2CN$) is shifted hypso- and hypochromically with respect to that of the dialkyl derivative **26** and even of **23**. Introduction of a second methylene group (compound **19**, $Z = CH_2{-}CH_2CN$) cancels this unfavorable spatial effect so the spectrum of compound **19** is normal.

The linear conformation of compound **19**, distinguished for its high $\mu_{\parallel}$ is only one from various possibilities. Thus, this compound neither gives linear association products nor reveals mesogenic properties. Nevertheless, it has a high virtual N → I transition temperature. The steric hindrance occurring at the benzene ring and related to the presence of CH_2CN, CH_2Br or CH_2COOH groups reduces the reaction of the substituent with the ring but also, what is more important, lowers the possibility of formation of contact complexes during collisions of molecules and increases the repulsive forces. There are no two-

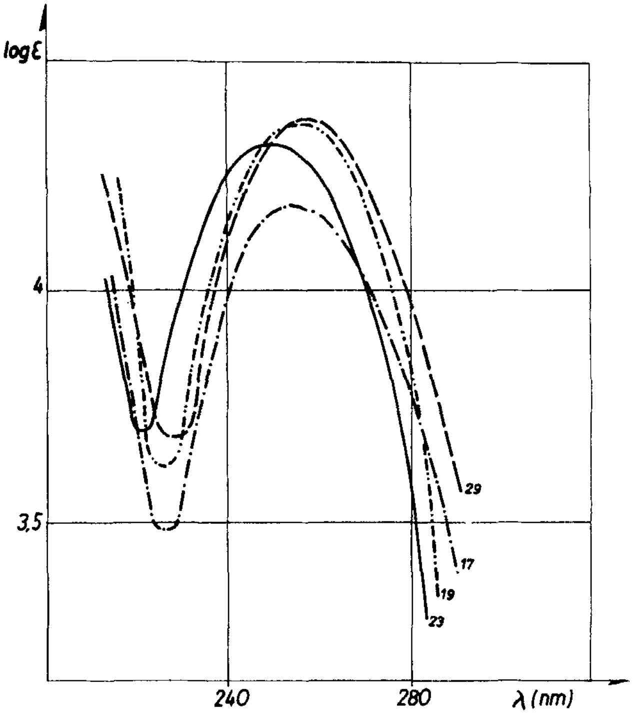
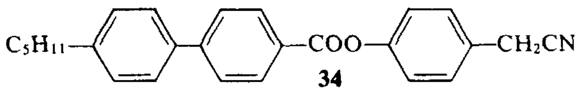


FIGURE 3 Electron spectra of compounds of general formula **1** with $Z = H$ **23**, $Z = CH_2CN$ **17**, $Z = CH_2—CH_2CN$ **19** and $Z = C_5H_{11}$ **29**.

ring compounds with these substituents that would reveal mesogenic features. However, the appearance of such features is possible in tri-nuclear compounds, e.g. ester **34**[33]



34

is a liquid-crystalline compound with phase transition temperatures K 155 S 165 N 173 I.

Compounds with terminal substituents classified in group D, whose mixtures with CPB have an abnormal dependence of the clearing points on composition are differentiated as regards structure. Also the effects of their presence in CPB are various. Compounds with terminal groups $C{\equiv}CH$, NH_2, $CH{=}CH_2$, NCO and CH_2COOH reveal an increase of the clearing points of the mixtures with increasing their concentrations in CPB. In all cases, the solid or solid-like phase and not the smectic phase precipitates on cooling of the solutions.

The efficiency of increasing the clearing point of the mixtures varies in the order (Figure 1a):

$$\underset{\mathbf{15}}{C{\equiv}CH} \approx \underset{\mathbf{8}}{NH_2} > \underset{\mathbf{20}}{CH{=}CH_2} \approx \underset{\mathbf{16}}{CH_2COOH} > \underset{\mathbf{18}}{NCO}$$

Among the compounds enumerated above only the one with C≡CH as the terminal group shows good solubility in CPB. It was possible, therefore, to investigate the properties of the solutions of this compound in a wide range of concentrations exceeding even the equimolar ratio. It was found that the variation of the clearing point with concentration was not proportional, and that the maximum value was obtained at an equimolar composition.

The clearing points of solutions of compounds **15**, **8**, **20**, **16** and **18** are inversely proportional to the concentration in 4-ethyl-4′-pentylazoxybenzene, decreasing with increasing concentration. The only exception was compound **20** with the substituent, $CH{=}CH_2$ (Figure 1b). Thus, only this compound has the virtual N → I transition temperature higher than the N → I for CPB. In the remaining compounds, the increase of the clearing points of the mixtures is related to a specific reaction. 4-Ethyl-4′-pentylazoxybenzene was selected as the second liquid-crystalline matrix in view of its properties differing from those of CPB. Between those compounds, a strong specific interaction occurs manifesting itself by the formation of an induced smectic S_A phase.[34] We expected, therefore, that if a compound reacts specifically with CPB, it will not react with the azoxy compound. Our results confirmed this supposition.

Compounds with terminal groups C≡CH, NH_2, CH_2COOH, $CH{=}CH_2$ and NCO yielded with CPB, pairs of linearly associated compounds. In the reactions of the first three compounds, probably hydrogen bonding also plays an important role, since only in this manner so can we explain the observed rise of the clearing points of mixtures of CPB with compounds having a CH_2COOH terminal group.

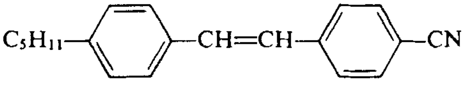
In the case of compounds with $CH{=}CH_2$ or NCO substituents the specific interaction seems to be small, since these compounds showed fairly high virtual temperatures of the N → I phase transition: 51.5°C and 30°C, respectively in the azoxy compound matrix.

Compounds with terminal groups I, CH_3CO and NCS, when mixed with CPB in a mole fraction of about 0.4, hardly affected the clearing temperature. One was independent of the concentration in the entire range or was slightly lowered but only for small concentrations such as was observed for the compound with the substituent CH_3CO.

Compounds with groups NCS and CH_3CO showed fairly good solubility in CPB making it possible to determine the N → I transition temperatures in a higher concentration range. Beginning with the concentration of 0.4 mole fraction, we observed a linear growth of the clearing temperature. This is, possibly, an indication that the temperature of the virtual N → I transition is higher for both compounds than in CPB. The abnormal behavior of compounds with the I, CH_3CO and NCS groups (**33**, **13**, **6**) in the concentration range below the mole fraction of 0.4 may be explained by the fairly high similarity of polarities and geometric structures of their molecules and molecules of CPB. These compounds can, therefore, replace each other in the dimers without any effect on the structure of the nematic liquid of the mixture as distinguished from pure CPB. In the range of higher concentrations of compounds **6** and **13**, the latter can appear in a form unbounded with CPB and so the molecules of one type (**6** or **13**) associate with each other. It is only then that the nematic solutions react to their presence as to a new species of a higher clearing temperature. Compounds **6** and **13** are also very similar to CPB in their complex forming ability with respect to azoxy compounds. When mixed with 4-ethyl-4′-*n*-pentylazoxybenzene they yield induced smectic S_A phases in a certain concentration range; the S_A → I transition temperature has a maximum value for a 1 : 1 composition. For mixtures of **6** or **13** with 4-ethyl-4′-*n*-pentylazoxybenzene, the nematic phase is observed only at concentrations below the 0.3 mole fraction, whereas for **2** the nematic phase is observed at higher temperatures in the entire concentration range.

In another work of ours, we studied the properties of CPB complexes with 4,4′-dialkylazoxy compounds in dilute solution of non-polar solvents.[26] We found that complexes were formed having a 1 : 1 composition and a fairly high stability constant, K. We suggested that the main contribution to this constant comes from the ΔS change due to the ordering of the molecules as a result of complexing. Compound **33** does not yield induced smectic phases with azoxy compounds, and its N → I transition temperature in the 4-ethyl-4′-*n*-pentylazoxybenzene matrix is as low as in the case of the compound with a CH_2Br terminal group.

Biphenyl compounds show a lower thermal stability of the mesophase as compared with compounds having central bridges. In our opinion, this lower stability is due to shorter molecular length of the biphenyl compounds. When compounds of the same molecular lengths are compared, e.g. **10** ($Z =$ CH═CHCN) and **35**, we observed no stability differences of the nematic phase in favor of compound **35**. Surprisingly compound **10** has a higher clearing point.



K 55.5°C N 101°C I[35] **35**

It might seem that the opposite should be true, since the **35** molecule is more coplanar and in **10** the phenyl rings are not precisely in one plane. A plot of the potential energy of the biphenyl molecule versus angle of rotation of the phenyl rings, providing only for the efficiency of the coupling of π electrons of both rings, shows a minimum for the planar conformation ($\sphericalangle\theta = 0°$). A potential energy plot, providing only for steric repulsion of hydrogen atoms in 2 and 2′ positions, has a minimum for the orthogonal conformation ($\sphericalangle\theta = 90°$). When both interactions are taken into account, the energy minimum is obtained for the intermediate values of angle θ.

The angle θ for biphenyl and its 4-substituted derivatives in the gaseous and liquid phases varies from 40°–45°.[36] When these compounds are dissolved in a nematic liquid, the angle θ decreases to 32°–38°.[37] In the solid state the molecules of biphenyl compounds are planar.[38] We can assume, therefore, that such a conformation also holds for the smectic phase, since it favors greater lateral interaction between the molecules. From Baran's calculations, we find that the barriers of rotation about the phenyl-phenyl bond are low and the biphenyl molecule easily undergoes deformation.[39] If the molecules of biphenyl derivatives are not planar in the nematic phase, then what are the factors that compensate for this unfavorable geometric shape? It seems that linear dimerization is this factor. The length of the dimer molecule corresponds to the length near the three-ring compound. Thus, the spatial effect connected with the possibility of torsion of the phenyl rings in biphenyl has a minor effect on the clearing point. This conclusion follows from comparing the mesogenic features of compounds **25** and **34**. In case of compounds **2** and **10**, the torsion does not seem to affect the stability of the complex and the exchange reaction, since the CN group orbitals of cylindrical shape can interact with equal force with the benzene ring of the second molecule irrespective of the rotation angle.

THE ROLE OF COUPLING

The effect of substituents has often been related to their capacity to react with the π electrons of the neighboring ring and to produce anisotropic polarization of the neighboring bonds.[40,41] One of the methods of characterizing the reaction of the substituent with the neighboring chromophore is to observe the changes of position and intensity of the characteristic band in the electronic spectrum. The electronic spectra of compounds **1** were measured in the near UV. Biphenyl and its derivatives have one band, i.e. band *p* in the range of 250–300 nm, which reveals the properties of a coupled π electron system. The maximum of the *p* band is shifted in the compounds tested towards higher wavelengths in the order:

$$\mathrm{H < C_5H_{11} \approx CH_2CN \approx CH_2CH_2Cl \approx CH_2Br \approx CH_2CH_2CN}$$
$$\mathrm{\approx CH_2CHClCN \approx CH_2COOH < Br < I < NH_2 < C{\equiv}CH \approx CN < N_3}$$
$$\mathrm{< C(CH_3){=}NOH \approx COOH < C(CH_3){=}NOC_2H_5 \approx CH{=}N{-}OH}$$
$$\mathrm{< COCH_3 \approx COC_5H_{11} \approx CHO \approx NCO < NCS < CH{=}CHCN}$$

and its intensity varies in the order:

$$\mathrm{CH_2CN < COCH_3 \approx CHO < H < CH_2CH_2CN < CH_2COOH < C_5H_{11}}$$
$$\mathrm{< CH_2CH_2Cl < CH_2CHClCN < COOH < Br < CH_2Br < CN}$$
$$\mathrm{< COC_5H_{11} < CH{=}NOH < C(CH_3){=}NOH < I < N_3}$$
$$\mathrm{< C(CH_3){=}NOC_2H_5 < NH_2 < C{\equiv}CH < CH{=}CHCN < NCO < NCS}$$

From these sequences of spectral properties variation, we can conclude that there is lack of closer correlation between the observed effect of the substituents on the spectra and on the mesogenic properties of the compounds. The electron spectrum reveals the features connected chiefly with the system of coupled bonds in the individual molecule and depends only weakly on other properties of the molecule, specially its total length and the orientation of the dipole moment. Thus, it is difficult and often irrational waiting conclusions about correlation from the above of the position and intensity $\lambda_{\max}$ of band *p*. The properties of the pairs of compounds **12** and **11** as well as **2** and **15** can serve as an example. The compounds in these pairs have electronic spectra of similar character (Figure 4) but their mesogenic properties are different. Thus compound **12** is a nematic while compound **11** is a smectic.

This difference of behavior is due to the different association capacities of these compounds. In Figure 5, the N → I phase transition temperatures versus calculated lengths of the molecules of these nematics and virtual nematics whose terminal groups lie in the plane of the molecule and do not associate via hydrogen bonds, are compared. A fairly good linear relationship is observed between the experimentally determined N → I transition temperatures and the lengths of the molecules. Compound **7** is an exception as it shows an excessively low clearing temperature considering the length of its molecule. Possibly, this is the result of the structure of the azide group $(-\overset{\oplus}{\underline{\mathrm{N}}}=\mathrm{N}=\overset{\ominus}{\underline{\mathrm{N}}}|)$ differing significantly from those of the remaining substituents.

This is a further confirmation of the already known fact[42,43] that the system of coupled bonds and the related bond polarizability anisotropy are not the structural features which determine whether or not the molecule will possess nematogenic properties. The important features here, is the length and rigidity

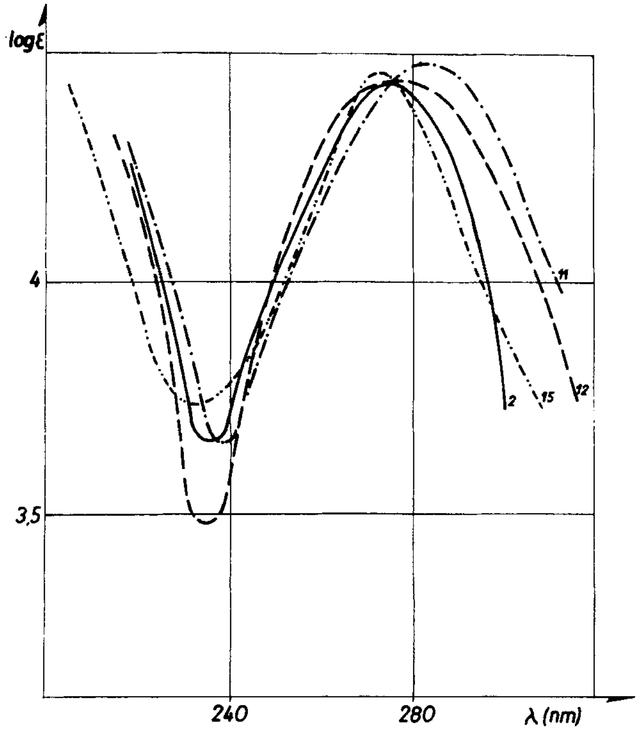


FIGURE 4 Electron spectra of compounds of the general formula **1** with $Z = \mathrm{CN}$ **2** and $Z = \mathrm{C{\equiv}CH}$ **15**; $Z = \mathrm{C(CH_3){=}NOH}$ **12** and $Z = \mathrm{C(CH_3){=}NOC_2H_5}$ **11**.

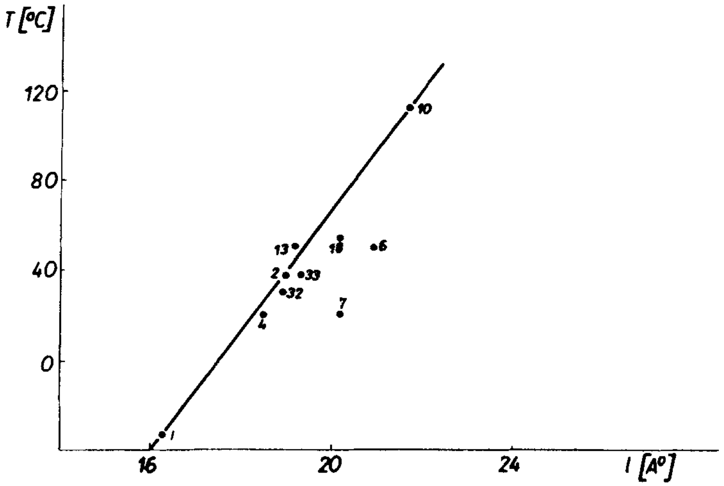


FIGURE 5 Variation of the N → I phase transition temperature with the molecule length (l). The temperatures of the virtual N → I transition have been determined in the compound **2** matrix.

of the molecule and its linear shape. The greater stability of the nematic phase in alkylcyclohexylbenzonitriles (PCH) and alkylbicyclohexylnitriles (CCH) as compared with that of the alkylcyanobiphenyls[41,42] is possibly related to the fact that polarization of the rings decreases in the order CCH < PCH < CPB. Thus, the molecules in the dimer shown in Figure 2a are ever more separated. The dimer becomes longer and the stability of the nematic phase increases.

FINAL REMARKS

The experimental data as well as the discussion presented in this work have revealed the possibility of creating the nematic phase in biphenyl derivatives-associates having a linear dimer structure. Such dimers exist already in the isotropic phase and it seems that this opinion can be extended to other types of compounds that is in accordance with the expectations of other authors[44] and with thermodynamic data. If we compare the changes of the thermodynamic functions ΔH_{N-I} and ΔS_{N-I} at the clearing point [T_{N-I}] for compounds differing solely by the terminal substituent, we find that compounds with terminal groups CN and NO_2 have lower values of ΔH_{N-I} and ΔS_{N-I} as compared with other compounds though their clearing temperatures are the highest.[45,46]

In our opinion, this can be explained solely by the fact that the molecules in the isotropic liquid are already considerably organized and nematic cybotactic structures are already present. The phase transition from such a partly ordered isotropic liquid to a nematic liquid is accompanied by small energy and entropy changes. The ordering increases in this case only a little and the phase transition heat is only a part of the total energy of interaction of the molecules in the mesophase and proportional to the achieved increase of ordering. Molecules with terminal groups favoring linear association are the most liable to undergo low range ordering in the isotropic liquid.

EXPERIMENTAL

Melting points and mesomorphic transition temperatures were determined using a PHMK heated stage and microscope with polarizers manufactured by VEB Analytic, Dresden. The studied compound was placed between two thin glass plates. The heating rate was less than 0.5°C/min at temperatures near the phase transition.

Liquid-crystalline phases were identified by Demus' method[8] by observing textures of the sample in polarized light under the microscope, and by testing their miscibility with already known and earlier classified liquid-crystalline biphenyl derivatives such as 4,4′-dihexylbiphenyl[8] (K 35 S_E 39.5 S_B 53.5 I)†, 4-hexyl-4′-hexanoilbiphenyl[7] (K 108 S_A 107 I)†, 4-ethylphenyl 4-*n*-pentylbiphenyl-4′-carboxylate[33] (K 106 S_A 125 N 168 I)†.

Virtual transitions were determined using the methods of Dave[47] and Gray[19] by extrapolating the clearing points of mixtures with CPB and with 4-ethyl 4′-*n*-pentylazoxybenzene.[48]

UV and VIS spectra were recorded using an Acta M-6 Beckmann apparatus in *n*-hexane solutions. The structures of the compounds were confirmed by IR (Specord 71 IR spectrometer) and NMR spectra (TESLA BS 487 B-80 MHz) and combustion analysis (Table I). The purity of the compounds was checked by thin-layer chromatography or for more volatile compounds, by gas chromatography.

4-Formyl-4′-pentylbiphenyl (**4**) 76 g (0.4 mole) of anhydrous $SnCl_2$ was added to 400 ml of anhydrous Et_2O and a stream of dry HCl passed through for 3 hr. A solution of 49.3 g (0.2 mole) of CPB (compound **2**) in 200 ml of Et_2O was rapidly added dropwise. Saturation with HCl was continued for an additional 1 hr, when the mixture was left to stand for 24 hr at room temperature. The pale yellow precipitate (complex **3**) was filtered, washed repeatedly with 100 ml of ether and treated with a stream of steam for 1 hr. The resulting oil was extracted into *n*-hexane, and the solution evaporated on a Rotavap. The residue was shaken with a saturated $NaHSO_3$ solution, the solid collected by filtration, washed twice with 100 ml ether and refluxed for 1 hr with 100 ml of 5% hydrochloric acid. The resulting oil was extracted into *n*-hexane and the extract dried over anhydrous $MgSO_4$, filtered through a layer of silica gel (7 cm thick and 3 cm width) and the hexane evaporated. The residue was distilled (0.3 mm Hg) and the distillate diluted with *n*-hexane, then the solution cooled to −20° and precipitated solid filtered to give 25 g of compound (**4**) in a 50% yield, m.p. 21.5°. T_{N-I} (19.5°); IR (film), 1650 cm^{-1} (C═O); n.m.r., δ 9.77 (s, 1, H—C═O).

*4-Isothiocyanato-4′-*n*-pentylbiphenyl* (**6**) 10 g (0.04 mole) of compound **8** was dissolved in benzene (saturated solution) and 3 ml (0.04 mole) CS_2 and 6 ml Et_3N were added and the solution placed in a refrigerator. After 45 hr, the pale yellow triethylammonium dithiocarbamate precipitate was filtered, washed with anhydrous ether and dried for 15 min in air. This salt was dissolved in 40 ml of chloroform, 6 ml of Et_3N added and the mixture cooled to 0°. Then 6 ml ethyl chloroformate was added dropwise with mixing. After 10 min, the

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†The phase transition temperatures have been determined by the present authors.

solution was allowed to warm to 20° (~1 hr) and then washed with 3N hydrochloric acid, twice with water and dried over anhydrous Na_2SO_4. The chloroform was removed from the filtrate on a Rotovap and the residue recrystallized twice from ethanol to give 8 g (78% yield) of compound **6**, K 53 S_E 74.5 I [Ref. 17, K 51 S_A 73 I]; IR (KBr), 2100 cm^{-1}, very strong band (—N=C=S).

*4-Azide-4′-*n*-pentylbiphenyl* (**7**) A solution 23.9 g (0.1 mole) of compound **8** in 500 ml of 1% aqueous HCl was heated to 80°. After cooling to 5°, a solution of 8.2 g $NaNO_2$ (0.12 mole) in 50 ml water was added dropwise during 2 hr and this solution stirred for 0.5 hr and then filtered. A solution of 7 g NaN_3 (0.12 mole) in 50 ml of water was added dropwise to the filtrate at 0°. After 0.5 hr, the precipitate formed was filtered and recrystallized twice from 95% ethanol to give 16 g (60% yield) of compound 7, m.p. 75°; IR (KBr), 2100 cm^{-1}, a very strong band $(\text{—}\underline{N}{=}\overset{\oplus}{N}{=}\overset{\ominus}{\underline{N}}|)$.

*4-(2-Chloro-2-cyanoethyl)-4′-*n*-pentylbiphenyl* (**9**) To a mixture of 100 ml acrylnitrile, 60 ml acetonitrile, 16.1 g (0.12 mole) $CuCl_2$ and 15.5 g (0.15 mole) tert-BuONO was added dropwise a solution of 23.9 g (0.1 mole) of 4-amino-4′-*n*-pentylbiphenyl **8** in 30 ml of acetonitrile.

As this solution was added, the temperature of the reaction solution rose to 30°; this temperature was maintained for an additional 1 hr. Then the mixture was poured into 100 ml of 20% aqueous hydrochloride and extracted twice with 100 ml Et_2O. The ether extract was washed with 20% HCl and dried over anhydrous $MgSO_4$. The solvent was removed from the filtrate on a Rotovap and the residue recrystallized once from methanol and twice from hexane (the first time it was heated to the boiling with silica gel in order to remove the color) to give 9.3 g (30% yield) of compound **9**, m.p. 46–50°; IR, the band characteristic for the CN group was not observed which is a characteristic feature of some α-substituted cyano compounds; n.m.r., δ 3.25 (d, 2, $Ar\text{—}\underline{CH}_2\text{—}CHClCN$), δ 4,4 (t, 1, —CHClCN); content of Cl: calcd. 11.37%, found 11.91%.

4-(2-Cyanoethenyl)-4′-pentylbiphenyl (**10**) A solution 15.6 g (0.05 mole) of compound **9** in 21 ml of Et_3N was refluxed for 6 hr. After cooling to RT, this solution was mixed with 140 ml of aqueous H_2SO_4. The resulting precipitate was filtered, washed with water until the filtrate became neutral and no Cl^- ions were present and then recrystallized twice from methanol to give 7 g (50% yield) of compound **10**, transitions temperatures: K 53 N 112 I; IR (KBr), 965 cm^{-1} (δ_{CH} in trans —CH=CH—), 1625 cm^{-1} (C=C), 2230 cm^{-1} (CN), n.m.r., δ 5.85 (d, 1, $\text{—}CH{=}\underline{CH}CN$, J_{HH}-trans, 16 Hz), doublet from $\underline{CH}{=}CHCN$ superimposed on the aromatic proton signal.

*O-Ethyl 4-acetyl-4'-*n*-pentylbiphenyl ketoxime ether* (**11**) 1.67 g of sodium was dissolved in 150 ml of anhydrous ethanol and then 14.2 g (0.05 mole) of ketoxime **12** and 10.5 g (0.07 mole) of ethyl iodide were added and the mixture refluxed 5 hr. Subsequently, this mixture was cooled, poured into a solution of 17 g NaOH in 250 ml water and extracted twice with 120 ml portions of chloroform. The extract was dried over anhydrous $MgSO_4$, the solvent removed by distillation and the residue thrice recrystallized from 95% ethanol to give 12.4 g (80% yield) of compound **11**, K 73 S_A 91 I; IR (KBr), absence of 3240 cm^{-1} band (OH); n.m.r., δ 2.15 (s, 3, CH_3—C=N—O—), δ 2.59 and 4.2 (t, 3 and k, 2 in CH_3—CH_2—O—N=).

*4-Acetyl-4'-*n*-pentylbiphenyl oxime* (**12**) A mixture of 26.6 g (0.1 mole) of ketone **13**, 100 ml of 95% ethanol, 9 g (0.12 mole) $NH_2OH \cdot HCl$ and 16.4 g (0.2 mole) CH_3COONa was heated for 5 hr on a steam bath. After cooling the precipitate was removed by filtration, washed with warm water, dried and recrystallized twice from ethanol to give 15 g (53% yield) of compound **13**, transition temperatures: K 139 N 144.5 I; IR (KBr) 3240 cm^{-1} (H—O—), n.m.r., δ 9.45 (s, 1, H—O—N=C—), δ 2.3 (s, 3, CH_3—C=).

4-Formyl-4'-pentylbiphenyl oxime (**5**) with transition temperatures K 126 N 141 I; IR (KBr) 3300 cm^{-1} (H—O—), n.m.r., δ 8.2 (s, 1, H—O—N=), δ 7.65 (H—C=) was obtained in an analogous manner.

*4-Ethynyl-4'-*n*-pentylbiphenyl* (**15**) A mixture of 26.6 g (0.1 mole) of compound **13**, 215 ml PCl_3 and 24 g PCl_5 was refluxed 48 hr. After cooling to RT, the reaction mixture was poured onto 250 g of crushed ice and extracted twice with 200 ml portions of Et_2O. The Et_2O extract was washed with 5% Na_2CO_3 and water and then dried over anhydrous $MgSO_4$. The ether was removed by distillation, the residue dissolved in hexane and the solution filtered through a silica gel layer 10 cm high and 3 cm width. The hexane was removed by distillation and the remaining mixture of chlorides **14** and **14a** dissolved in 75 ml anhydrous ethanol. Next, 15 g of solid KOH was added and the mixture refluxed for 40 hr. After cooling to RT, this mixture was poured onto 200 g of crushed ice in 300 ml H_2O and extracted with Et_2O. The Et_2O extract was washed with water, dried over anhydrous $MgSO_4$, the ether was removed by distillation and the residue recrystallized twice from hexane to give 5 g (20% yield) of compound **15**; m.p. 81°, IR, 3300 cm^{-1} (H—C≡), n.m.r., δ 2.95 (s, 1, H—C≡).

*4'-*n*-Pentylbiphenylacetic acid* (**16**) A mixture of 26.6 g (0.1 mole) of the ketone **13**, 5.2 g sulfur and 30 ml morpholine were refluxed for 7 hr. After cooling to RT, the reaction mixture was diluted with 50 ml ethanol, and the resulting precipitate filtered and washed with 50 ml of ethanol. The thiomorpholide obtained was refluxed with 180 ml of 70% aqueous ethanol and 180 ml of 50% NaOH solution for 8 hr. Then the alcohol was removed on a Rotovap and the residue diluted with 200 ml of hot water acidified and cooled. The resulting precipitate was filtered, washed with water, dried recrystallized from ethyl acetate and sublimed to give 14.3 g (51% yield) of compound **16**, m.p. 168°; IR (KBr) 1690 and 1720 cm^{-1} (CO in COOH) and 2400–3400 cm^{-1} wide band (OH in COOH), n.m.r., δ 3.7 (s, 1, Ar—$\underline{CH_2}$—COOH), δ 6.45 (COO$\underline{H}$).

*4-Isocyanate-4′-*n*-pentylbiphenyl* (**18**) A solution of 10 g (0.1 mole) Et_3N in 40 ml of acetone was added dropwise to a solution of 22.8 g (0.085 mole) of acid **17** in 150 ml of acetone cooled to 0° and followed by a solution of 12 g (0.11 mole) ethyl chloroformate in 40 ml of acetone. Then, the content was stirred for 30 min at 0° and a solution of 8.45 g (0.13 mole) NaN_3 in 30 ml water added dropwise. After stirring 1 hr, the mixture was poured into 400 g ice and water and extracted three times with 50 ml toluene. The toluene extract was dried over anhydrous $MgSO_4$ for 12 hr in a refrigerator. The filtered toluene solutions were introduced dropwise into a three-necked flask and heated to 90°—giving vigorous evolution of N_2. After the addition was concluded, heating was continued for 1 hr, the mixture diluted with 200 ml carbon tetrachloride and filtered. The solvents were removed from the filtrate and the solid residue recrystallized twice from hexane to give 10 g (45% yield) of compound **18**, m.p. 132°; IR, 2150 cm^{-1} (—N=C=O).

*4-(2-cyanoethyl)-4′-*n*-pentylbiphenyl* (**19**) A mixture of 28.5 g (0.1 mole) of compound **21**, 6.1 g (0.125 mole) NaCN and 200 ml diethylene glycol was heated at 120° for 3 hr with stirring. Then the mixture was poured into 500 ml of water and extracted with chloroform using 3 × 50 ml portions. The extract was dried over anhydrous $MgSO_4$, and the solvent evaporated. The solid residue was dissolved in hexane and the solution passed through a column (20 cm high and 3 cm width) filled with silica gel. The eluate contained mainly unreacted chloro derivatives **21**, whereas the cyano derivatives were adsorbed on the gel. The column was subsequently eluated with chloroform, the solvent removed from the eluent and the residue recrystallized twice from hexane to give 11 g (40% yield) of compound **19**, m.p. 66°; IR, 2250 cm^{-1} (—CN), n.m.r., δ 2.55 (t, 2, Ar—$\underline{CH_2}$—CH_2—CN), δ 2.92 (t, 2, —$\underline{CH_2}$—CN).

4-Vinyl-4′-pentylbiphenyl (**20**) Compound **21** heated with an ethanolic KOH solution in a way similar to that described above for the mixture of chlorides **14** and **14a** was converted to compound **20** in a 80% yield, m.p. 107–112°. This material was contaminated with a small quantity of the polymer and is not stable. On storage it oxidizes and polymerizes† IR (KBr), 1625 cm^{-1} (C═C), 890 and 980 cm^{-1} (non-flat deformating vibration of CH in the vinyl group), n.m.r., characteristic spectrum of the vinyl group $H_CC{=}C\,H_AH_B$, δ 5.17 (d, 1, H_A), δ 5.62 (d, 1, H_B), δ 6.62 (k, 1, H_C).

*4-(2-chloroethyl)-4′-*n*-pentylbiphenyl* (**21**) 6.7 g (0.05 mole) of anhydrous $AlCl_3$ was suspended in 20 ml of anhydrous Et_2O and introduced dropwise into a suspension of 0.95 g (0.025 mole) $LiAlH_4$ in 20 ml anhydrous Et_2O. Then a solution of 30.1 g (0.1 mole) 4-chloroacetyl-4′-*n*-pentylbiphenyl **22** in 40 ml of anhydrous $CHCl_3$ was added dropwise during 30 min with stirring and the mixture was refluxed for 18 hr. After this time 20 ml of ethyl acetate, 25 ml concentrated hydrochloric acid and 100 ml Et_2O were successively added in order to decompose excess $LiAlH_4$. The organic layer was separated, washed three times with water and dried over anhydrous Na_2SO_4. The solvents were distilled from the filtrate and the residue recrystallized twice from an acetone-methanol (1:1) mixture after cooling to −20° to give 20 g (70% yield) of compound **21**, m.p. 49°; n.m.r., δ 2.97 (t, 2, Ar—$\underline{CH}_2$—CH_2Cl), δ 3.59 (t, 2, —CH_2—Cl), content of Cl: calcd. 12.37%, found 12.85%.

*4-(Bromomethyl)-4′-*n*-pentylbiphenyl* (**24**) A mixture of 22.4 g (0.1 mole) pentylbiphenyl **17**, 3.4 g (0.11 mole) paraformaldehyde, 12.5 g (0.12 mole) NaBr and 50 ml of acetic acid were heated to 80°. At this temperature a solution prepared from sulfuric acid (20 ml, $d = 1.84$) and acetic acid (20 ml) was added dropwise during 1 hr. Heating at 80° was continued for 25 hr upon which the mixture was cooled, diluted with water (100 ml) and extracted twice with 200 ml CCl_4. The CCl_4 extract was washed with water, a 5% Na_2CO_3 solution, water and then dried over anhydrous $MgSO_4$. The CCl_4 was removed from the filtrate on a Rotovap and the residue distilled at 198° (1 mm Hg). The distillate solidified and was recrystallized twice from *n*-hexane to give 15.4 g (48.5% yield) of compound **24**, m.p. 76°; n.m.r., δ 4.45 (s, 2, Ar—$\underline{CH}_2$—Br).

*4-Cyanomethyl-4′-*n*-pentylbiphenyl* (**25**) A mixture of 31.7 g (0.1 mole) of compound **24**, 10 g (0.15 mole) KCN, 20 ml H_2O and 50 ml ethanol was refluxed for 4 hr. The ethanol was removed by distillation and the residue diluted with 150 ml of water. The resulting crystals were filtered and recrystallized twice from hexane to give 20 g (75% yield), m.p. 84°, IR 2250 cm^{-1} (CN), n.m.r., δ 3.67 (s, 2, Ar—$\underline{CH}_2$—CN).

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† In the IR spectrum, the 890, 980 and 1625 cm^{-1} bands disappear and a new strong band is developed at 1680 cm^{-1}.

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