Thermotropic Liquid Crystals from Planar Chiral Compounds: [2.2]Paracyclophane as a Mesogen Core

by **Valeria I. Rozenberg*** and **Elena L. Popova**

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova 28, 117813 Moscow, Russia (e-mail: lera@ineos.ac.ru)

and **Henning Hopf***

Department of Organic Chemistry, Technical University of Braunschweig, Hagenring 30, D-38106 Braunschweig (e-mail: H.Hopf@tu-bs.de)

New thermotropic mesomorphic compounds containing a [2.2]paracyclophane (PC) unit were synthesized and investigated (*Scheme*). Carboxylic acids were selected as the starting PC building blocks. The influence of structural features on the stability of the mesomorphic phases was studied (*Figs. 1* and *2*): for this purpose, the structures of the PC-carboxylate unit and the organic fragment of the aryl-ester moiety were varied systematically. Esters derived from PC-monocarboxylic acid did not exhibit liquid-crystalline (LC) properties, while diaryl PC-dicarboxylates favored mesomorphism. Dicarboxylate substituents arranged in the *para*-position provided LC phases in a broad temperature range and considerably increased the mesomorphic interval in comparison with that of the structurally related pseudo-*para* PC derivatives.

Introduction. – Unique physical properties, providing wide application in electro-optic devices and particularly the recent discovery of new mesophases, such as antiferroelectric, ferrielectric, and twist-grain boundary phases, have put chiral liquid-crystalline (LC) materials in the centre of liquid-crystal research [1][2]. Historically, up to now, most chiral LC compounds contain molecules incorporating a centre of chirality. More recently, compounds with planar and axial chirality are beginning to attract the growing interest of researchers dealing with LC materials. The unique geometry of this type of compounds provides a rigid interaction between the origin of the symmetry-breaking chirality and the mesogenic unit, thus resulting in a definite fixation of the source of chirality in a LC matrix.

In principle, planar chirality could drastically change the physical properties of the resultant LC material: *1*) In terms of molecular structure, a rigid steric coupling between the transverse dipole, chiral centre, and the mesogen rod should maximize the local ferroelectric polarization [3], allowing consideration of the above compounds as possible chiral dopants for ferroelectric compositions, which are able to confer a high value of spontaneous polarization (P_s) to the achiral host [4]. *2*) Electro-optical effects exhibited by LC materials such as electroclinic effects or nonlinear optical (NLO) properties are expected to be larger for compounds with rigid interaction between the chiral and optical portions of the molecule [5].

However, the bulkiness of the structural units necessary to realize an axis or a plane of chirality significantly disturbs the desired rigid rod-like shape of the molecule, thus creating a serious obstacle to achieving stable mesomorphic properties. So far, only a

few examples of optically active compounds with planar or axial chirality exhibiting LC behaviour have been reported. These include cyclohexylideneethanone derivatives [6], compounds containing a chiral biphenyl core [7], allene derivatives [8], and liquid crystals derived from butadiene(tricarbonyl)iron complexes [9]. Also the first 1,3-unsymmetrically disubstituted optically active LC ferrocene derivative was recently reported [10][1]). In all the above cases, the investigated compounds had to be prepared by multistage synthesis – leading to low overall yields, or compounds were obtained which are chemically or photochemically unstable. Moreover, only a narrow temperature interval of smectic phases was observed in most cases[2]). This is probably the reason for lack of systematic studies of physical properties of compounds with planar and axial chirality as well as of their practical application. The ease of functionalization, optical resolution (introduction of even one substituent into the aromatic ring or the molecular bridges produces planar chirality of the PC molecule), and high stability of [2.2]paracyclophane (=tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene; PC) derivatives towards light, oxidation, and high temperatures [12] make them unique candidates in this study.

In the present study, we want to assess the mesogenic potential of the PC unit, as well as to establish the characteristic features of PC-containing compounds concerning mesomorphism. In particular, a search of the structural features that provide increased stability of the mesomorphic behaviour of the PC derivatives was performed. Towards this end, the structures of *a*) the PC unit and *b*) of the organic fragment (substituent) were varied systematically.

Results and Discussion. – *Synthesis.* Three starting building blocks are commonly used to construct LC compounds: aldehydes, phenols, and carboxylic acids, and they have often been employed to build-up imino and ester groups, respectively. *Schiff* bases derived from aldehydes are less important for practical applications because of their tendency to hydrolyze. The phenolic [2.2]paracyclophanol is quite unreactive; however, with aromatic acid chlorides it reacts to give esters that have significantly higher melting points than their benzene analogues (with benzene unit instead of PC). On the other hand, PC-carboxylic acids provide esters that melt approximately at the same temperatures as structurally related benzene derivatives, and they are readily available. Therefore, carboxylic acids of PC were chosen as the most appropriate building blocks to construct LC compounds.

The general approach used in the synthesis of the investigated PC derivatives was to construct separately a phenolic part and to attach this subsequently as an ester moiety to the PC-carboxylic acid structural block (*Scheme*). Standard esterification conditions (pyridine) were used for the reaction of PC-carbonyl chlorides with aromatic phenols. To study the influence of the structure of the aryl-ester moieties on mesogenic

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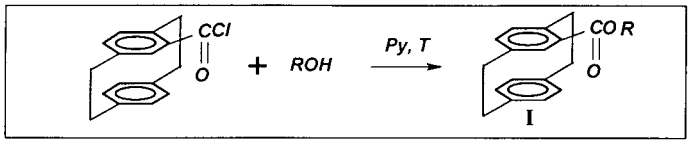
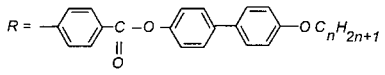
[1]) Two examples of optically active ferrocene-containing LC compounds have been reported previously [11]. However, in these cases, chirality was introduced into the peripheral side chain by means of an asymmetric C-atom.

[2]) Exceptions are allene derivatives for which smectic C phases were observed over a broad temperature range [8]. However, these compounds possess moderate thermal stability only, which largely depends on the substitution pattern at the allene moiety.

Scheme

a) Monosubstituted PC derivatives (compounds of series **I**) :

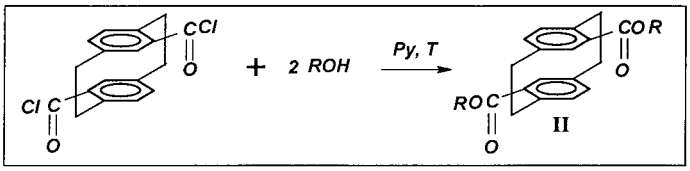


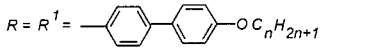


Ia $n = 8$

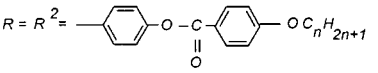
Ib $n = 12$

b) Disubstituted PC derivatives (compounds of series **II** and **III**):

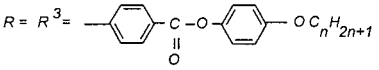




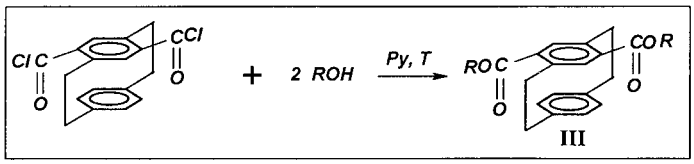
II a-g $n = 5–11$

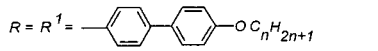


II h, i $n = 10, 14$

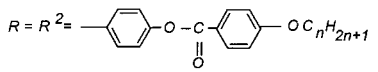


II j, k $n = 10, 14$

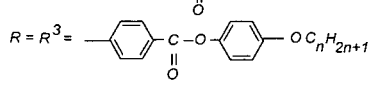




III a, b $n = 6, 14$



III c $n = 14$



III d $n = 14$

behaviour, three types of phenols were tested to construct disubstituted PC derivatives (*Scheme*).

Mesogenic Properties. a) *Monosubstituted PC Derivatives* **Ia**,**b**. The investigated monosubstituted PC derivatives **Ia** and **Ib** reveal no mesomorphic behaviour. They melt directly into an isotropic liquid; also, no LC phases were detected on cooling of the samples from the isotropic melt – compounds crystallized directly from the liquid

phase. The lack of LC properties could be probably explained by the unfavourable molecular shape (L-shape) and repulsive interactions introduced by the PC core.

b) *Disubstituted Pseudo*-para-*PC Derivatives* **IIa**–**k**. In our search for mesogenic structures derived from [2.2]paracyclophane, we next turned to disubstituted compounds that could provide a more elongated molecular shape, compared to that of monosubstituted derivatives, thus favoring mesomorphism. We furthermore considered it useful to compare the mesomorphic behaviour of PC derivatives with that of the corresponding compounds containing a ferrocene unit, which can be viewed as the most closely related analogue of PC, both systems possessing a double-layered structure. Although we do not consider ferrocene derivatives to be promising candidates in our study of LC compounds with planar chirality (rather complex resolution techniques, relatively narrow interval of LC phases exhibited in most cases), the main construction principles elaborated for ferrocenomesogens [13] appear to be useful for the investigation of the LC behaviour of PC derivatives. However, the structure/mesogenic property relationship determined for ferrocene-containing LC compounds cannot be applied to PC derivatives automatically since the mesomorphic behaviour could be significantly influenced by the structural peculiarities of each of these molecules.

Historically, the ferrocene 1,1′-diesters bis(4′-alkoxy-[1,1′-biphenyl]-4-yl) ferrocene-1,1′-dicarboxylates were reported as the first mesogenic ferrocene derivatives [14]. X-Ray diffraction studies indicated that these compounds adopt a '*transoid*' conformation ('S' shape) in the crystalline and mesomorphic states [15], which approximately corresponds to the pseudo-*para* substitution pattern in paracyclophanes. The structurally related PC analogues **IIa**–**g** were hence synthesized (*Fig. 1*).

Mesomorphic behaviour was investigated by means of differential scanning calorimetry (DSC) and polarized microscopy (PM). Compounds were investigated at various scanning rates (see *Exper. Part*), and coincident results were obtained in all cases. Phase-transition temperatures of the investigated PC derivatives are presented in *Fig. 1*. Only three ferrocene derivatives from the reported series [14] ($n = 4-11$) show mesomorphic behaviour (*Fig. 1*): the compounds with $n = 5$ and 6 exhibit a monotropic smectic C (SmC) phase in a narrow temperature interval, while the compound with $n = 11$ gives rise to a monotropic smectic A (SmA) phase. In contrast, all structurally related PC derivatives exhibit a stable enantiotropic nematic phase over a relatively broad temperature range, which can be easily identified by the appearance of the nematic droplets immediately below the clearing point that consolidate on cooling to display the characteristic marbled texture. The temperature interval of the nematic phase is nearly independent of the alkyl chain length. This observation is of interest since usually the nematic stability decreases as the paraffinic chain becomes longer. Long-chain derivatives with $n > 6$ also exhibit a short monotropic SmA phase. Within the cooling temperature regimes (5 and 10°/min) used, it separates in the form of grains, and crystallization takes place parallel with its formation. However, when samples are kept at temperatures 5–10° higher than T_{cryst} for 30 min, a typical focal conic texture with homeotropic domains develops.

To further investigate the importance of structural features on the liquid-crystalline behaviour, we examined the influence of the nature of the organic aryl-ester moiety on the mesomorphic tendency. PC Derivatives **IIh** and **IIi** with the ester moieties R^2 and **IIj**

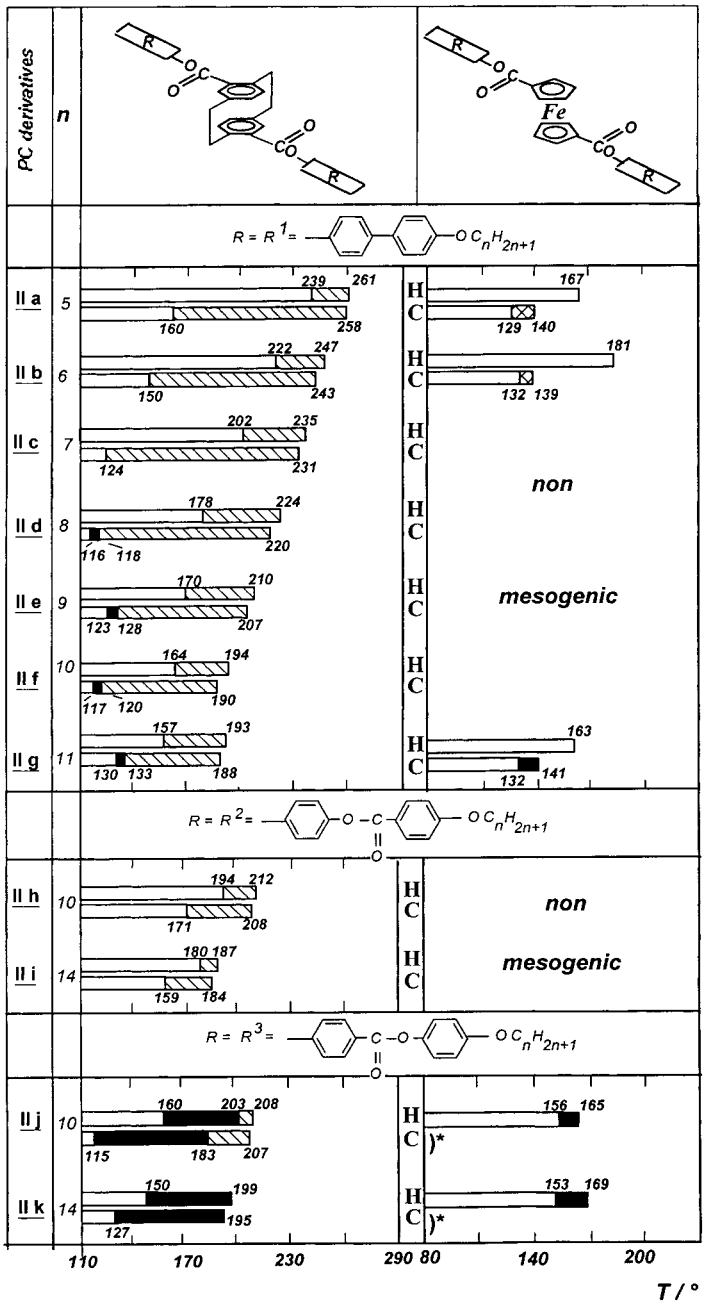


Fig. 1. *Phase-transition temperatures of PC derivatives* **IIa**–**k**, *compared with those of structurally related ferrocene analogues.* The data for ferrocene derivatives are from [14][16] for the compounds containing the corresponding ester moieties R^1, R^2 or R^3. H = Heating cycle, C = cooling cycle.)*, no reported data. crystal, nematic phase, smectic A phase, smectic C phase.

and **IIk** with R^3 were synthesized for this purpose. The organic fragments R^2 and R^3 have similar chemical compositions but differ in orientation of the interior ester linkages. Paracyclophanecarboxylates containing the ester moiety R^2 exhibit an enantiotropic nematic phase in a narrow temperature interval (structurally related ferrocene analogous were nonmesogenic [16]). PC-Containing compounds containing the ester moiety R^3 exhibit a broad interval of SmA phase (ferrocene analogues also exhibited a tendency to form smectic phases; however, these were detected only over a narrow temperature interval [16]). Benzene derivatives containing substituents of type R^2 and R^3 revealed the same mesogenic tendencies with respect to the mesophase type [17][18] as those observed for the investigated cyclophane-containing compounds: as suggested in [18] both structural (unfavourable 'bent' shape of fragment R^2) and electronic factors can explain the different mesogenic tendency of the derivatives with fragments R^2 and R^3.

c) *Disubstituted* para-*PC Derivatives* **IIIa**–**d**. To study the influence of the substituent position on the mesophase behaviour of paracyclophane derivatives, compounds containing the same type of substituents (R^1, R^2 or R^3) in *para*-position of the cyclophane moiety were synthesized, and the mesomorphic behaviour was compared with that of pseudo-*para*-PC analogues, as well as with the structurally related ferrocenomesogenes [19][20].

As in the case of pseudo-*para*-substituted paracyclophane derivatives, compounds with the ester moiety R^3 reveal superior mesogenic properties in the investigated series and a pronounced tendency to form smectic phases (*Fig. 2*).

Broad intervals of the SmA phase, exhibiting a typical focal-conic texture with homeotropic domains under PM are observed for **IIId**. Compounds containing R^1 show a nematic phase, as well as SmA phase in the case of the long-chain derivative **IIIb** ($n = 14$). PC Derivatives with the ester moiety of type R^2 display only nematic behaviour. Thus, the LC tendency of *para*-substituted PC derivatives depending on the nature of the substituents remains unchanged, compared with the pseudo-*para*-substituted structures.

However, in contrast to the structurally related pseudo-*para* analogues, *para*-substituted PC derivatives exhibit a considerable lowering of the melting point and increased mesomorphic ranges (this relates to all three types of ester moieties R^1, R^2 and R^3). Thus, the *para*-disubstituted PC structure is a stronger mesomorphic promoter than the one containing the substituents in pseudo-*para* position (for identical ester moieties). Therefore, for the investigated paracyclophane-containing compounds, mesomorphic strength follows the series: *para*- > pseudo-*para*- > mono-substitution. The above tendencies are similar to the data obtained for the ferrocene framework [13]. Thus, in spite of the fact that PC derivatives show superior mesogenic properties compared to the ferrocene-containing compounds, the main principles elaborated for the construction of LC double-layered molecules are comparable. It is hence likely that rigid organic moieties exhibiting similar molecular shapes will behave analogously as well.

Conclusions. – The results presented demonstrate that, by careful combination of structural factors, [2.2]paracyclophane derivatives that exhibit stable mesomorphic behaviour over a wide temperature range can be produced, and different types of

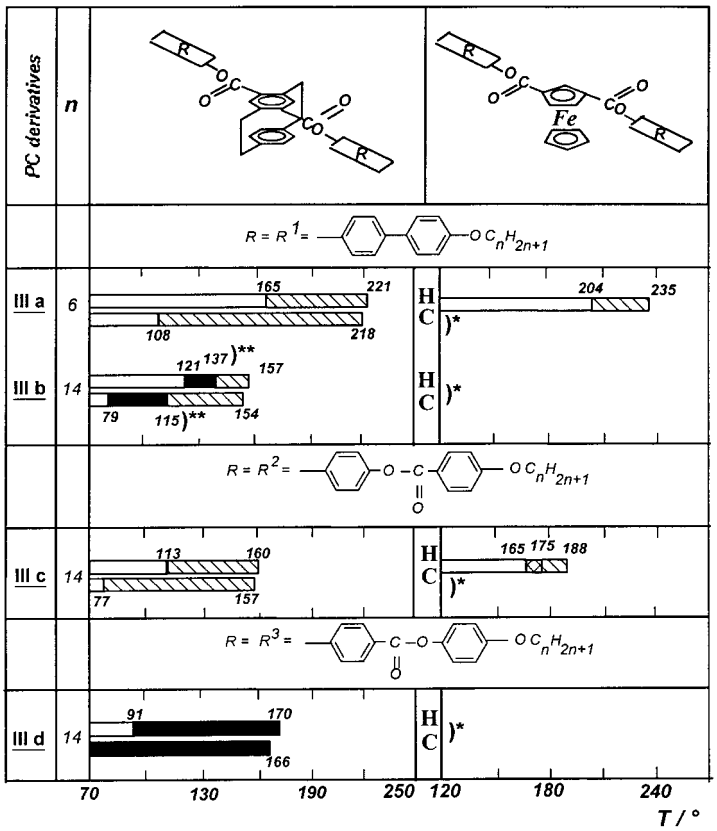


Fig. 2. *Phase-transition temperatures of PC derivatives* **IIIa**–**d**, *compared with those of structurally related ferrocene analogous.* The data for ferrocene derivatives are from [19][20] for the compounds containing the corresponding ester moieties R^1 or R^2. H = heating cycle, C = cooling cycle.)*, no reported data;)**, phase transition resolved by polarized microscopy only. Identification of the mesophases, see *Fig. 1.*

mesophases can be generated. The mesomorphic properties depend on both the structure of the initial cyclophane block and the nature of the organic substituents and their position. Due to their unfavourable molecular shape, the investigated mono-substituted paracyclophane derivatives do not reveal LC behaviour, while disubstitution favors mesomorphism. *para*-Substitution in the PC unit provides mesophases over a broad temperature range and considerably increased mesomorphic intervals in comparison with structurally related pseudo-*para*-PC derivatives. Thus, appropriately substituted paracyclophanes can serve as a valuable framework for the design of novel LC compounds with planar chirality.

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Experimental Part

1. *General*. Pyridine was distilled over KOH prior to use. Other reagents were purchased from *Aldrich* and were used without purification. All reactions were carried out under N_2. Column chromatography (CC): silica gel *60*, 70–230 mesh (*Merck*, Darmstadt). Transition temp. (onset point of endotherm or exotherm) and enthalpies were determined with a differential scanning calorimeter *Rheometric Scientific DSC SP*; all compounds were studied at various scanning rates (5 and 10° min^{-1}) under N_2. Optical studies were conducted by means of the *Olympus BX-50* system microscope equipped with a *Linkam LTS-350* variable-temp. stage. *IR Spectra: Nicolet 320-FT-IR* spectrometer; in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker DRX-400* (400.13 and 100.6 MHz, for ^{1}H and ^{13}C, resp.); $CDCl_3$ as solvent; δ in ppm rel. to $SiMe_4$ as internal standard, J in Hz. MS: *Finnigan MAT 8430*, EI (70 eV); in *m*/*z* (rel. %). Elemental analyses were performed in the Analytical Laboratory of the Department of Pharmaceutical Chemistry, Technical University Braunschweig.

2. *[2.2]Paracyclophanecarboxylic Acids. [2.2]Paracyclophane-4-carboxylic Acid* (= *Tricyclo[8.2.2.2^{4,7}]-hexadeca-4,6,10,12,13,15-hexaene-5-carboxylic Acid*) was synthesized according to [21].

[2.2]Paracyclophane-4,16-dicarboxylic Acid (= *Tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene-5,11-dicarboxylic Acid*) [22] was obtained from 4,16-dibromo[2.2]paracyclophane [23] by lithiation followed by carboxylation under the same conditions as described for the preparation of [2.2]paracyclophane-pseudo-*o*-dicarboxylic acid [24]. This provided [2.2]paracyclophane-4,16-dicarboxylic acid in 77% yield.

[2.2]Paracyclophane-4,7-dicarboxylic Acid (= *Tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene-5,15-dicarboxylic Acid*). Dimethyl [2.2]paracyclophane-4,7-dicarboxylate [25] (3 g, 9.26 mmol) in MeOH/H_2O 1:1 (400 ml) was treated with an excess of K_2CO_3. The mixture was boiled overnight, concentrated to *ca*. 100 ml, and acidified with conc. HCl soln. The precipitate was filtered off, thoroughly washed with H_2O, and dried: 2.44 g (89%). M.p. > 250° (dec.). IR (KBr): 2924*s*, 2894*m*, 2854*m*, 1686*s*, 1414*s*, 1282*s*. ^{1}H-NMR ((D$_6$)DMSO): 2.81–3.00 (*m*, 4 H, CH_2CH_2); 3.13–3.20 (*m*, 2 H, CH_2CH_2); 3.91–3.99 (*m*, 2 H, CH_2CH_2); 6.45–6.55 (*m*, 4 arom. H); 7.13 (*s*, 2 arom. H); 12.89 (br. *s*, 2 COOH). MS: 296 (20, M^+), 148 (4), 104 (100), 78 (16). Anal. calc. for $C_{18}H_{16}O_4$: C 72.96, H 5.44; found: C 72.90, H 5.61.

3. *Phenolic Biphenyl and Benzene Derivatives. 4′-(Alkyloxy)-[1,1′-biphenyl]-4-ols* (R^1OH). The mixture of equimolar amounts of [1,1′-biphenyl]-4,4′-diol and alkyl bromide, excess of K_2CO_3, and a catalytic amount of NaI were stirred in 1-methylpyrrolidin-2-one (NMP) overnight at 70°. The mixture was poured into H_2O and the precipitate filtered off, thoroughly washed with H_2O, and dried. CC (silica gel, CH_2Cl_2) gave the desired phenolic derivatives in 65–75% yield.

4-Hydroxyphenyl 4-(Alkyloxy)benzoates (R^2OH). The 4-(alkyloxy)benzoic acids [26] were converted to the corresponding acid chlorides with $SOCl_2$. These were reacted with hydroquinone in pyridine [27]. The final phenolic derivatives were purified by CC (silica gel, CH_2Cl_2).

4′-(Alkyloxy)-[1,1′-biphenyl]-4-yl 4-Hydroxybenzoate (ROH) *or 4-(Alkyloxy)phenyl 4-Hydroxybenzoate* (R^3OH). The 4-hydroxybenzoic acid (its OH function protected as the methyl carbonate [27]) was converted to the corresponding acid chloride with oxalyl chloride. The acid chloride was treated with 4′-(alkyloxy)-[1,1′-biphenyl]-4-ol (or 4-(alkyloxy)phenol for the preparation of disubstituted PC derivatives) in pyridine as described in [27]. Subsequent removal of the protecting group was accomplished by stirring with aq. ammonia in EtOH [28] to give the desired phenolic derivatives, which were recrystallized from EtOH.

4. *PC Esters* **Ia**,**b**, **IIa**–**k**, *and* **IIIa**–**d**: *General Procedure*. The PC-dicarboxylic acid (0.4 mmol) (or the PC-monocarboxylic acid for the preparation of mono-substituted **Ia**,**b**) was converted with $SOCl_2$ (3 ml) to the corresponding acid chloride by boiling in $CHCl_3$ (15 ml) for 4 h. After evaporation, the residue was dried under reduced pressure. The acid chloride and the aromatic phenolic derivative (0.75 mmol) in pyridine were boiled for 6 h under N_2. Then the mixture was cooled and poured into dil. HCl soln. The precipitate was filtered off, thoroughly washed with H_2O, and dried. The product was dissolved in CH_2Cl_2 and the soln. was passed through a short silica gel plug. The solvent was evaporated and the residue recrystallized from MeOH/CH_2Cl_2 2:1.

4-{[[4′-(Octyloxy)[1,1′-biphenyl]-4-yl]oxy}carbonyl}phenyl [2.2]Paracyclophane-4-carboxylate (= *4-{[[4′-Octyloxy)[1,1′-biphenyl]-4-yl]oxy}carbonyl}phenyl Tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene-5-carboxylate*; **Ia**): Yield 0.21 g (81%). M.p. 160–162°. ^{1}H-NMR ($CDCl_3$): 0.90 (*t*, Me); 1.24–1.54 (*m*, 10 H, 5 CH_2); 1.76–1.85 (*m*, 2 H, CH_2); 2.89–2.94 (*m*, 1 H, CH_2CH_2 (PC)); 3.03–3.29 (*m*, 6 H, CH_2CH_2 (PC)); 4.01 (*t*, CH_2O); 4.14–4.21 (*m*, 1 H, CH_2CH_2 (PC)); 6.51–6.66 (*m*, 5 arom. H (PC)); 6.78 (*dd*, ^3J = 7.8, ^4J = 1.9, 1 arom. H (PC)); 6.99 (*d*, J = 8.7, 2 arom. H); 7.28 (*d*, J = 8.7, 2 arom. H); 7.38 (*d*, ^4J = 1.9, 1 arom. H (PC)); 7.42 (*d*, J = 8.7, 2 arom. H); 7.52 (*d*, J = 8.7, 2 arom. H); 7.61 (*d*, J = 8.7, 2 arom. H); 8.35 (*d*, J = 8.7, 2 arom. H). MS: 652 (70, M^+), 235 (100), 131 (86), 104 (32). Anal. calc. for $C_{44}H_{44}O_5$: C 80.95, H 6.79; found: C 81.08, H 6.87.

4-{{[4′-(Dodecyloxy)[1,1′-biphenyl]-4-yl]oxy}carbonyl}phenyl [2.2]Para-cyclophane-4-carboxylate (= *4-{{[4′-(Dodecyloxy)[1,1′-biphenyl]-4-yl]oxy}carbonyl}phenyl Tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene-5-carboxylate*; **Ib**): Yield 0.22 g (78%). M.p. 146–147°. ^{1}H-NMR ($CDCl_3$): 0.89 (*t*, Me); 1.23–1.54 (*m*, 18 H, 9 CH_2); 1.75–1.85 (*m*, 2 H, CH_2); 2.88–2.93 (*m*, 1 H, CH_2CH_2 (PC)); 3.03–3.29 (*m*, 6 H, CH_2CH_2 (PC)); 4.00 (*t*, CH_2O); 4.14–4.21 (*m*, 1 H, CH_2CH_2 (PC)); 6.51–6.66 (*m*, 5 arom. H (PC)); 6.77 (*dd*, ^3J = 7.8, ^4J = 1.9, 1 arom. H (PC)); 6.98 (*d*, *J* = 8.7, 2 arom. H); 7.28 (*d*, *J* = 8.7, 2 arom. H); 7.38 (*d*, ^4J = 1.9, 1 arom. H (PC)); 7.41 (*d*, *J* = 8.7, 2 arom. H); 7.52 (*d*, *J* = 8.7, 2 arom. H); 7.61 (*d*, *J* = 8.7, 2 arom. H); 8.34 (*d*, *J* = 8.7, 2 arom. H). MS: 708 (68, M^+), 235 (100), 131 (78), 104 (28). Anal. calc. for $C_{48}H_{52}O_5$: C 81.32, H 7.39; found: C 81.61, H 7.45.

Bis[4′-(pentyloxy)[1,1′-biphenyl]-4-yl] [2.2]Paracyclophane-4,16-dicarboxylate (= *Bis[4′-(pentyloxy)[1,1′-biphenyl]-4-yl] Tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene-5,11-dicarboxylate*; **IIa**): Yield 0.25 g (81%). ^{1}H-NMR: *Table*. MS: 772 (34, M^+), 185 (91), 131 (100). Anal. calc. for $C_{52}H_{52}O_6$: C 80.80, H 6.78; found: C 80.81, H 6.61.

Table. *^{1}H-NMR Data of PC Derivatives* **IIa**–**k** *and* **IIIa**–**d**. Data in italics are coincident for all members of the noted series.

	Protons of the aliphatic chain (OCH_2 ------ CH_2 ------ $(CH_2)_k$ ------ $CH_3)_2$				Bridge CH_2CH_2	Protons of the aromatic ring of PC moiety	Aromatic protons
	(*t*, 4 H)	(*m*, 4 H)	(*m*, 4*k* H)	(*t*, 6 H)			
IIa	4.02		1.35–1.53	0.95			
b	4.01		1.30–1.53	0.92			
c	4.02		1.27–1.53	0.92	*2.96–3.08* (*m*, 2 H)	*6.69* (*d*, ^3J, 2 H)	*7.00* (*d*, *J* = 8.7, 4 H)
d	4.01	*1.78–1.86*	1.23–1.53	0.91	*3.23–3.32* (*m*, 4 H)	*6.92* (*dd*, ^3J, ^4J, 2 H)	*7.30* (*d*, *J* = 8.6, 4 H)
e	4.02		1.23–1.53	0.91	*4.17–4.26* (*m*, 2 H)	*7.43* (*d*, ^4J, 2 H)	*7.54* (*d*, *J* = 8.7, 4 H)
f	4.01		1.23–1.53	0.90			*7.64* (*d*, *J* = 8.6, 4 H)
g	4.01		1.23–1.53	0.89			
IIh	4.05	*1.78–1.88*	*1.24–1.53*	*0.89*	*2.96–3.08* (*m*, 2 H)	*6.67* (*d*, ^3J, 2 H)	*6.99* (*d*, *J* = 8.9, 4 H)
i	4.06				*3.23–3.32* (*m*, 4 H)	*6.89* (*dd*, ^3J, ^4J, 2 H)	*7.32* (*s*, 8 H)
					4.15–4.24 (*m*, 2 H)	*7.40* (*d*, ^4J, 2 H)	*8.17* (*d*, *J* = 8.9, 4 H)
IIj	*3.97*	*1.75–1.84*	*1.23–1.53*	*0.89*	*2.98–3.09* (*m*, 2 H)	*6.70* (*d*, ^3J, 2 H)	*6.95* (*d*, *J* = 9.0, 4 H)
k					*3.24–3.33* (*m*, 4 H)	*6.91* (*dd*, ^3J, ^4J, 2 H)	*7.14* (*d*, *J* = 9.0, 4 H)
					4.15–4.24 (*m*, 2 H)	*7.43* (*d*, ^4J, 2 H)	*7.40* (*d*, *J* = 8.7, 4 H)
							8.33 (*d*, *J* = 8.7, 4 H)
IIIa	*4.02*	*1.78–1.86*	1.32–1.53	0.92	*2.94–3.05* (*m*, 2 H)		*7.00* (*d*, *J* = 8.7, 4 H)
b			1.24–1.53	0.89	*3.14–3.24* (*m*, 2 H)	*7.48* (*s*, 2 H)	*7.32* (*d*, *J* = 8.6, 4 H)
					3.26–3.36 (*m*, 2 H)	*6.63–6.72* (*m*, 4 H)	*7.54* (*d*, *J* = 8.7, 4 H)
					4.15–4.25 (*m*, 2 H)		*7.65* (*d*, *J* = 8.6, 4 H)
c	4.06	1.79–1.88	1.24–1.53	0.89	2.93–3.04 (*m*, 2 H)		6.99 (*d*, *J* = 8.9, 4 H)
					3.11–3.22 (*m*, 2 H)	7.48 (*s*, 2 H)	7.34 (*s*, 8 H)
					3.24–3.38 (*m*, 2 H)	6.63–6.70 (*m*, 4 H)	8.17 (*d*, *J* = 8.9, 4 H)
					4.13–4.23 (*m*, 2 H)		
d	3.97	1.75–1.85	1.24–1.53	0.89	2.95–3.07 (*m*, 2 H)		6.95 (*d*, *J* = 9.0, 4 H)
					3.12–3.23 (*m*, 2 H)	7.46 (*s*, 2 H)	7.14 (*d*, *J* = 9.0, 4 H)
					3.27–3.39 (*m*, 2 H)	6.61–6.70 (*m*, 4 H)	7.43 (*d*, *J* = 8.7, 4 H)
					4.14–4.24 (*m*, 2 H)		8.34 (*d*, *J* = 8.7, 4 H)

Bis[4′-(hexyloxy)[1,1′-biphenyl]-4-yl] [2.2]Paracyclophane-4,16-dicarboxylate (= *Bis[4′-(hexyloxy)[1,1′-biphenyl]-4-yl] Tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene-5,11-dicarboxylate*; **IIb**): Yield 0.26 g (81%). ^{1}H-NMR: *Table*. MS: 801 (10, M^+), 531 (90), 131 (100). Anal. calc. for $C_{54}H_{56}O_6$: C 80.97, H 7.05; found: C 80.67, H 7.00.

Bis[4′-(heptyloxy)[1,1′-biphenyl]-4-yl] [2.2]Paracyclophane-4,16-dicarboxylate (= *Bis[4′-(heptyloxy)[1,1′-biphenyl]-4-yl] Tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene-5,11-dicarboxylate*; **IIc**): Yield 0.26 g (78%). ^{1}H-NMR: *Table*. MS: 829 (12, M^+), 545 (100), 131 (66). Anal. calc. for $C_{56}H_{60}O_6$: C 81.13, H 7.29; found: C 81.16, H 7.30.

Bis[4′-(octyloxy)[1,1′-biphenyl]-4-yl] [2.2]Paracyclophane-4,16-dicarboxylate (= *Bis[4′-(octyloxy)[1,1′-biphenyl]-4-yl] Tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene-5,11-dicarboxylate*; **IId**): Yield 0.28 g (81%). ^{1}H-NMR: *Table*. MS: 857 (8, M^+), 559 (100), 131 (66). Anal. calc. for $C_{58}H_{64}O_6$: C 81.27, H 7.53; found: C 81.20, H 7.59.

Bis[4′-(nonyloxy)[1,1′-biphenyl]-4-yl] [2.2]Paracyclophane-4,16-dicarboxylate (= *Bis[4′-(nonyloxy)[1,1′-biphenyl]-4-yl] Tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene-5,11-dicarboxylate*; **IIe**): Yield 0.29 g (82%). ^{1}H-NMR: *Table.* MS: 885 (5, M^+), 185 (74), 131 (100). Anal. calc. for $C_{60}H_{68}O_6$: C 81.41, H 7.74; found: C 81.37, H 7.89.

Bis[4′-(decyloxy)[1,1′-biphenyl]-4-yl] [2.2]Paracyclophane-4,16-dicarboxylate (= *Bis[4′-(decyloxy)[1,1′-biphenyl]-4-yl] Tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene-5,11-dicarboxylate*; **IIf**): Yield 0.30 g (82%). ^{1}H-NMR: *Table.* MS: 913 (2, M^+), 587 (94), 131 (100). Anal. calc. for $C_{62}H_{72}O_6$: C 81.54, H 7.95; found: C 81.67, H 7.91.

Bis[4′-(undecyloxy)[1,1′-biphenyl]-4-yl] [2.2]Paracyclophane-4,16-dicarboxylate (= *Bis[4′-(undecyloxy)[1,1′-biphenyl]-4-yl] Tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene-5,11-dicarboxylate*; **IIg**): Yield 0.32 g (85%). ^{1}H-NMR: *Table.* MS: 941 (10, M^+), 601 (100), 131 (58). Anal. calc. for $C_{64}H_{76}O_6$: C 81.66, H 8.14; found: C 81.50, H 8.27.

Bis{4-{[4-(decyloxy)benzoyl]oxy}phenyl} [2.2]Paracyclophane-4,16-dicarboxylate (= *Bis{4-{[4-(decyloxy)-benzoyl]oxy}phenyl} Tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene-5,11-dicarboxylate*; **IIh**): Yield 0.29 g (72%). ^{1}H-NMR: *Table.* MS: 1001 (8, M^+), 631 (54), 261 (100). Anal. calc. for $C_{64}H_{72}O_{10}$: C 76.77, H 7.25; found: C 76.69, H 7.33.

Bis{4-{[4-(tetradecyloxy)benzoyl]oxy}phenyl} [2.2]Paracyclophane-4,16-dicarboxylate (= *Bis{4-{[4-(tetradecyloxy)benzoyl]oxy}phenyl} Tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene-5,11-dicarboxylate*; **IIi**): Yield 0.35 g (79%). ^{1}H-NMR: *Table.* MS: 1112 (10, M^+), 690 (60), 317 (100). Anal. calc. for $C_{72}H_{88}O_{10}$: C 77.67, H 7.97; found: C 77.30, H 7.82.

Bis{4-{[4-(decyloxy)phenoxy]carbonyl}phenyl} [2.2]Paracyclophane-4,16-dicarboxylate (= *Bis{4-{[4-(decyloxy)phenoxy]carbonyl}phenyl} Tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene-5,11-dicarboxylate*; **IIj**): Yield 0.34 g (85%). ^{1}H-NMR: *Table.* MS: 1001 (5, M^+), 631 (28), 121 (100). Anal. calc. for $C_{64}H_{72}O_{10}$: C 76.77, H 7.25; found: C 76.81, H 7.32.

Bis{4-{[4-(tetradecyloxy)phenoxy]carbonyl}phenyl} [2.2]Paracyclophane-4,16-dicarboxylate (= *Bis{4-{[4-(tetradecyloxy)phenoxy]carbonyl}phenyl} Tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene-5,11-dicarboxylate*; **IIk**): Yield 0.36 g (81%). ^{1}H-NMR: *Table.* MS: 1112 (10, M^+), 687 (100), 121 (78). Anal. calc. for $C_{72}H_{88}O_{10}$: C 77.67, H 7.97; found: C 77.43, H 8.01.

Bis[4′-(hexyloxy)[1,1′-biphenyl]-4-yl] [2.2]Paracyclophane-4,7-dicarboxylate (= *Bis[4′-(hexyloxy)[1,1′-biphenyl]-4-yl] Tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene-5,15-dicarboxylate*; **IIIa**): Yield 0.28 g (87%). ^{1}H-NMR: *Table.* MS: 800 (10, M^+), 531 (100), 186 (28). Anal. calc. for $C_{54}H_{56}O_6$: C 80.97, H 7.05; found: C 80.95, H 6.75.

Bis[4′-(tetradecyloxy)[1,1′-biphenyl]-4-yl] [2.2]Paracyclophane-4,7-dicarboxylate (= *Bis[4′-(tetradecyloxy)[1,1′-biphenyl]-4-yl] Tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene-5,15-dicarboxylate*; **IIIb**): Yield 0.34 g (83%). ^{1}H-NMR: *Table.* MS: 1025 (8, M^+), 643 (100), 186 (48). Anal. calc. for $C_{70}H_{88}O_6$: C 82.00, H 8.65; found: C 82.17, H 8.69.

Bis{4-{[4-(tetradecyloxy)benzoyl]oxy}phenyl} [2.2]Paracyclophane-4,7-dicarboxylate (= *Bis{4-{[4-(tetradecyloxy)benzoyl]oxy}phenyl} Tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene-5,15-dicarboxylate*; **IIIc**): Yield 0.34 g (76%). ^{1}H-NMR: *Table.* MS: 1113 (5, M^+), 573 (50), 121 (100). Anal. calc. for $C_{72}H_{88}O_{10}$: C 77.67, H 7.97; found: C 77.70, H 7.99.

Bis{4-{[4-(tetradecyloxy)phenoxy]carbonyl}phenyl} [2.2]Paracyclophane-4,7-dicarboxylate (= *Bis{4-{[4-(tetradecyloxy)phenoxy]carbonyl}phenyl} Tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene-5,15-dicarboxylate*; **IIId**): Yield 0.32 g (72%). ^{1}H-NMR: *Table.* MS: 1113 (3, M^+), 317 (100). Anal. calc. for $C_{72}H_{88}O_{10}$: C 77.67, H 7.97; found: C 77.63, H 7.92.

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