Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Mesophase behaviour of 2,5-dibenzoyloxy-*p*-benzoquinone derivatives and tetrahydrobenzene tetraesters

Sibylle Berg[a]; Volker Krone[a]; Helmut Ringsdorf[a]; Udo Quotschalla[b]; Helmut Paulus[b]
[a] Institut für Organische Chemie, Universität Mainz, Mainz, F. R. Germany [b] Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Darmstadt, F. R. Germany

To cite this Article Berg, Sibylle , Krone, Volker , Ringsdorf, Helmut , Quotschalla, Udo and Paulus, Helmut(1991) 'Mesophase behaviour of 2,5-dibenzoyloxy-*p*-benzoquinone derivatives and tetrahydrobenzene tetraesters', Liquid Crystals, 9: 2, 151 — 163

To link to this Article: DOI: 10.1080/02678299108035495

URL: http://dx.doi.org/10.1080/02678299108035495

LIQUID CRYSTALS, 1991, VOL. 9, NO. 2, 151–163

Mesophase behaviour of 2,5-dibenzoyloxy-*p*-benzoquinone derivatives and tetrahydrobenzene tetraesters

by SIBYLLE BERG, VOLKER KRONE and HELMUT RINGSDORF
Institut für Organische Chemie, Universität Mainz,
J.-J.-Becher-Weg 18–20, D-6500 Mainz, F.R. Germany

UDO QUOTSCHALLA and HELMUT PAULUS
Institut für Physikalische Chemie, Technische Hochschule Darmstadt,
Petersenstrasse 20, D-6100 Darmstadt, F.R. Germany

(*Received 12 March 1990; accepted 17 August 1990*)

The synthesis of 2,5-dibenzoyloxy-*p*-benzoquinone derivatives, their products after reduction and tetraesters from tetrahydroxybenzene prepared from those products is described. Their phase behaviour was investigated by differential scanning calorimetry and polarizing microscopy and is discussed in terms of their detailed structure.

1. Introduction

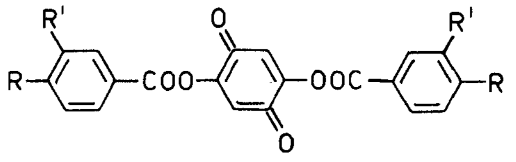
Calamitic liquid-crystalline benzoquinone derivatives have received little interest in the past [1], although they may have interesting properties; as possible agents for oxidations in the liquid-crystalline state, liquid-crystalline charge-transfer complexes, liquid-crystalline conductors [1] or transesterification reactions of benzoyloxyderivatives as active esters in the liquid-crystalline state. This work is concerned with the synthesis of 2,5-dibenzoyloxy-*p*-benzoquinones, for which only halogen substituted derivatives are known [1], their products after reduction and some closely related tetraesters of tetrahydroxybenzene. Relations between structure and the liquid-crystalline properties of the 2,5-dibenzoyloxy-*p*-benzoquinones is detailed. In addition, the phase behaviour of the tetraesters of tetrahydroxybenzene are discussed as model compounds for polyesters with laterally fixed mesogens in the main chain [2] and for polyesters with cross-shaped mesogens [3].

2. Synthesis and phase behaviour

The 2,5-di(*p*-alkoxybenzoyloxy)-*p*-benzoquinones **1–6** (see table 1 (*a*)) were synthesized from 2,5-dihydroxy-*p*-benzoquinone (Aldrich) with *p*-(*n*-alkoxy)- benzoic acid chlorides [4] (see scheme 1). Due to a disparity between the reaction conditions and the optimum pH for the carbonyl reaction, the esterification according to several common procedures such as with pyridine, DMF or DMAP failed. In addition, an azeotropic condensation of the diol with the corresponding acids did not succeed. The 2,5-dihydroxy-*p*-benzoquinone as a vinylog dicarboxylic acid ($pK_1 = 2{\cdot}73$ [5]) is stronger for instance than chloracetic acid. Thus, strong acid conditions are required. The esterification works in the presence of a moderate excess of the alkoxybenzoic acid chlorides at 100–120°C without any bases and with an average yield of *c.* 10–50 per cent. The hydrogen chloride resulting from the reaction must be driven out with a stream of dry nitrogen to avoid chlorination of the benzoquinone. It is advisable to follow the reaction progress by titration of the hydrochloric acid and to stop the reaction when 80 per cent of this has been released.

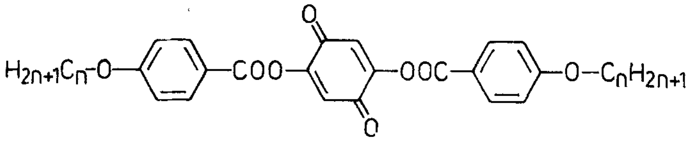
Table 1. Transition temperatures and enthalpies for the 2,5-dibenzoyloxy-*p*-benzoquinone derivatives.

(*a*)



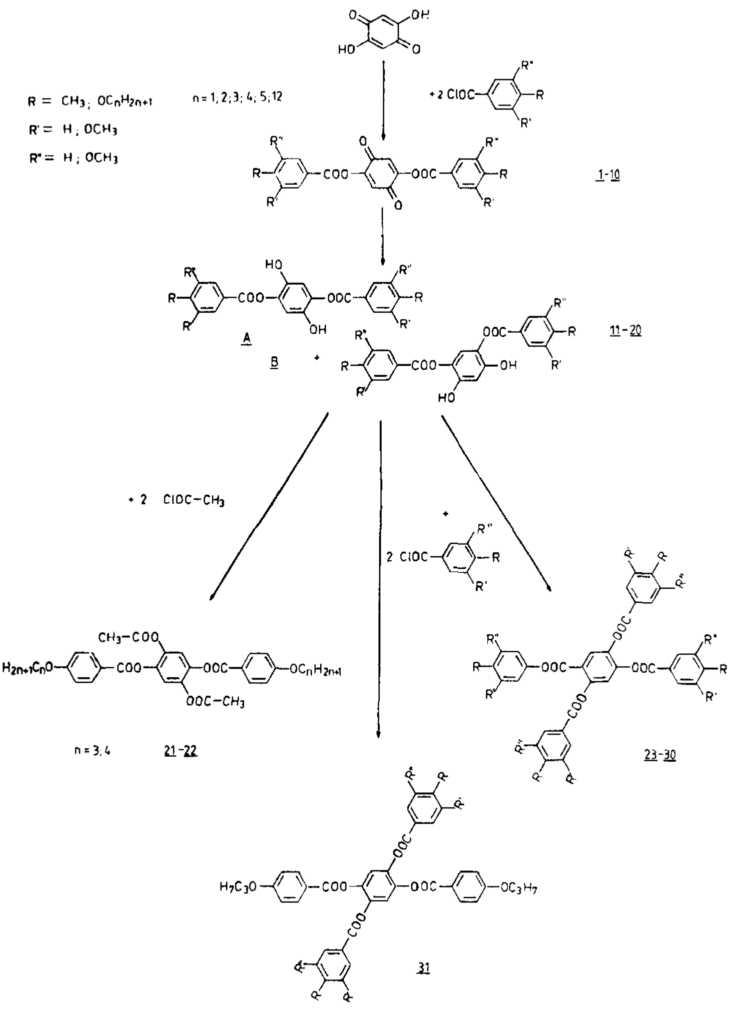
Quinone No.	*n*	Transition temperatures†/°C	Transition enthalpies†/kJ mol^{-1}		
			ΔH_{CLC}	ΔH_{SN}	ΔH_{NI}
1	1	C 215 N 252 I(d),	52		0·9–1·7
2	2	C 207 N 251 I(d),	61		1·8
3	3	C 155 N 217 I(d),	46		1·7
4	4	C 134 N 214 I(d),	39		2·5
5	5	C 123 N 191 I(d)	47		2·0
6	12	C_1 70 C_2 111 S 144 N 154 I	51	4·5	3·6

(*b*)



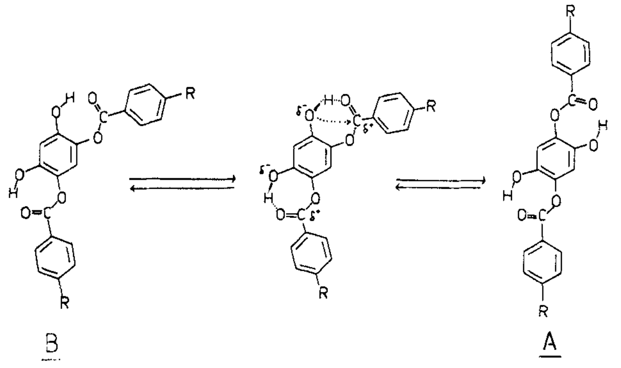
Quinone No.	R'	R	Transition temperatures†/°C	Transition enthalpies†/kJ mol^{-1}	
				ΔH_{CLC}	ΔH_{LC}
7	H	CH_3	C 268 I(d)	69	—
8	OCH_3	OCH_3	C 208 I(d)	69	—
9	H	$OCH_2CH(CH_3)C_2H_5$	C_1 117 C_2 121 CH 129 I	28	1·0–1·4

† Values determined by DSC; the scan rate was 20°C/min. At the clearing temperature all quinone derivatives are unstable and decompose, with instability increasing with increasing clearing temperature, C_1, C_2, crystalline; S, smectic; N, nematic; CH, cholesteric; ΔH_{CCL}, melting enthalpy; ΔH_{SN}, transition enthalpy between the smectic and nematic state; ΔH_{NI} or ΔH_{LCI}, enthalpy at the clearing temperature.



Scheme 1. Synthetic route to the tetraesters of tetrahydroxybenzene.

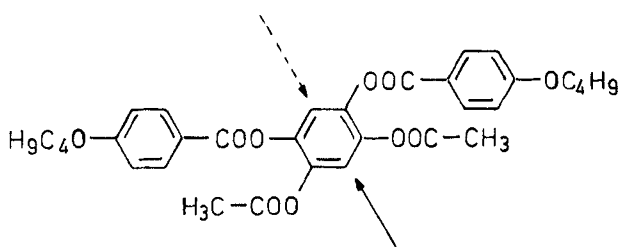
The same procedure was used to synthesize 2,5-di(*p*-methylbenzoyloxy)-*p*-benzoquinone **7** from methylbenzoic acid chloride, 2,5-bis(3,4-dimethoxybenzoyloxy)-*p*-benzoquinone **8** from 3,4-dimethoxybenzoic acid chloride and 2,5-di(*p*-((-)2-methyl)butoxybenzoyloxy)-*p*-benzoquinone **9** from *p*-((-)2-methylbutoxy)benzoic acid chloride (see table 1 (*b*)). The latter acid chloride was synthesized from (-)2-methylbutanol to prepare the tosylate derivative analogous to a common procedure [6], etherifying with *p*-hydroxybenzoic acid and chlorinating the product with phosphorus pentachloride. The esterification of 2,5-dihydroxy-*p*-benzoquinone with 2,6- and 2,4-dimethoxybenzoic acid chloride did not succeed, probably because of steric hindrance by the substituent in the ortho position of the acid chlorides. An esterification with 3,4,5-trimethoxybenzoic acid chloride succeeded (**10**), but an analytically-clean product could only be isolated after the reduction of the crude product to **20** (see table 4). All 2,5-dibenzoyloxy-*p*-benzoquinone derivatives are air and moisture sensitive. Their phase behaviour is summarized in table 1.



Scheme 2. Equilibrium of the reduction products of 2,5-di(*p*-alkoxybenzoyloxy)-*p*-benzoquinone derivatives caused by neighbouring effects.

The reduction of the 2,5-dibenzoyloxy-*p*-benzoquinone derivatives leads not only to the corresponding and expected 2,5-dibenzoyloxy-*p*-hydroquinone derivatives **11–20 A** but also to the transesterified 4,6-dibenzoyloxyresorcinol derivatives **B** (see scheme 1). The transesterification probably takes place during a two-step reduction with a semiquinone anion in the first step. In solution an additional transesterification mechanism should probably exist (see scheme 2) which keeps products **A** and **B** in equilibrium. This would explain why it was not possible to isolate pure products of either species until now. In thin layer chromatography only a fraction with a diffuse R_f value occurs. NMR spectroscopically determined compositions of the reduction products **11–20** are given in the experimental part (see table 4).

Interesting and, at the same time, not yet understood is that when, for instance, the mixture **13 A, B** is esterified under conditions given later, only the centrosymmetric products **21, 31** could be isolated in high yields (87 and 83 per cent). It appears that only the hydroquinone derivative **A** takes part in this further esterification reaction (see scheme 1) and is taken away from the equilibrium with the corresponding resorcine derivative (see scheme 2). The structure of the tetraesters **21, 22** were verified by ^{1}H NMR spectroscopy (see figure 1). Because of the centrosymmetry, both hydrogen atoms of the central benzene ring are identical (7·25 ppm). The NMR spectrum changes significantly when these esters come into contact with silica gel during a chromatographic purification. Instead of the spectrum of the pure 1,4-diacetyloxy-2,5-di(*p*-butoxybenzoyloxy)benzene **22** we observe a mixed spectrum of this component with 1,5-diacetyloxy-2,4-di(*p*-butoxybenzoyloxy)benzene after silica gel chromatography.



The 1,5-diacetyloxy-2,4-di(*p*-butoxybenzoyloxy)benzene now has two different hydrogen atoms at the central benzene ring which appear additionally at about 7·19 and 7·35 ppm.

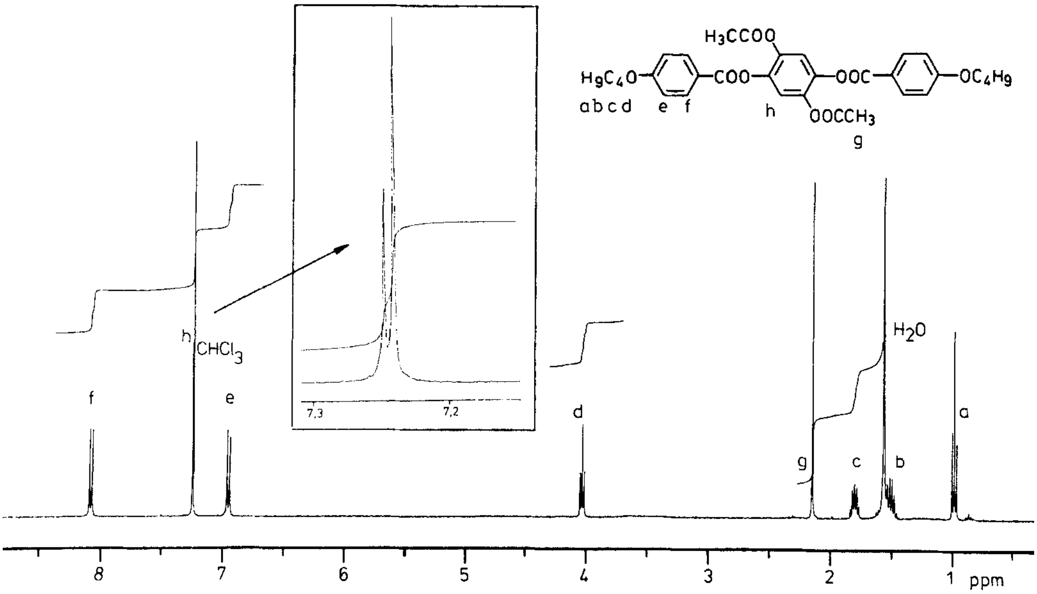


Figure 1. ^{1}H NMR spectrum of the tetraester **22**.

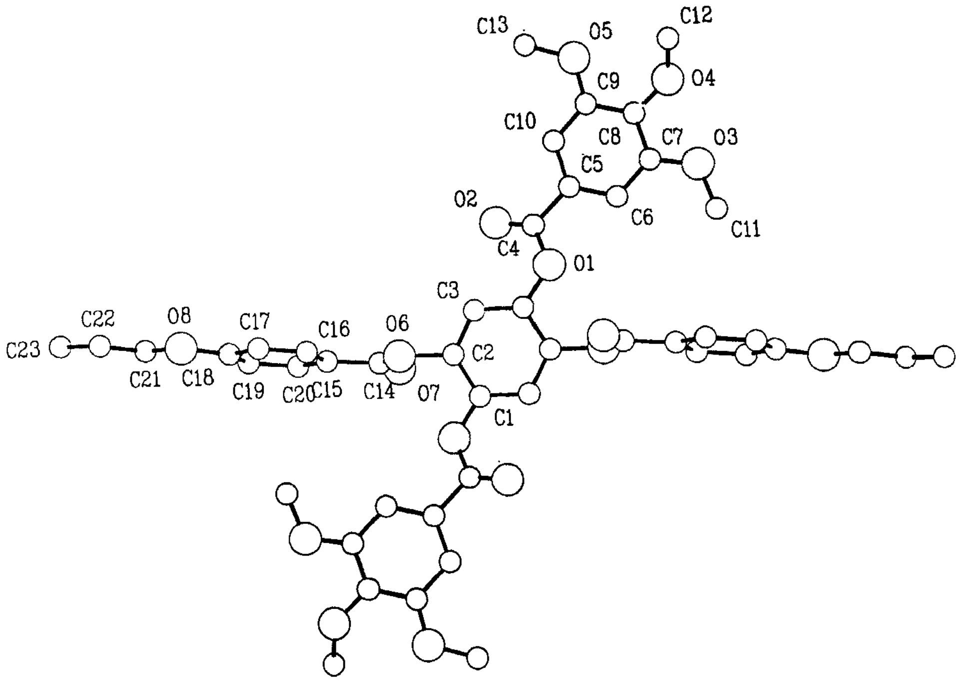
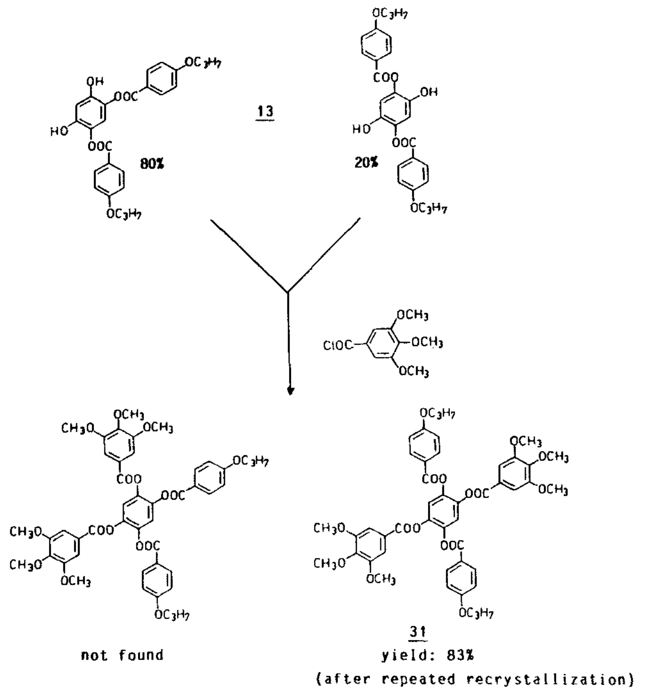


Figure 2. Structure of ester **31** resulting from X-ray analysis.



Scheme 3. Reaction of the mixture of the reduction products **13** to give the centrosymmetric ester **31**.

For the highly symmetric tetrabenzoic ester **31** it is not possible to clarify the absolute configuration by NMR spectroscopy. The structure was verified by X-ray analysis as shown in figure 2. The unexpected reaction process again occurs for the tetraester **31** in scheme 3, emphasizing the composition of the adducts and the high yield of the clean product. The same situation, that is, only the centrosymmetric hydroquinone derivatives react with acid chlorides, has been found in many polycondensation reactions [2, 3].

3. Discussion

The plot of the melting and clearing temperatures of the quinone derivatives **1–6** versus the length of the terminal groups (see figure 3) shows a phase behaviour typical for low molecular liquid crystals: the transition temperatures drop with increasing length of the terminal groups. At the same time, an odd–even effect is superimposed. Derivatives with short alkyloxy groups ($n = 1$–5) show only nematic phases with typical nematic schlieren textures and droplets at the clearing point; the derivative with long dodecyloxy groups exhibits an additional smectic phase of the S_C *or* S_A type. This suggests that the two oxygens at the central benzoquinone ring represent no major lateral disturbance. Otherwise we should expect only nematic phases [3, 7] also with long terminal groups. If the methoxy groups are exchanged by methyl groups (**7**) or, instead of the two methoxy substituents, four (**8**) terminal methoxy groups are introduced, the mesophase behaviour is lost completely (see table 1). The substitution

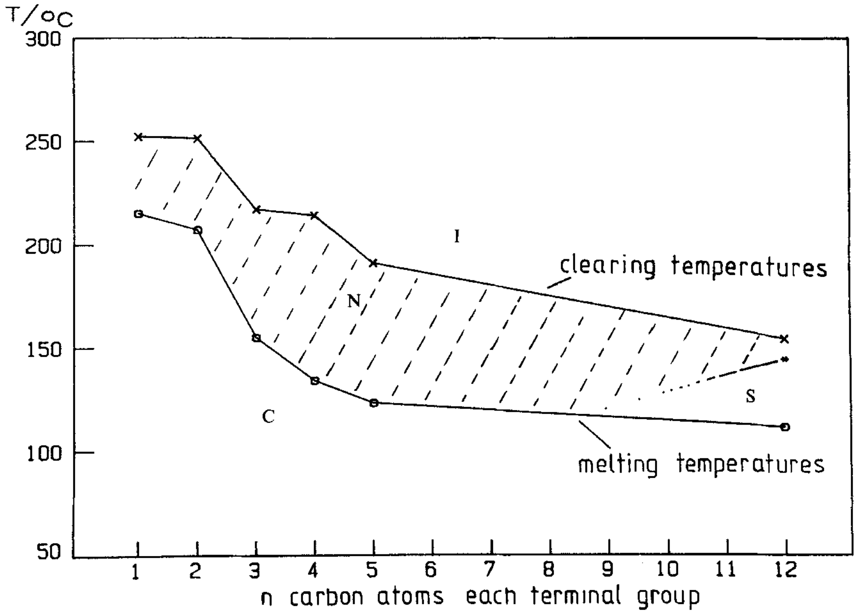


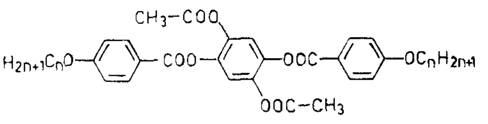
Figure 3. Terminal group length dependence of transition temperatures for the quinone derivatives **1–6**.

of *n*-butyloxy or *n*-pentyloxy groups respectively for (-)2-methylbutoxy groups (**9**) leads to a drastic decrease in the clearing temperature. A cholesteric mesophase with a blue–green selective reflection is then observed.

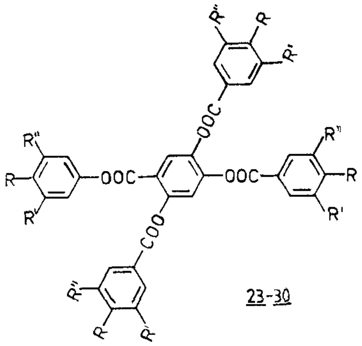
While the mixtures (containing **A** and **B**) of the reduction products (**11–20**) show no mesophase behaviour, some of the tetraesters of tetrahydroxybenzene (**21–31**) astonishingly do (see table 2). Indeed, the esters **21, 22** with two acetoxy groups as small lateral substituents do not possess any mesophases, not even monotropic ones. In contrast, the esters **25, 26, 27** with four large 4-(*n*-alkoxy)benzoyloxy groups show monotropic nematic phases with characteristic schlieren textures and droplets at the clearing point under the polarizing microscope. With increasing length of the terminal groups, the melting points decrease. The relation between the structure and the clearing temperatures cannot yet be given. The ester **26** has the highest nematic–isotropic transition temperature which is closest to the melting point. It seems possible that more favourable terminal groups could lead to enantiotropic behaviour. As far as the shape of the molecules (**23–31**) is concerned, they should be more cross-like than rod-like. That any additional branching by the introduction of (-)2-methylbutoxy groups (**28**) or additional methoxy groups at the aromatic rings (**29–31**) shows no mesomorphism points to a non-discotic behaviour of these esters. In the special case of ester **30**, a glass transition is easily reached by quenching.

In contrast to the low molecular weight tetraesters of the tetrahydroxybenzene discussed here, polyesters containing these cross-shaped mesogens show enantiotropic mesophases with much higher transition temperatures [3]. Moreover, the polymeric analogues of esters **21, 22**, where mesogenic cores have been bonded laterally via diacid dichlorides, form mesophases [2].

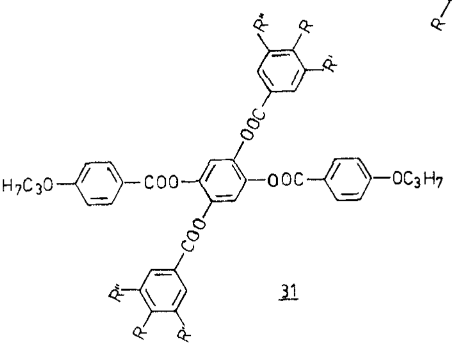
Table 2. Phase behaviour of the tetrabenzoic acid esters of 1,2,4,5-tetrahydroxybenzene.



21-22



23-30



31

Ester No.	Terminal groups R	R′	R″	Phase transition temperatures‡/°C	Transition enthalpies† /kJ mol^{-1}
21	($n=3$)			C† 181–182 I	
22	($n=4$)			C† 180 I	
23	$-CH_3$	-H	-H	C 239 I	54
24	$-OCH_3$	-H	-H	C 223 I	58
25	$-OC_3H_7$	-H	-H	C 160 I (N 115)†	45
26	$-OC_4H_9$	-H	-H	C 123 I (N 121)	72
27	$-OC_5H_{11}$	-H	-H	C 122 I (N 103)†	59
28	$-OCH_2\overset{CH_3}{\overset{\vert}{C}}HC_2H_5$	-H	-H	C 121 I	48
29	$-OCH_3$	$-OCH_3$	-H	C 249 I	96
30	$-OCH_3$	$-OCH_3$	$-OCH_3$	g 71 C 266 I	102
31	$-OCH_3$	$-OCH_3$	$-OCH_3$	C† 205 I	

† Values observed by polarization microscopy.

‡ Values determined by DSC; the scan rate was 10°C/min.

4. Experimental part

4.1. *2,5-Dibenzoyloxy-*p*-benzoquinone derivatives* (1–10)

0·1 mol of the appropriate benzoic acid chloride derivative [4, 8] was placed in a Schlenk-tube and mixed carefully with 0·04 mol of 2,5-dihydroxy-*p*-benoquinone (Aldrich). A gas-inlet with a strong stream of dried nitrogen was dipped into the heterogenous mixture. The tube was then plunged into a bath preheated to 120°C. In

Table 3. Yields, elemental analyses and synthetic conditions of the 2,5-dibenzoyloxy-*p*-benzoquinone derivatives (formula see scheme 1).

					Elemental analysis				Synthetic conditions	
				Yield in	Calculated		Found			
No.	R	R′	R″	%	%C	%H	%C	%H	Recrystallized in	Remarks
1	OCH_3	H	H	52	64·71	3·95	63·83	3·92	$CHCl_3$	
2	OC_2H_5	H	H	30	66·05	4·62	66·33	4·69	$CHCl_3$	5 hours 120°C
3	OC_3H_7	H	H	51	67·23	5·21	66·91	5·53	THF	
4	OC_4H_9	H	H	48	68·29	5·73	67·91	5·88	Acetone	†
5	OC_5H_{11}	H	H	54	69·22	6·20	68·88	6·30	Acetone	†
6	$OC_{12}H_{25}$	H	H	11	73·71	8·43	74·10	8·58	Cyclohexane	8 hours 120°C†
7	CH_3	H	H	43	70·21	4·28	69·17	4·19	THF	
8	OCH_3	OCH_3	OCH_3	32	61·54	4·30	61·77	4·33	$CHCl_3$/acetone	‡
9	$OCH_2\overset{CH_3}{\overset{\vert}{C}}HC_2H_5$	H	H	16	69·22	6·20	68·81	6·14	*n*-Hexane	†
10	OCH_3	OCH_3	OCH_3	23	59·09	4·58	58·05	4·60	$CHCl_3$/*n*-hexane	§, ‖

† Washing only with ether, in the case of **6** only with ligroin.

‡ Stirring for 9 hours at 120°C and 2 hours at 180°C.

§ Stirring for 4 hours at 130°C.

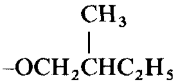
‖ An analytically clean product could not be isolated after this stage.

the normal case, the reaction mixture was stirred for 2 hours under these conditions (deviations from this are noted in table 3). The reaction progress can be followed via the expelled hydrogen chloride by titration against potassium hydroxide. At a turnover of 80 per cent the reaction was stopped to avoid higher amounts of by-products. It should be noted that small amounts of other components of the reaction mixture were also expelled but this hardly influences the reaction. After cooling to room temperature, the mixture was washed a few times with dry ether, cool acetone and in the case of **1**, **2** with chloroform (deviations from these conditions are noted in table 3). The products are recrystallized from solvents listed in table 3.

4.2. *Mixtures of 2,5-dibenzoyloxyhydroquinone A and 4,6-dibenzoyloxyresorcinol B derivatives* (**11–20**)

A concentrated aqueous solution of 20 g of sodium dithionite was shaken with a concentrated solution of 10 g of the appropriate 2,5-dibenzoyloxybenzoquinone derivative in THF. The organic phase quickly lost its colour. The aqueous phase was separated and the reduction products were precipitated by adding pure water to the organic phase. The white, crystalline precipitate was recrystallized twice from acetone. It proved favourable to use water containing acetone for derivatives with short terminal groups. Derivative **16** was recrystallized from a mixture of THF and hexane.

Table 4. Yields, compositions and elemental analyses of the reduction products **11–20**.

				Yield in	Composition†		Elemental analysis		
No.	R	R′	R″	%	%A	%B		%C	%H
11	$-OCH_3$	-H	-H	61	20	80	Calc.	64·39	4·42
							Found	64·10	4·43
12	$-OC_2H_5$	-H	-H	74	20	80	Calc.	65·75	5·06
							Found	65·88	5·20
13	$-OC_3H_7$	-H	-H	69	20	80	Calc.	66·94	5·61
							Found	66·40	5·66
14	$-OC_4H_9$	-H	-H	86	20	80	Calc.	68·01	6·11
					60‡	40‡	Found	67·56	5·87
15	$-OC_5H_{11}$	-H	-H	42	20	80	Calc.	68·96	6·56
							Found	68·45	6·43
16	$-OC_{12}H_{25}$	-H	-H	59	15	85	Calc.	73·50	8·69
							Found	72·72	8·66
17	$-CH_3$	-H	-H	24	/	/	Calc.	69·84	4·79
							Found	69·18	5·28
18	$-OCH_3$	$-OCH_3$	-H	41	20	80	Calc.	61·28	4·71
							Found	61·91	5·20
19	 $-OCH_2\overset{\overset{CH_3}{\vert}}{C}HC_2H_5$	-H	-H	46	85	15	Calc.	68·93	6·50
							Found	67·94	6·42
20	$-OCH_3$	$-OCH_3$	$-OCH_3$	26	15	85	Calc.	58·87	4·94
							Found	59·06	5·16

† The compositions of the mixtures were determined by NMR spectroscopic.

‡ The composition deviates when the reduction is realized in the absence of any moisture in cooled THF in the presence of a Pd/C catalyst.

Table 5. Yields, melting temperatures and elemental analyses of the tetraesters **21–31**.

R	R′	R″	Phase transition temperatures/°C‡	Yield in %	Elemental analysis		
						%C	%C
See formula table 2			C 181–182 I†	87	Calc.	65·45	5·49
					Found	65·29	5·50
See formula table 2			C 180 I†	53	Calc.	66·43	5·92
					Found	66·23	5·95
$-CH_3$	-H	-H	C 239 I	99	Calc.	74·26	4·92
					Found	73·94	5·01
$-OCH_3$	-H	-H	C 223 I		Calc.	67·25	4·45
					Found	66·91	4·56
$-OC_3H_7$	-H	-H	C 160 I (*N* 115)†	58	Calc.	69·86	5·86
					Found	69·44	5·90
$-OC_4H_9$	-H	-H	C 123 I (*N* 121)	53	Calc.	70·91	6·43
					Found	70·40	6·07
$-OC_5H_{11}$	-H	-H	C 122 I (*N* 103)†	90	Calc.	71·82	6·92
					Found	71·33	6·89
$-OCH_2\overset{\overset{CH_3}{\mid}}{C}HC_2H_5$	-H	-H	C 121 I	71	Calc.	71·82	6·92
					Found	71·63	6·86
$-OCH_3$	$-OCH_3$	-H	C 249 I	60	Calc.	62·84	5·27
					Found	62·69	4·85
$-OCH_3$	$-OCH_3$	$-OCH_3$	g 71 C 266 I	80	Calc.	59·61	5·87
					Found	59·43	5·01
See formula table 2			C* 205 I§	83	Calc.	64·63	5·42
					Found	64·28	5·40

† Values observed by polarization microscopy.

‡ Values determined by DSC, the scan rate was 10°C/min.

§ Quenching leads to a glass transition instead of crystallization.

4.3. *Tetraester derivatives of 1,2,4,5-tetrahydroxybenzene* (21–31)

0·3 g of the appropriate mixture (**11–20**) of 2,5-di(*p*-alkoxybenzoyloxy)-hydroquinone and 4,6-di(*p*-alkoxybenzoyloxy)resorcinol was dissolved in 5 ml of dry pyridine and treated with a 2·2-fold amount of the desired acid chloride under stirring. After stirring overnight, the tetraesters **23–30** were isolated by evaporating the pyridine in vacuum, dissolving the sample in chloroform and separating over a short silica gel column. The esters were recrystalized several times from acetone until the tetraesters were chromatographically pure. The tetraesters **21, 22** and **31** were poured into cold water. The crystalline, white precipitate was removed and washed alternately with cold dilute hydrochloric acid and sodium hydrogen carbonate several times. Afterwards, the esters were neutralized with water and recrystallized from ethanol.

4.4. *Characterization methods*

All of the quinones prepared, mixtures of the reduction products and tetraesters, were additionally characterized by ^1H NMR spectra. Furthermore, IR, ^{13}C NMR spectra and special experiments for selected members of each group of esters were investigated to confirm the structure. Examples of these investigations are now given. The thermal behaviour of the compounds was examined by a DSC-2C differential scanning calorimeter (Perkin–Elmer). The peak maxima were taken as transition temperatures. The textures were observed with a POL-BK II polarizing microscope (Leitz) equipped with a FP 5 hot stage (Mettler). The X-ray reflections were collected on a four cycle diffractometer (Stoe Stady). The solution of the structure was made with help of the programmes SHELX76, and SHELX86, using direct methods. The structure was plotted with the use of PLUTO, a special package for plotting X-ray data.

IR (KBr) of **9**: 1750 cm^{-1} (C=O, ester); 1690 cm^{-1} (C=O, quinone); 1640 cm^{-1} (C=C, quinone); 1610 cm^{-1}, 1585 cm^{-1} and 1520 cm^{-1} (C=C, arom.).

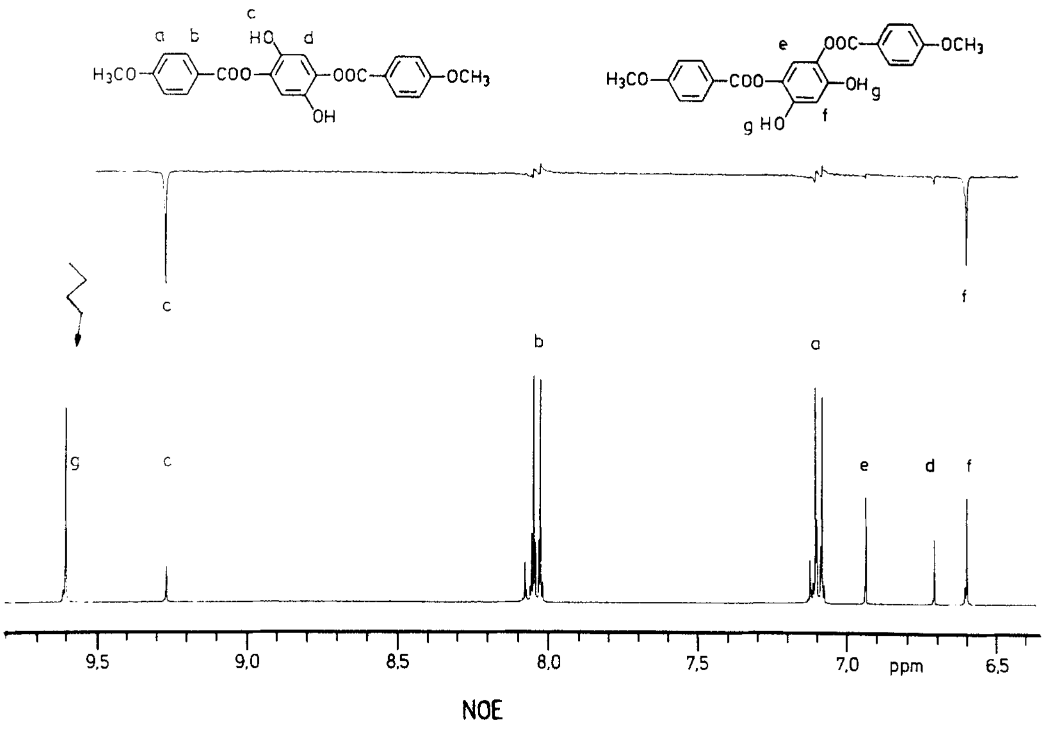
^{1}H NMR of **9** (400 MHz in $CDCl_3$): (in ppm) = 8·05 (d, 4 H, arom.), 6·95 (d, 4 H, arom.), 6·81 (s, 2 H, quinone), 3·85 (m, 4 H, OCH_2), 1·89 (m, 2 H, CH), 1·45 (m, 4 H, CH_2–CH_3), 1·03 (d, 6 H, CH–CH_3), 0·95 (t, 6 H, CH_2–CH_3).

^{13}C NMR of **1** ($CDCl_3$): (in ppm) = 180·3 (C=O, quinone), 164·7 (C–O, arom.), 162·9 (COO), 152·7 (C–O, quinone), 132·9 (CH=C–COO, arom.), 114·1 (CH=C–O, arom.), 122·1 and 119·9 (C–COO, arom. and CH, quinone), 55·6 (OCH_3).

IR (KBr) of **19**: 3440 cm^{-1} (OH); 1725 cm^{-1} (C=O, ester); 1610 cm^{-1}, 1590 cm^{-1} (C=C, arom.).

^{1}H NMR of **14** (400 MHz in acetone-d_6): (in ppm) = 8·51 and 8·24 (ss, 2H, OH), 8·1 (m, 4 H, arom.), 7·08 (m, 4 H, arom.), 6·67, 6·83 and 6·98 (sss, 2 H, CH in central rings, see later, 4·1 (m, 4 H, OCH_2), 1·78 and 1·5 (mm, 8 H CH_2), 0·98 (m, 6 H, CH_3).

^{1}H NMR of **11** with a NOE differential spectrum (400 MHz in acetone-d_6).



^{1}H NMR of **31** (400 MHz in $CDCl_3$): (in ppm) = 8·01 (d, 4 H, arom. in –C_6H_4–O–C_3H_7), 7·52 (s, 2 H, CH central arom. ring), 7·28 (s, 4 H, arom. in –$C_6H_2(OCH_3)_3$), 6·86 (d, 4 H, arom. in –C_6H_4–O–C_3H_7), 3·95 (t, 4 H, OCH_2), 3·87 (s, 6 H, p-OCH_3), 3·73 (s, 12, m-OCH_3), 1·8 (m, 4 H, CH_2-CH_3), 1·02 (t, 6 H, CH_2CH_3).

References

[1] Sevostayanov, V. P., Zarov, Y. M., and Gnilomedova, T. I., 1976, *Zh. Org. Khim.*, **12,** 2400; 1977, *Chem. Abstr.*, **86,** 139567j.

[2] Krone, V., Ringsdorf, H., Ebert, M., Hirschmann, H., and Wendorff, J. H., 1991, *Liq. Crystals*, **9,** 165.

[3] Krone, V., Ringsdorf, H., Ebert, M., Hirschmann, H., and Wendorff, J. H., 1991, *Liq. Crystals*, **9,** 195.

[4] Pierce, J. S., Salsbury, J. M., and Fredericksen, J. M., 1942, *J. Am. Chem. Soc.*, **64,** 1961.

[5] Schwarzenbach, G., and Suter, H., 1941, *Helv. chim. Acta,* **24,** 617.

[6] 1955, *Organic Synthesis*, Vol. 3 (Wiley), p. 366.

[7] Weißflog, W., and Demus, D., 1983, *Cryst. Res. Technol.*, **18,** 21; 1984, *Ibid.*, **19,** 271.

[8] Bennett, G. M., and Jones, B., 1939, *J. chem. Soc.*, p. 420.