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Liquid-Crystalline Behavior and Constitutional Analysis of 1,5-Dimethoxynaphthalene Dicarboxylic Acid Derivatives

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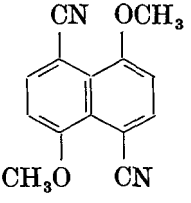
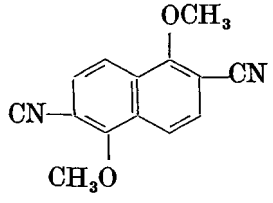
Summary—G. Lohaus[1] obtained a compound from 1,5-dimethoxynaphthalene and chlorosulphonyl isocyanate. On the basis of its reactivity alone and by spectroscopic examination it was not possible to determine whether compound (a) or compound (b) was concerned (the substance showed no mesomorphic behavior).

(a)



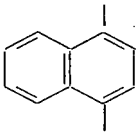
(b)



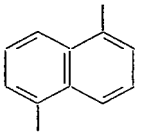
It was known from the literature[2] (Wiegand) that disubstituted naphthalenes (1,4-, 1,5 and 2,6-derivatives) as a function of their constitution can form liquid-crystalline phases with varying mesomorphic ranges. An attempt was therefore made, starting on the one hand from the dicarbonic acid obtained by saponification of the dinitrile and on the other, by means of an independent synthesis, to obtain dicarboxylic acid esters of types (a) or (b) which would form liquid-crystalline phases and to classify the liquid crystals in terms of the known liquid-crystalline 1,4-, 1,5- and 2,6-substituted compounds with the aim of drawing conclusions therefrom as to the constitution of the acids, resp. the primary product, the dinitrile. So it could be proved that the dinitrile is present in the (a) form.

Introduction

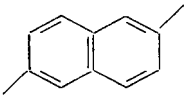
It is known regarding several derivatives of the disubstituted naphthalene nucleus that a very distinct dependence exists between the position of the substituents and the tendency to form liquid-crystalline phases. Typical bifunctional derivatives of naphthalene for which liquid-crystalline phases exist are the following dianisal-diaminonaphthalenes:



1,4- (resp. 5,8-)



1,5- (resp. 4,8-)



2,6- (resp. 3,7-)

With identical substituents, the generally valid rule was found that the 2,6-derivatives have a much greater tendency towards liquid-crystalline order, as demonstrated by the following example:

TABLE 1 Physical Constants of Dianisal-diaminonaphthalene

Isomer	1,4-	1,5-	2,6-
Range of the liquid-crystalline phase	79 °C	86 °C	167 °C
Clarification point	263 °C	282 °C	356 °C
Melting point	184 °C	196 °C	189 °C

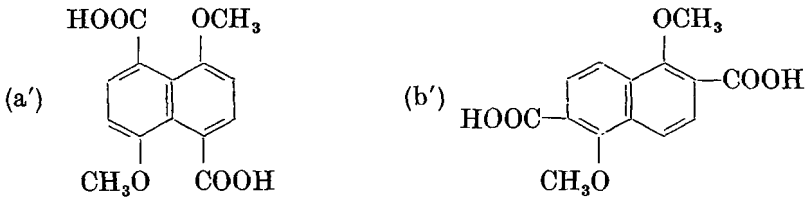
In another case, studied by Gray and Jones,[3] the 4- and the 5-*n*-alkoxy-1-naphthoic acids and the 7-*n*-alkoxy-2-naphthoic acids exhibit no mesophases whereas the 6-*n*-alkoxy-2-naphthoic acids are mesomorphic.

It was expected that two identically substituted derivatives of (a) and (b) with relatively long substituents in the positions of CN-groups would exhibit liquid-crystalline behavior and that the one with the broader mesophase and higher clarification point could be assigned to constitution (b). The method of synthesis

and IR spectra were used to support the findings, which resulted in assignment of the CH-overtone bands to the essentially equal substitution types (a) and (b) see Fig. 1. Such a distinction is not possible *a priori*; both forms contain 2 neighboring CH-groups which in each case are separated by 3 C-atoms. The same applies in principle to the NMR spectra which show the two *ortho*-coupled pairs of aromatic protons in the original dinitrile but which do not allow a distinction between structure (a) or (b).

Method of Synthesis (general)

The first step to obtain elongated molecules from type (a) and (b) was to start with two different carboxylic acids, corresponding to (a') and (b')



In one case we started with the nitrile (a) *or* (b), made by Lohaus, and saponified to the free acid. In the other case we proceeded as described by Hemmelmayr.[4] Using 1,5-dihydroxynaphthalene, one obtains with potassium hydrogen carbonate (see later) a dicarboxylic acid which can be transformed into its dimethyl ether. The only important fact is that these acids, synthesized by different methods, represent different compounds having the same elementary composition. This has been proved by IR analysis and by comparison of the melting points. Fig. 2 shows the IR spectrum of the " Lohaus acid ", Fig. 3 that of the free and Fig. 4 that of the methoxy-substituted " Hemmelmayr acid ". The constitutional formulas given in these figures correspond to the final result of this investigation.

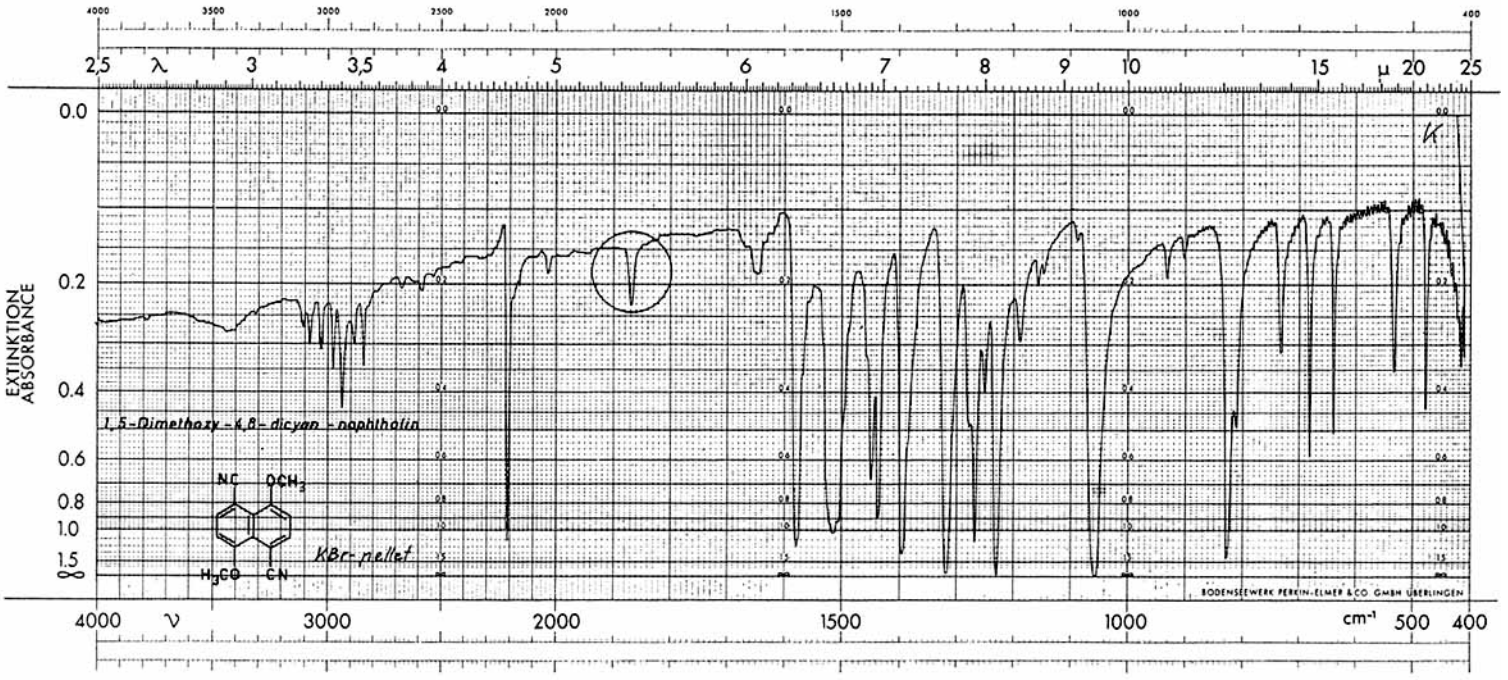


Figure 1

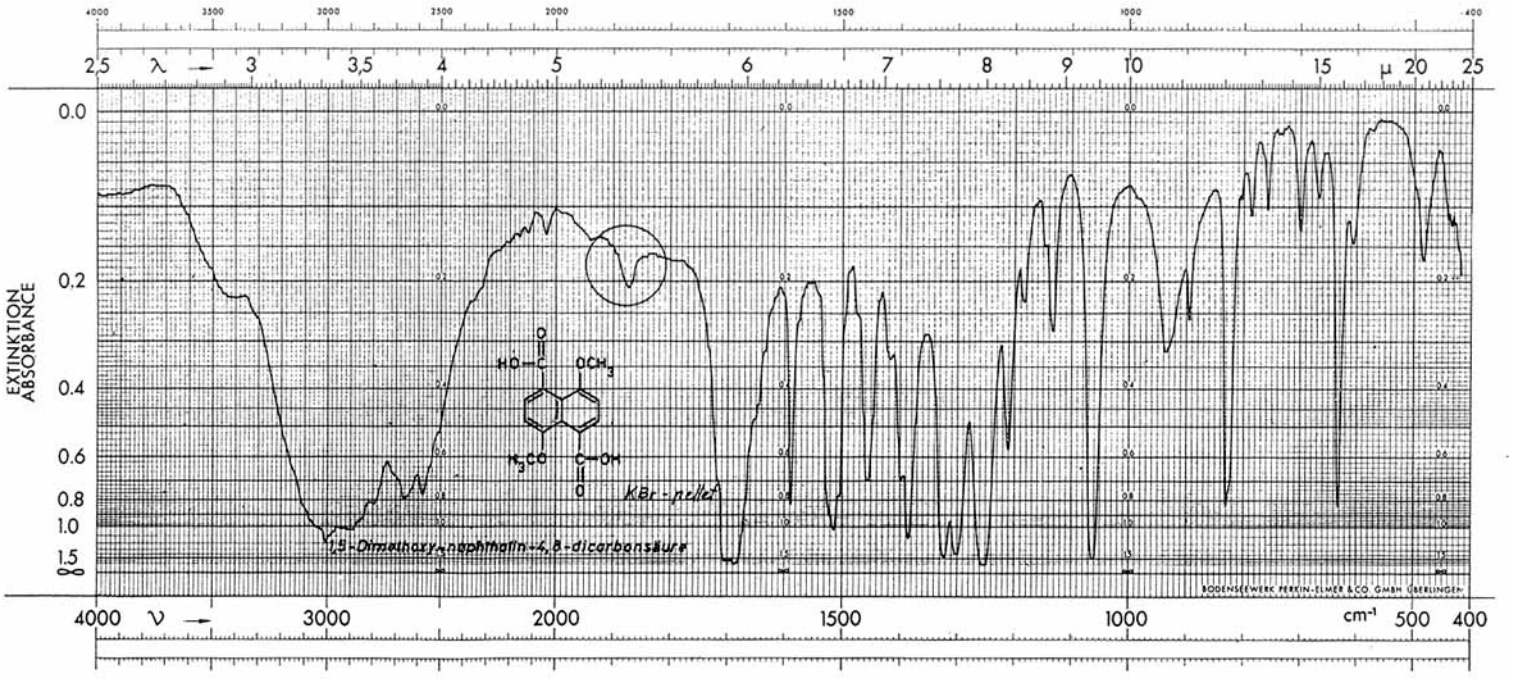


Figure 2

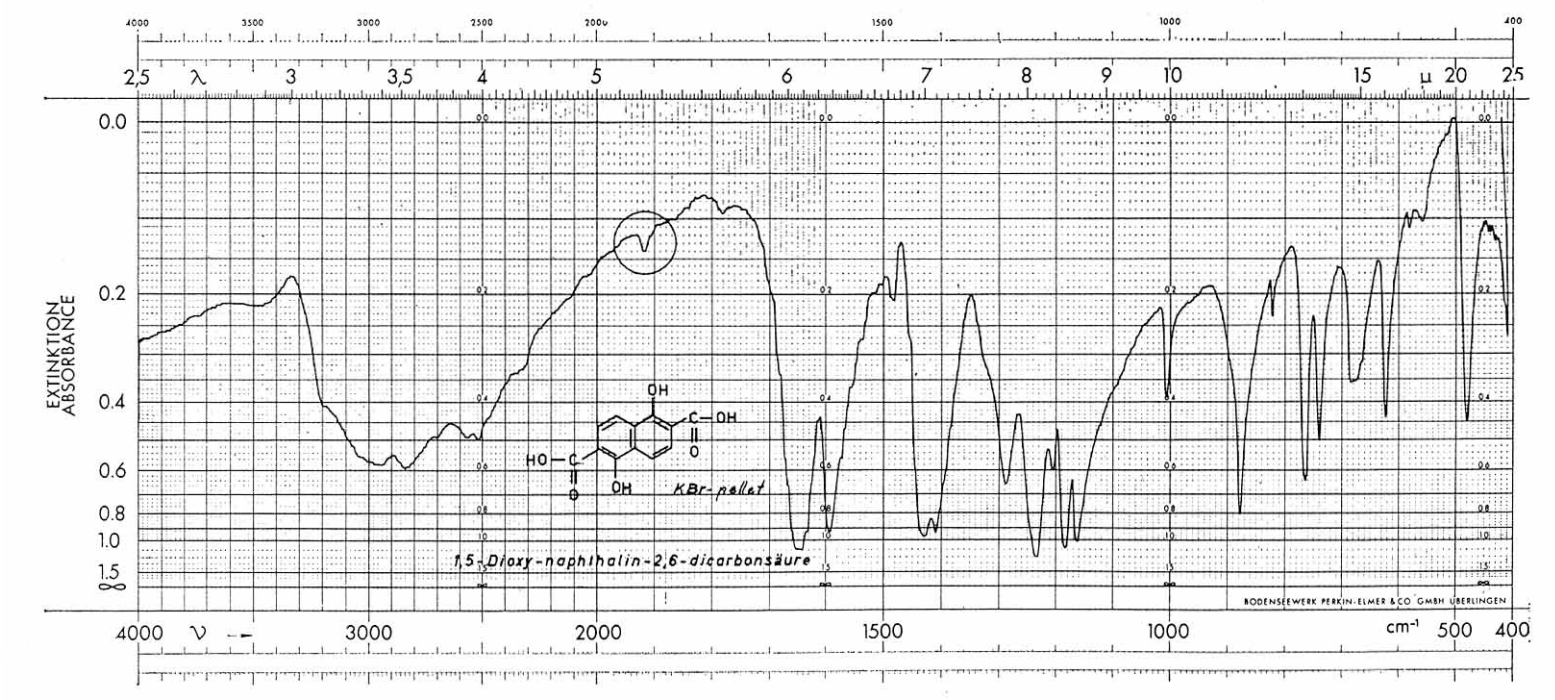


Figure 3

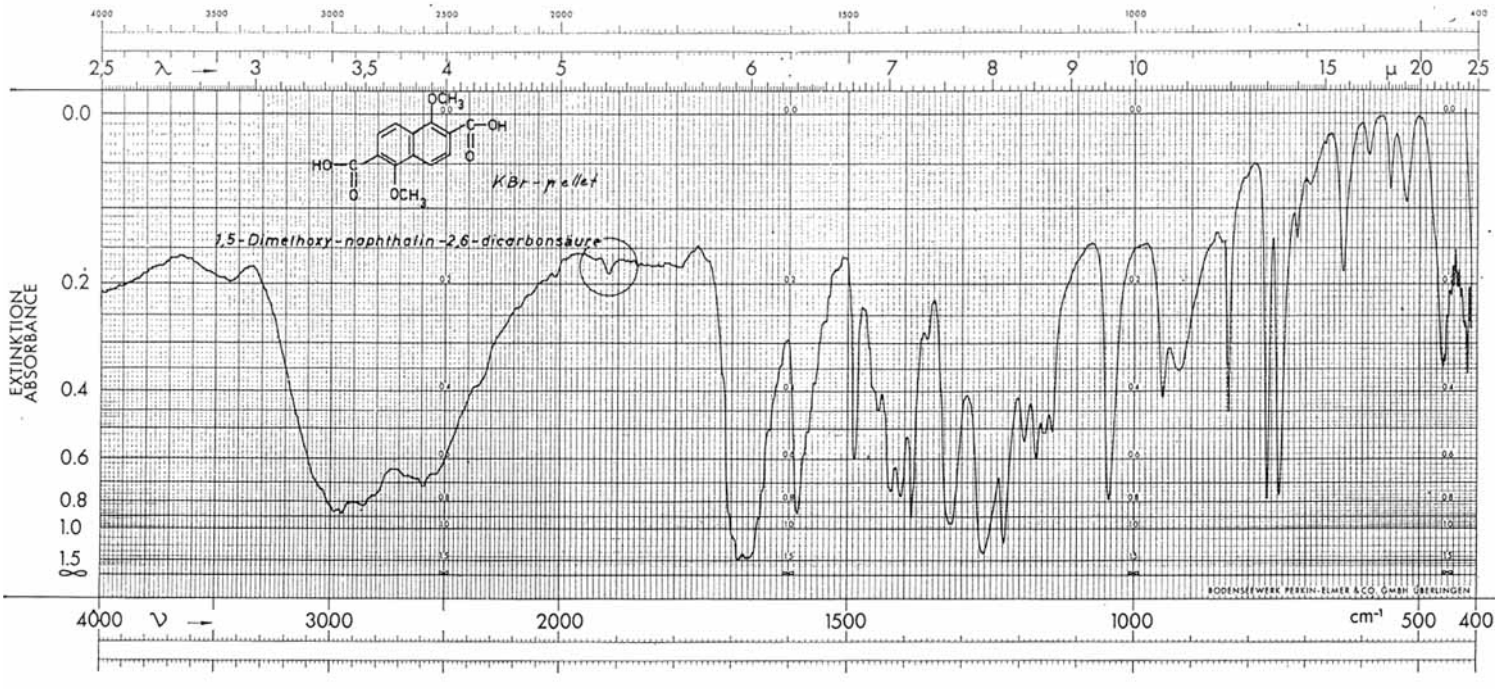
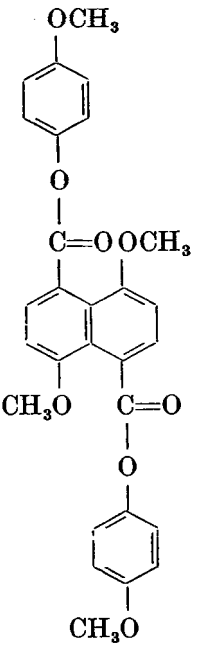


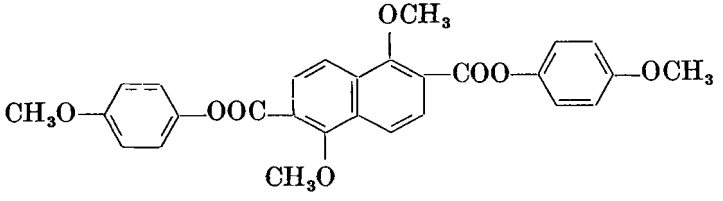
Figure 4

As we knew from our previous work that the 4′-*n*-alkyl-hydroquinone esters of terephthalic acid are liquid-crystalline, we tried to obtain the compounds (a″) and (b″) from (a′) and (b′):

(a″)

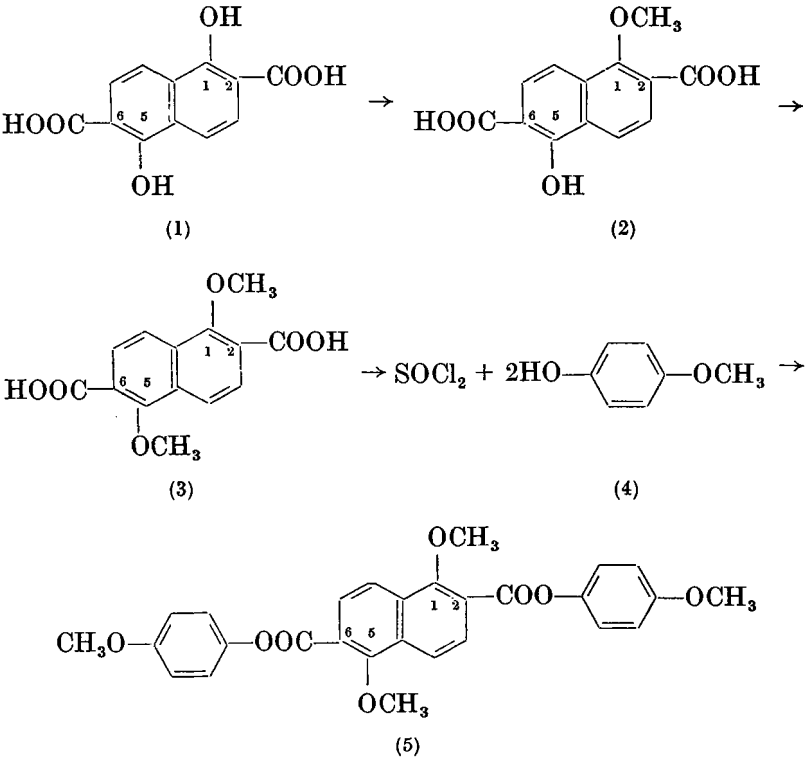


(b″)



The diester of the Lohaus acid was prepared by reaction with thionyl chloride to give the acid chloride. Then, by reaction with hydroquinone monomethyl ether the methoxy hydroquinone ester could be obtained (for details of synthesis see later, and for characteristics of the substance see Table 2). As expected, the compound exhibited a nematic phase.

Another ester, presumably the 2,6-diester was synthesized in the following way, starting with the acid of Hemmelmayr:



This ester (5) showed with respect to the former one an enhanced liquid-crystalline behavior (see Table 2), having the higher clarification point and the broader mesophase (Table 2). Details of synthesis are given in the appendix; for characteristics of the substance see Table 2.

Discussion

The two dimethoxynaphthalene dicarboxylic acids clearly have different constitutions (IR spectra Nos. 2 and 4). Spectrum No. 2 (carboxylic acid from nitrile) reveals an overtone band at 1870

cm^{-1} which can be recognized at the same point in the nitrile spectrum (Fig. 1). The other dimethoxy dicarboxylic acid (spectrum Fig. 4) has a constitution that is considerably different from Fig. 2, and the substitution type shown by Fig. 4 is exactly the same as that represented by Fig. 3, the latter being the parent substance of the methoxy-compound.

If it is assumed that the latter substance has the formula stated by Hemmelmayr, then the substitution type (a) can be considered as confirmed for our compound. Otherwise and independently the proof of constitution regarding mesomorphic behavior is given as follows. Table 2 shows the melting points and the clarification points of the two esters.

TABLE 2 Physical Constants of the Isomeric Esters

	(a) Ester derived from Lohaus' compound	(b) Ester derived from Hemmelmayr's synthesis
Melting point	235–236 °C	218,5 °C
Clarification point	275 °C	286–287 °C
Existence of the mesophase	40 °C	68 °C

If we assume that the higher clarification point and the broader mesophase, i.e. the higher mesomorphic stability correspond to the longer molecule, it follows that the compound (b) (Table 2) is the 1,5,2,6-diester, synthesized from the acid of Hemmelmayr. This statement also can be taken as a proof for the constitution given by this author. The ester derived from the nitrile of Lohaus has the 1,5,4,8-constitution, corresponding to the lower clarification point (275 °C as against 286–287 °C) and the smaller range of 40 °C compared with 68 °C for the liquid crystalline phase of the 1,5,2,6-compound (Table 2, (a)). However, these differences are not as marked as in the case of the two-fold substituted naphthalene derivatives. However, this levelling effect is understandable and follows from the increased breath of the tetrasubstituted molecules.

In conclusion it should be noted that the present case is the first in which liquid-crystalline melting compounds of the four-fold substituted naphthalene nucleus have been obtained. A main goal of our work in the field of liquid crystals is to synthesize systematically such mesomorphic compounds and to test compounds for specific solvent action suited for isomer separation in gas-liquid chromatography.

APPENDIX

Synthesis in Detail

Synthesis of the diester (a'') or (b'') from the dicarboxylic acid

9,1 g (1,5-)-dimethoxynaphthalene-(x,x')-dicarboxylic acid (0.033 mol) with 50 ml thionyl chloride and 0.5 ml dimethyl formamide are heated for 2 hours on a water bath, the $SOCl_2$ is distilled off *in vacuo* and the remaining dicarboxylic acid chloride dispersed in 250 ml dry pryidine. A solution of 20 g hydroquinone-monomethyl ether (about 0.15 mol) in 100 ml dry pyridine is added dropwise with stirring and subsequently stirred for 48 hours at room temperature. The diester is formed as a yellowish-white precipitate which is filtered, washed with pyridine, water and ethanol and dried at 120 °C. In this way approximately 8 g crude ester are obtained. After recrystallizing twice from decahydronaphthalene, about 4 g of the white, crystalline diester of the Lohaus acid are obtained (melting point 235–236 °C, clarification point 275 °C, nematic mesophase). Melting point of the Lohaus acid is 302–304 °C.

Analysis

calculated	*found*
68.85% C	68.7% C
4.95% H	5.0% H
26.2% O	26.4% O
100.0%	100.1%

Synthesis of 1,5-*dihydroxynaphthalene*-2,6-*dicarboxylic acid*

For the synthesis and constitution of this dihydroxynaphthalene-dicarboxylic acid, cf. F. Hemmelmayr.[4]

The yellow recrystallized 1,5-dihydroxynaphthalene-2,6-dicarboxylic acid which is obtained in high yield from 1,5-dihydroxynaphthalene and $KHCO_3$, decomposes, without melting, above 320 °C.

Analysis

calculated	*found*
58.06% C	58.0% C
3.25% H	3.3% H
38.7% O	38.5% O
100.0%	99.8%

1-*hydroxy*-5-*methoxynaphthalene*-2,6-*dicarboxylic acid*

Owing to the low solubility of the Na-salt of 1,5-dihydroxy naphthalene-2,6-dicarboxylic acid, methylation was carried out in a solution or N-methylpyrrolidone, the monomethyl ether derivative at first being obtained.

75 g 1,5-dihydroxynaphthalene-2,6-dicarboxylic acid are dissolved in 900 ml N-methylpyrrolidone and 600 ml 2 N NaOH. To the solution are added simultaneously dropwise (in 60–70 minutes) 400 ml 2 N NaOH and 150 ml dimethyl sulphate at 46–48 °C, stirring continued for 1 hour at 50–55 °C and the mixture then heated for a further 1–2 hours to 60–70 °C in order to destroy the excess dimethyl sulphate. After cooling, the mixture is acidified with dilute hydrochloric acid, hydroxy-methoxy-naphthalene-dicarboxylic acid dimethyl ester being formed as a yellowish precipitate. The ester is saponified with potassium hydroxide solution and the dicarboxylic acid is precipitated with HCl, filtered off, washed with water and dried (yield of crude acid 51 g).

After recrystallization from ca. 12 l glacial acetic acid, 23 g

1-hydroxy-5-methoxynapththalene-2,6-dicarboxylic acid in the form of yellow crystals is obtained (melting point 258–261 °C).

Analysis

calculated	*found*
59.5% C	59.4% C
3.84% H	3.9% H
36.65% O	36.8% O
100.0%	100.1%

1,5-*dimethoxynaphthalene*-2,6-*dicarboxylic acid*

This compound is prepared by the continued methylation of hydroxymethoxynaphthalene dicarboxylic acid, by dissolving 20 g of the dicarboxylic acid in 250 ml 2 N NaOH solution and at the same time adding dropwise an additional 250 ml of 2N NaOH solution and 100 ml dimethyl sulphate at 40–50 °C, in the course of which the yellowish-white dimethyl ether dimethyl ester is precipitated. Stirring is continued for another hour at 60–70 °C in order to destroy the excess dimethyl sulphate. The ester is filtered off and saponified with sodium hydroxide solution and the acid precipitated with HCl. After recrystallization from 70% alcohol the pure acid is obtained in the form of yellowish-white needles (melting point 296–297 °C).

Analysis

calculated	*found*
60.9% C	61.0% C
4.3% H	4.3% H
34.8% O	34.9% O
100.0%	100.2%

1,5-*dimethoxynaphthalene*-2,6-*dicarboxylic acid diester of hydroquinone-monomethyl ether*

The same procedure as described above for the Lohaus isomer was used for esterification. The diester (melting point 218,5 °C,

clarification point 286–287 °C) was obtained after recrystallization from dioxane and ethyl acetate and exhibited a nematic phase.

Analysis

calculated	*found*
68.85% C	69.0% C
4.95% H	4.9% H
26.2% O	26.3% O
100.0%	100.2%

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