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Liquid Crystalline Properties of Terminally Substituted Benzylideneanilines[1]

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The preparation and mesomorphic characteristics of certain anils (*p*-alkoxybenzylidene-*p*'-alkylanilines and *p*-alkoxybenzylidene-*p*'-alkoxyanilines) are described. Fifteen new compounds were found to exhibit nematic behavior below 100°C. The structural effects of the terminal substituents on nematic temperature range are discussed. It has been found that the anils containing *n*-alkyl substituents in the *p*-position of the aniline moiety exhibit mesophases in a much lower temperature range than those containing *n*-alkoxy substituents. Among *p*-isoalkoxybenzylideneanilines, all compounds except one are non-mesomorphic.

Recently, the electro-optic properties of liquid crystals have attracted considerable attention because of their application for display.[2] The term liquid crystal or mesomorphic state means a unique state of matter intermediate between a crystalline solid and a normal isotropic liquid.[3] A special class of mesomorphic material called nematic liquid crystal changes its transparency when an electric field is applied to its thin film.

Since low temperature nematic materials are desirable for a practical display device, efforts have been made for their preparation.[4–6] With this purpose in view, we prepared and characterized twenty three new anils, three of which were reported[5,6] as low temperature mesomorphic materials.

Results and Discussion

The terminally substituted anils we prepared are given in Table 1 along with their transition temperatures. The compounds are classified into the following three types according to their molecular constitutions.

I: *p*-*n*-Alkoxybenzylidene-*p*'-*n*-alkylanilines
II: *p*-Isoalkoxybenzylidene-*p*'-*n*-alkylanilines
III: *p*-Isoalkoxybenzylidene-*p*'-*n*-alkoxyanilines

A great number of *p*-*n*-alkoxybenzylidene-*p*'-*n*-alkoxyanilines (type IV) are known to exhibit mesomorphisms.[7,8] However, mesomorphic properties of other anils with less polar or branched substituents are scarcely known.

The compounds of type I contain no oxygen atom in the substituent of the aniline moiety. As the atom is polar and considered to contribute to intermolecular terminal cohesion between ordered mesomorphic molecules, it is of great interest to investigate the mesomorphic properties of the compounds. In this study, sixteen new compounds of this type were synthesized. Elemental analyses of most of them are given in Table 2.

Weygand and Gabler[9] studied *p*-*n*-nonyloxybenzylidene-*p*'-*n*-alkylanilines, which were found to exhibit smectic mesophases and no nematic mesophase when they have an ethyl or higher alkyl substituent in aniline moiety. Almost all the compounds of type I presented here, however, exhibit enantiotropic mesophases, as shown in Table 1.

It is notable that in homologous series of *p*-*n*-alkoxy-

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[1] Presented in part at the 3rd. Symposium on Structural Organic Chemistry, Hiroshima, November, 1970.

[2] G. H. Heilmeier, *Sci. Amer.*, **222**, 100 (1970).

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[9] C. Weygand and R. Gabler, *Naturwissenschaften*, **27**, 28 (1938).

Table 1. Transition temperatures of terminally substituted anils, X-C_6H_4-CH=N-C_6H_4-Y

Compd.	X	Y	Temp. °C of transition to		
			Smectic	Nematic	Isotropic
Ia	n-C_3H_7O	C_2H_5			67
Ib	n-C_4H_9O	C_2H_5	[39]	51.5[48]	66[62.5]
Ic	n-$C_5H_{11}O$	C_2H_5		56	61
Id	n-$C_6H_{13}O$	C_2H_5		59	71.5
Ie	n-$C_7H_{15}O$	C_2H_5	58	64	70
If	n-$C_8H_{17}O$	C_2H_5	65	71	75
Ig	n-$C_{16}H_{33}O$	C_2H_5	71		75.5
Ih	CH_3O	n-C_3H_7		45.5[42]	60.5[57]
Ii	C_2H_5O	n-C_3H_7		75.5[76]	87.5[97]
Ij	n-C_3H_7O	n-C_3H_7		57.5	68
Ik	n-C_4H_9O	n-C_3H_7		54	82.5
Il	n-$C_5H_{11}O$	n-C_3H_7		57	74.5
Im	n-$C_6H_{13}O$	n-C_3H_7	65	66.5	82.5
In	n-$C_7H_{15}O$	n-C_3H_7	62.5	71.5	79.5
Io	n-$C_8H_{17}O$	n-C_3H_7	68	82	85
Ip	n-C_3H_7O	n-C_4H_9		42	55
IIq	*iso*-C_3H_7O	CH_3			87
IIr	*iso*-$C_5H_{11}O$	C_2H_5			41.5
IIIs	*iso*-C_3H_7O	OCH_3			102
IIIt	*iso*-C_3H_7O	OC_2H_5			104
IIIu	*iso*-$C_5H_{11}O$	OC_2H_5		(89)	112
IIIv	*iso*-C_3H_7O	On-C_4H_9			89
IIIw	*iso*-$C_5H_{11}O$	On-C_4H_9			105

a) Values in parentheses denote monotropic transition.
b) Values in brackets are taken from Refs. 5 and 6.

Table 2. Analytical data of mesomorphic anils

Compd.	Formula	Calcd %			Found %		
		C	H	N	C	H	N
Ib	$C_{19}H_{23}NO$	81.10	8.24	4.99	81.02	8.45	4.90
Ic	$C_{20}H_{25}NO$	81.31	8.53	4.74	81.28	8.60	4.65
Id	$C_{21}H_{27}NO$	81.51	8.80	4.53	81.34	8.81	4.47
Ie	$C_{22}H_{29}NO$	81.69	9.04	4.33	81.63	9.18	4.17
If	$C_{23}H_{31}NO$	81.85	9.26	4.15	81.73	9.32	4.06
Ig	$C_{31}H_{47}NO$	82.79	10.53	3.11	83.04	10.69	2.97
Ih	$C_{17}H_{19}NO$	80.20	7.56	5.53	79.77	7.42	5.33
Ii	$C_{18}H_{21}NO$	80.86	7.92	5.24	81.02	8.00	5.14
Ij	$C_{19}H_{23}NO$	81.10	8.24	4.98	81.33	8.48	4.84
Ik	$C_{20}H_{25}NO$	81.31	8.53	4.74	81.47	8.64	4.68
Il	$C_{21}H_{27}NO$	81.51	8.80	4.53	81.77	9.13	4.43
Ip	$C_{20}H_{25}NO$	81.31	8.53	4.74	81.23	8.57	4.56

benzylidene-*p'*-ethylanilines and *p*-*n*-alkoxybenzylidene-*p'*-*n*-propylanilines the smectic phase first appears at C_7-ether[10] and C_6-ether, respectively, while in the series of *p*-*n*-alkoxybenzylidene-*p'*-ethoxyanilines[7] and *p*-*n*-alkoxybenzylidene-*p'*-*n*-propoxyanilines[8] the smectic properties begin at their respective C_9-ethers.

The compounds of type II, which are characterized by their terminal substituents of bulky branched groups as well as less polar *n*-alkyl groups, are non-mesomorphic in two cases.

The compounds of type III have a branched and a *n*-alkoxy substituent. Five compounds of this type were prepared. Only one compound IIIu exhibited monotropic nematic behavior.

Effect of Alkyl Substituents. Various transition temperatures for the homologous series of *p*-*n*-alkoxybenzylidene-*p'*-ethylanilines (type I) and *p*-*n*-alkoxybenzylidene-*p'*-ethoxyanilines (type IV) *vs.* the length of their alkoxy chain (total carbon and oxygen atoms) are plotted in Fig. 1. Those of *p*-*n*-alkoxybenzylidene-*p'*-*n*-propylanilines (type I) and *p*-*n*-alkoxy-

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[10] Flannery and Haas report the smectic phase of C_4-ether[6].

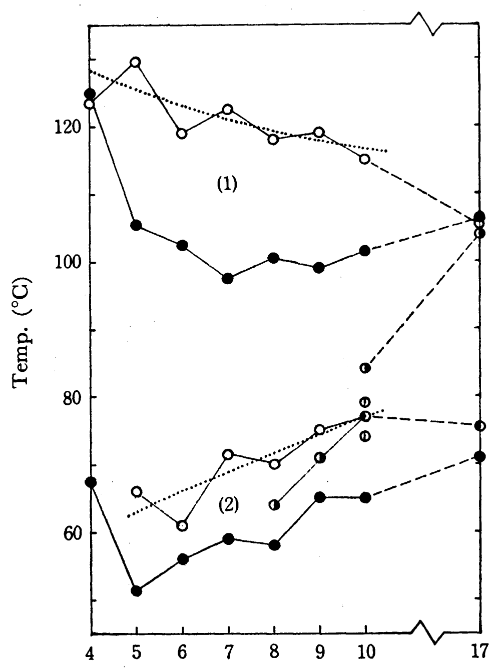

Fig. 1. Transition temperature for the series, (1) p,p'-n-$ROC_6H_4CH=NC_6H_4OC_2H_5$[7] and (2) p,p'-n-$ROC_6H_4CH=NC_6H_4C_2H_5$.
●: crystal-mesomorphic or -isotropic, ○: nematic-isotropic, ◐: smectic-isotropic, ◑: smectic-nematic, ⦶: smectic I-smectic II (Data for nonyloxy derivative from Ref. 9)

benzylidene-p'-n-propoxyanilines (type IV) are similarly plotted in Fig. 2.

From a comparison of crystal-mesomorphic and nematic-isotropic transition temperatures for the corresponding compounds of type I and type IV, it was found that both transition temperatures for each compound of type I are much lower than those for the corresponding compound of type IV. The features for the compounds of the former type are considered to be due to the decrease of the terminal intermolecular attraction resulting from the lack of a polar oxygen atom in the substituent of aniline moiety. As a matter of fact, smectic phases appear at a shorter alkoxy chain length in these compounds than in the compounds of type IV, because smectic stability increases when terminal attraction decreases and lateral interaction becomes relatively predominant.

It is known that nematic-isotropic transition temperatures for a homologous series lie on two smooth curves, one related to the members with an even-numbered chain and the other to those with an odd-numbered chain. In Figs. 1 and 2, dotted lines are drawn in the middle of the above mentioned two curves. The lines show that the temperatures for the compounds of type I have an unusual rising tendency with the growing chain length, while those for the compounds of type IV have a usual[11,12] falling tendency.

These phenomena can be explained by assuming a

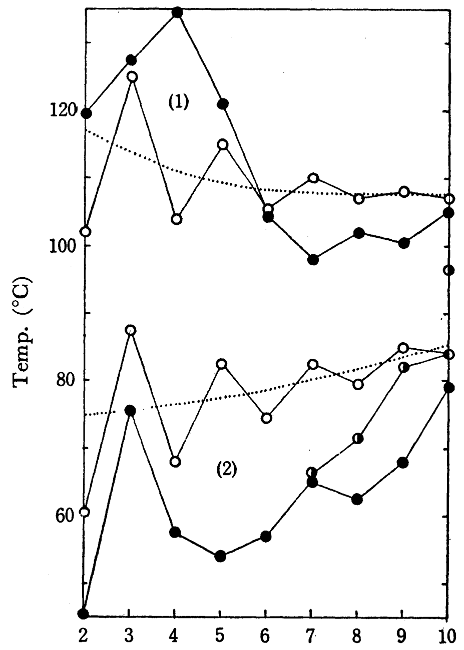

Fig. 2. Transition temperature for the series, (1) p,p'-n-$ROC_6H_4CH=NC_6H_4OC_3H_7$[8] and (2) p,p'-n-$ROC_6H_4CH=NC_6H_4C_3H_7$.
●: crystal-mesomorphic or -isotropic, ○: nematic-isotropic, ◐: smectic-isotropic, ◑: smectic-nematic
(Data for nonyloxy derivative in (2) are referred from Ref. 9.)

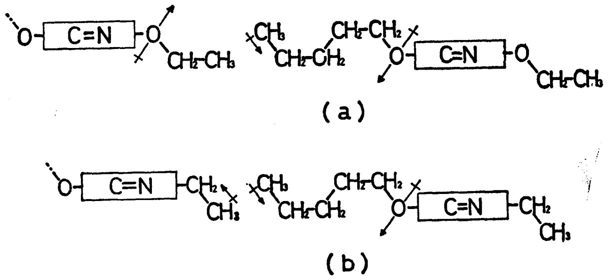

Fig. 3. Head-to-tail arrangement of neighboring molecules (a) compounds of the type IV (b) compounds of the type I.

head-to-tail molecular arrangement in which central C=N bondings of neighboring anils are in the same direction.[13] In the compounds of type IV as shown in Fig. 3(a), the terminal attraction between neighboring molecules is caused mostly by the interaction between dipoles of C–O–C groups. The contribution of other kinds of interactions such as related to the induced dipole moment of terminal methyl group are probably smaller. The nematic-isotropic transition temperatures for these compounds have falling tendency with the growing chain length because of decrease of the interaction between the dipoles. On the other hand, in the compounds of type I as shown in Fig. 3(b), the terminal attraction between

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[11] C. Weygand and R. Gabler, *Z. physik. Chem.*, **B48**, 148 (1941).

[12] G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Chap. IX, Academic Press, London and New York (1962), p. 197.

[13] The possibility of a head-to-head or tail-to-tail molecular arrangement, where the C=N bondings of neighboring molecules are in opposite direction to each other, cannot be ruled out. However, it will be impossible to explain the phenomena by assuming this arrangement.

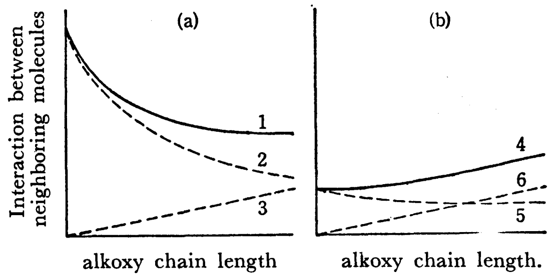

Fig. 4. Terminal interaction *vs.* alkoxy chain length
(a) for the compounds of type IV, (b) for the compounds of the type I, curve 1 and 4: total interaction, curve 2: interaction related to two O atoms, curve 3: interaction such as related to polalizability of terminal CH_3 group, curve 5: interaction related to terminal CH_3 group and O atom, curve 6: interaction to two terminal CH_3 group

neighboring molecules is caused by the interaction between the dipole of the C–O–C group in one molecule and the induced dipole of the terminal methyl group in the other molecule and by the interaction between the induced dipoles of the terminal methyl groups in both molecules. The former interaction becomes weaker with the growing alkoxy chain length, but the latter becames stronger because of increase of the induced dipole. The rising tendency is considered to be due to the superiority of the latter interaction. A schematic explanation is given in Fig. 4.

Effect of Odd- and Even-numbered Length of Terminal Chain. In Figs. 1 and 2, the well known change of nematic-isotropic transition temperatures can be seen between homologues containing odd and even numbers of carbon atoms in the terminal substituent of benzylidene moiety. Figure 5 gives the plots of nematic-isotropic transition temperatures for several series of *p-n*-alkoxybenzylidene-*p*′-*n*-alkylanilines. Similar changes are found also with regard to the terminal chain length of aniline moiety.

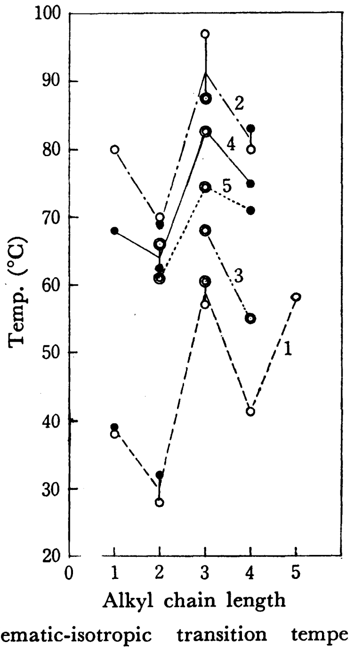

Fig. 5. Nematic-isotropic transition temperature for *p*-alkoxybenzylidene-*p*′-alkylanilines.

(1) $CH_3O-\langle\bigcirc\rangle-CH=N-\langle\bigcirc\rangle-R$
(2) $C_2H_5O-\langle\bigcirc\rangle-CH=N-\langle\bigcirc\rangle-R$
(3) $C_3H_7O-\langle\bigcirc\rangle-CH=N-\langle\bigcirc\rangle-R$
(4) $C_4H_9O-\langle\bigcirc\rangle-CH=N-\langle\bigcirc\rangle-R$
(5) $C_5H_{11}O-\langle\bigcirc\rangle-CH=N-\langle\bigcirc\rangle-R$

◎: present study, ○: Ref. 5, ●: Ref. 6

When the alkoxy chain length is defined as the number of oxygen plus carbon atoms, and the alkyl chain length as that of carbon atoms, curves of nematic-isotropic transition temperatures related to an odd-numbered chain length lie always above those related to an even-numbered chain length. It is notable that the feature is decided by the altered chain length of one moiety, independent of the chain length of the other moiety.

The behavior can be explained by considering the direction of polarizability of terminal methyl group as suggested by Gray.[12] Using the cog-wheel conformation for the substituted chain, the terminal C–C bond in the odd-numbered chain lies in the direction of the preferred axis of the molecules, but in the even-numbered chain it makes an angle with this axis. Therefore, the terminal intermolecular attraction is considered to be stronger in the molecules containing odd-numbered terminal chain. It is inferred that an oxygen atom in ether bonding makes one unit like a methylene group in this conformation and its polarity has nothing to do with the alternative behavior of the transition temperatures.

Let us consider curves 1 and 2 in Fig. 5. The terminal situations of neighboring molecules are exhibited schematically in Figs. 6 and 7 for the compounds related to curves 1 and 2, respectively. (A), (B) and (C) represent 2, 3, and 4 of alkyl chain length of aniline moiety. It is understood that the terminal intermolecular cohesion of the odd-numbered chain of the aniline moiety should be stronger than that of the even-numbered chain, independent of the chain length of the benzylidene moiety. As the terminal C–C bond of the benzylidene moiety of compounds in Fig. 7 lies in the direction of the preferred axis of the molecule, the terminal cohesion in these compounds should be stronger than that of corresponding compounds in Fig. 6. Thus, a compound with the terminal situation of (A) or (C) has a lower nematic-isotropic transition temperature than a homologous one with

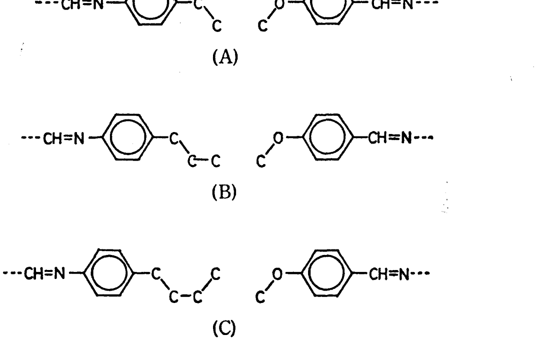

Fig. 6. Terminal situation of neighboring molecules of *p*-methoxybenzylidene-*p*-alkylanilines.

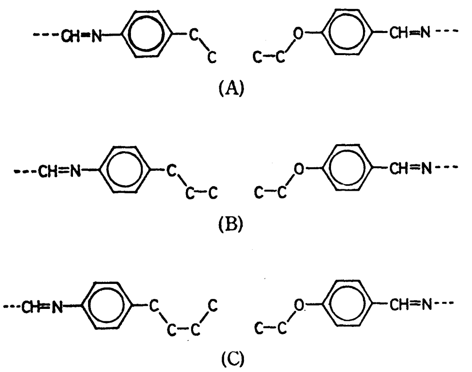

Fig. 7. Terminal situation of neighboring molecules of *p*-ethoxybenzylidene-*p*′-alkylanilines.

terminal situation of (B). The series in Fig. 6 exhibit the transition at a lower temperature than that in Fig. 7.

The consideration is in line with the aspects of curves 1 and 2 of Fig. 5. All the other data on the alternation of nematic-isotropic transition temperatures of anils can be explained as well.

Effect of Branched Chain Substituent. The bulky effect of the branched substituent was expected to weaken the intermolecular cohesion and to make the mesomorphic transition temperatures of type II and III compounds low as was the case with 4′-isoalkoxybenzylidene-1-aminonaphthyl-4-azobenzene.[11] However, all the compounds of these types do not exhibit mesomorphic behavior except for IIIu. The results suggest that the compounds do not possess sufficient intermolecular cohesion for mesomorphic ordering because of too bulky effect.

However, both the nematic-isotropic and the crystal-nematic transition temperatures of the compound IIIu are actually lower than those of the corresponding compound of type IV by about ten degrees. If the melting point of non-mesomorphic materials can be assumed to correspond to the crystal-mesomorphic transition temperature of mesomorphic ones, similar lowering effects are found in a comparison of these temperatures of the compounds of type II or III and the corresponding compounds of type I or IV.[7,8]

Experimental

Materials. p-*Alkoxybenzaldehydes*: *p*-*n*-Propoxybenzaldehyde (bp 91—92°C/2 mmHg), *p*-isopropoxybenzaldehyde[14], *p*-*n*-butoxybenzaldehyde (bp 111—112°C/2 mmHg), *p*-*n*-amyloxybenzaldehyde (bp 114—116°C/2 mmHg), *p*-isoamyloxybenzaldehyde (bp 110—111°C/2 mmHg), *p*-*n*-hexyloxybenzaldehyde[14], *p*-*n*-heptyloxybenzaldehyde (bp 136—137°C/2 mmHg), *p*-*n*-octyloxybenzaldehyde (bp 152—154°C/2 mmHg) and *p*-*n*-hexadecyloxybenzaldehyde[14] were prepared from *p*-hydroxybenzaldehyde and the corresponding alkylbromide by refluxing in ethanol.[15] The yields were 60—80%. All the aldehydes obtained were identified by IR-spectroscopy, and exhibited the following peaks: $\nu_{\max}^{\text{film}}$ 2925, 2850 (aliphatic C–H), 2730 (aldehyde C=H), 1695 (C=O), 830 cm^{-1} (*p*-substituted).

p-*alkoxyanilines*: *p*-Anisidine and *p*-phenetidine were obtained from commercial sources and distilled. *p*-*n*-Butoxyaniline was prepared by the reduction of *p*-*n*-butoxynitrobenzene.[16]

p-*Alkylanilines*: *p*-Toluidine and *p*-ethylaniline were obtained from commercial sources and distilled. *p*-*n*-Propylaniline and *p*-*n*-butylaniline were prepared by a method similar to that of Read and Mullin[17] (bp 74—76, 80—86°C/2 mmHg, respectively).

Preparation of Substituted Benzylideneanilines. Equimolar quantities of the appropriate benzaldehyde and aniline were mixed, warmed at about 50°C for a quarter of an hour and then cooled to room temperature until crystalline products appeared. It was necessary to cool the mixture with dry ice-acetone for the synthesis of Ib and Ip.

Since no crystals appeared in the syntnesis of Ih and IIr, the mixture was dissolved in benzene containing a catalytic amount of benzenesulfonic acid, and refluxed for about three hours to remove water azeotropically.[4] After the removal of solvent, the residue was cooled in dry ice-acetane to crystallize.

The products were purified by recrystallization from ethanol. All anils were obtained in 60—85% yield after recrystallization. The absorption band at 1625—1630 cm^{-1} (C=N stretching[18]) in IR-spectra, not belonging to raw materials, confirms the formation of anils.

Determination of Transition Temperature. The melting point and mesomorphic transition temperature were determined with an electrically heated microscope block in conjugation with a projection system. The mesomorphic states of the compounds were readily distinguished by their typical textures.[19]

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[14] Only isolated from extract and not distilled.

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[16] C. Weygand and G. Gabler, *ibid.*, **71B**, 2399 (1938).

[17] R. R. Read and D. B. Mullin, *J. Amer. Chem. Soc.*, **50**, 1763 (1928).

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[19] G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Chap. II, Academic Press, London and New York (1962) p. 17.