Mesomorphism and Chemical Constitution. Part II. The* trans-p-n-*Alkoxycinnamic Acids.*

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[Reprint Order No. 4908.]

Thirteen pure *trans-p-n*-alkoxycinnamic acids have been prepared, and their mesomorphic transition temperatures determined. The mesomorphic properties are compared with those exhibited by the 6-*n*-alkoxy-2-naphthoic acids. The variations from previously determined transition temperatures for these cinnamic acids are discussed.

COMPARISON of the mesomorphic properties of the 6-*n*-alkoxy-2-naphthoic acids (Part I *) with those of the *trans-p-n*-alkoxycinnamic acids (Bennett and Brynmor Jones, *J.*, 1939, 420) reveals differences not to be expected in compounds which display such similarity of constitution. Unlike the naphthoic acids, the series of cinnamic acids shows no regularity of the upper transition points, or of smectic–nematic, and smectic–isotropic transition points. Moreover, hexadecyloxycinnamic acid exhibits a nematic phase, whilst the corresponding naphthoic acid is purely smectic. The only similarities between the two series would seem to be that all the ethers examined, from methyl upwards, exhibit mesomorphism, and that smectic properties are introduced, with a monotropic phase, in the nonyl ethers. The octadecyloxycinnamic acid was not examined by Bennett and Brynmor Jones (*loc. cit.*), but this has now been done in order to make the series of cinnamic acids comparable with the series of naphthoic acids. This acid melts at 120·5° to a smectic state, which changes to the isotropic liquid at 157·5°, without showing any nematic phase. When these values were added to a graph of the recorded constants for the cinnamic acids, they seemed misplaced in relation to the lower members. The series of *trans-p-n*-alkoxycinnamic acids (methyl—decyl, dodecyl, hexadecyl, and octadecyl) was therefore prepared afresh, and the transition points redetermined in the electrically heated block recently described (Gray, *Nature*, 1953, **172**, 1137). The new values for the transitions (solid–nematic or smectic, smectic–nematic, and smectic or nematic–isotropic) are tabulated on p. 1468.

When these values are plotted against the number of carbon atoms in the alkyl chain, the transition temperatures exhibit regularities similar to those already reported for the *p-n*-alkoxybenzoic acids (Gray and Brynmor Jones, *J.*, 1953, 4179) and the 6-*n*-alkoxy-2-naphthoic acids (Part I, *J.*, 1954, 683). The upper transition points now lie on two smooth curves, the upper representing the ethers with an even number, and the lower curve those with an uneven number, of carbon atoms in the alkyl group. These curves fall gradually, and are joined by the rising curve which passes through the smectic–nematic and smectic–isotropic transition points of the nonyl, decyl, dodecyl, hexadecyl, and octadecyl ethers. Like the analogous ethers of the benzoic and naphthoic acids, the hexadecyl and octadecyl ethers are purely smectic, as proved by their appearance from the isotropic state in bâtonnets. Thus, the resemblance between the alkoxycinnamic acids and the 6-*n*-alkoxy-2-naphthoic acids is very close. Both series show a regularity of the transition points, with smectic

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* Part I, *J.*, 1954, 683.

phases appearing at the nonyl ether. There is, moreover, a general decrease in the stability of the mesophases with increasing chain length, and an increasing stability of the smectic phases with increasing molecule length up to the hexadecyl ether; thereafter there is a slight decrease to the upper transition point of the octadecyl ether. The qualitative agreement between the two series would have been complete had the smectic phase of nonyloxycinnamic acid been monotropic, as reported earlier. However, repeated preparation and purification of this compound gave in all cases the constants now quoted, with an enantiotropic smectic phase of length 5·5°.

	Temp. of transition to			Phase length of	
Alkyl group	smectic	nematic	isotropic	smectic	nematic
Methyl	—	173·5°	190°	—	16·5°
Ethyl	—	194	198·5	—	4·5
Propyl	—	167	184·5	—	17·5
Butyl	—	156	189·5	—	33·5
Pentyl	—	139·5	179·5	—	40
Hexyl	—	153	181·5	—	28·5
Heptyl	—	148	175	—	27
Octyl	—	146	174·5	—	28·5
Nonyl	138·5°	144	171	5·5°	27
Decyl	136	150·5	169	14·5	18·5
Dodecyl	132	157	165	25	8
Hexadecyl	118	—	159	41	—
Octadecyl	120·5	—	157·5	37	—

In their principal characteristics, the agreement between the two series is good. It was, of course, not to be expected that the similarity would be any closer, and that, for instance, the phase lengths of analogous ethers would be identical or that the maximum phase lengths would occur at the same point in each series. The naphthoic acids should have higher m. p.s than the cinnamic acids. This in fact is the case in nine of the thirteen ethers, but probably varying factors affect the m. p. It is even more significant that in all cases the upper transition points of the naphthoic acids are higher than those of the cinnamic acids. Therefore, the mesophases of the former are more stable. The average upper transition temperature for the naphthoic acids is 192·1°, and for the cinnamic acids 176·5°—a difference of 15·6°. The smectic–nematic and smectic–isotropic transition temperatures are much closer, and are higher in the naphthoic acids in only three of the five cases. The average value for the naphthoic acids (153°) is indeed less by 0·6° than the average of 153·6° for the cinnamic acids. It is possible, therefore, that the naphthalene system gives rise to a greater overall thermal stability of the mesophases, but that, relative to the nematic phases, the smectic phases of the latter are, on the average, slightly more stable.

The order of mesomorphic stability for three series of acids is as shown below, where the figures represent the average fall in the upper transition points.

$$\text{6-}n\text{-Alkoxy-2-naphthoic acids} \xrightarrow{15\cdot6^\circ} trans\text{-}p\text{-}n\text{-Alkoxycinnamic acids} \xrightarrow{31\cdot4^\circ} p\text{-}n\text{-Alkoxybenzoic acids}$$

$$\xrightarrow{\text{Decreasing thermal stability of the mesophases}}$$

It is noteworthy that these decreases are accompanied by a decrease in the number of double bonds in the system, and further evidence is forthcoming to verify this.

The above values vary substantially from those obtained by Bennett and Brynmor Jones (*loc. cit.*), and there may be a number of contributory reasons for the differences. When the earlier measurements were made, the higher alkyl halides (especially $C_7H_{15}X$ to $C_{12}H_{25}X$) were not readily obtained pure and, although the analyses for the corresponding alkoxycinnamic acids were satisfactory, the acids may not have been free from isomers. However, in addition, these compounds are sensitive to sunlight and heat, and when some of the original samples, prepared some 15 years ago, were re-examined there was in many cases almost a complete loss of mesomorphic characteristics. For example, the nonyl ether, reported to have m. p. 141° and upper transition point 163°, melted to the isotropic liquid over the range 137—141°. Samples of the acids prepared afresh for this investigation showed reduced mesomorphic properties when set aside—the rapid deterioration in sunlight points to isomerisation. When octadecyloxycinnamic acid was exposed to sunlight during 3 months, the original constants of 120·5° and 158° fell to 117° and 151—154°. The last transition was so indefinite that, had it not been previously known that the sample was purely smectic, the presence of a short nematic phase between 151° and 154° would have been suspected. Such behaviour may account for the reported observation of a short nematic phase in the hexadecyl ether.

These compounds are also affected by heat, as shown by the behaviour of the nonyl ether. This was heated in an oil-bath at 160° for 1 hour, the nematic melt was cooled, and the m. p. determined. The material softened at 126°, and flowed at 136° to a turbid melt, which cleared at 157—164°. The constants of the pure acid are 138·5°, 144°, and 171°. Moreover, after this treatment no definite smectic phase was detectable on cooling the isotropic liquid on a slide. This confirms the earlier report of a monotropic smectic phase in this compound.

To minimise these risks in the present investigation, a fresh slide was mounted for the determination of each transition point, and no sample was exposed to light or high temperatures for more than 2—3 minutes.

No difference was found in the enantiotropic polymorphic transition of the hexyloxycinnamic acid, or in the textures of the mesophases reported by Bennett and Brynmor Jones.

The *trans-p-n*-alkoxycinnamic acids were prepared by condensing the *p-n*-alkoxybenzaldehydes with malonic acid in pyridine (piperidine as catalyst). This method is more satisfactory than the homologous alkylation of *trans-p*-hydroxycinnamic acid (Bennett and Brynmor Jones, *loc. cit.*). For example, the octadecyl ether was prepared by both of these methods. The constants, 120·5° and 157·5°, for the acid prepared by the former method were obtained after only two crystallisations from glacial acetic acid, whereas they were obtained for the material prepared by the second method only after seven crystallisations—two from glacial acetic acid, three from benzene, and two from absolute ethyl alcohol. More readily purified compounds are therefore obtained by the condensation method.

EXPERIMENTAL

Determination of the Mesomorphic and Polymorphic Transition Temperatures.—The approximate transitions for solid–nematic and smectic, smectic–nematic, and smectic and nematic–isotropic were first determined in a wide m. p. capillary tube in a well-stirred paraffin bath. The electrically heated block (Gray, *loc. cit.*) was raised to within 5° of each value, and a thin section of the acid, obtained by melting between a glass slide and a cover slip, inserted in the slide slot. The temperature was then raised at less than 2°/min. until each transition had occurred. A fresh slide was mounted for each transition, and no specimen was exposed to light or heat for more than 2—3 min. The corrected values obtained are tabulated above.

Preparation of Materials.—p-n-*Alkoxybenzaldehydes.* *p*-Hydroxybenzaldehyde (12·2 g., 0·1 mol.), anhydrous potassium carbonate (60 g., 0·4 mol.), *cyclo*hexanone (80 ml.), and the *n*-alkyl bromide or iodide (0·16 mol.) were refluxed and agitated vigorously. Alkylation was complete after 1—3 hr., the mixture then being pale yellow or colourless. The solution was decanted from the potassium carbonate, which was washed with ether. The washings were added to the *cyclo*hexanone extract, and both solvents distilled off on the water-bath under reduced pressure. The residual *p-n*-alkoxybenzaldehydes were then distilled under reduced pressure, and obtained as colourless liquids or low-melting solids (65—75% yield). The yields of the hexadecyl and octadecyl ethers were never more than 60%—their high b. p.s resulted in

TABLE 1.

Alkyl group	B. p.	Found, %		Formula	Required, %	
		C	H		C	H
Et	106°/3 mm.	71·9	6·5	$C_9H_{10}O_2$	72·0	6·7
Pr	144°/14 mm.	73·3	7·4	$C_{10}H_{12}O_2$	73·2	7·3
$C_{10}H_{21}$	185°/4 mm.	77·9	10·0	$C_{17}H_{26}O_2$	77·85	9·9
$C_{12}H_{25}$	194°/8 mm.	78·6	10·4	$C_{19}H_{30}O_2$	78·6	10·4
$C_{16}H_{33}$	230°/3 mm.	79·9	10·9	$C_{23}H_{38}O_2$	79·8	11·0
$C_{18}H_{37}$	240°/2 mm.	80·2	11·2	$C_{25}H_{42}O_2$	80·2	11·2

charring during distillation. The butyl to nonyl ethers have been prepared, and their b. p.s recorded, by Weygand and Gabler (*J. pr. Chem.*, 1940, **155**, 332). Table 1 gives the b. p.s and analyses for the remainder of the series. The dodecyl, hexadecyl, and octadecyl aldehydes are waxy solids of m. p.s 24°, 34°, and 48·5° respectively.

trans-p-n-*Alkoxycinnamic acids.* The *p-n*-alkoxybenzaldehyde (0·02 mol.), malonic acid (3·2 g., 0·04 mol.), pyridine (8 ml.), and piperidine (3 drops) were heated at 100° for 3 hr. The mixture was poured on ice (25 g.) and concentrated hydrochloric acid (25 ml.). The precipitate was collected, washed with dilute hydrochloric acid and water, and crystallised from 98% acetic acid. The yields of the colourless products were 90—100% and, after a total of three crystallisations from 98% acetic acid, the m. p.s were constant. The analyses for these acids are in Table 2.

TABLE 2.

Alkyl group	Found, %		Formula	Required, %		Alkyl group	Found, %		Formula	Required, %	
	C	H		C	H		C	H		C	H
Me	67·3	5·5	$C_{10}H_{10}O_3$	67·4	5·6	C_8H_{17}	73·7	8·7	$C_{17}H_{24}O_3$	73·9	8·7
Et	68·7	6·3	$C_{11}H_{12}O_3$	68·8	6·25	C_9H_{19}	74·3	9·0	$C_{18}H_{26}O_3$	74·5	9·0
Pr	69·7	6·8	$C_{12}H_{14}O_3$	69·9	6·8	$C_{10}H_{21}$	74·8	9·2	$C_{19}H_{28}O_3$	75·0	9·2
Bu	70·9	7·2	$C_{13}H_{16}O_3$	70·9	7·3	$C_{12}H_{25}$	76·1	9·5	$C_{21}H_{32}O_3$	75·9	9·65
C_5H_{11}	71·9	7·7	$C_{14}H_{18}O_3$	71·8	7·7	$C_{16}H_{33}$	77·3	10·4	$C_{25}H_{40}O_3$	77·3	10·3
C_6H_{13}	72·6	8·1	$C_{15}H_{20}O_3$	72·6	8·1	$C_{18}H_{37}$	78·1	10·7	$C_{27}H_{44}O_3$	77·9	10·6
C_7H_{15}	73·3	8·5	$C_{16}H_{22}O_3$	73·3	8·4						

The authors thank the Distillers Co. Ltd. and Imperial Chemical Industries Limited for grants to the Department.

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[*Received, December* 21*st*, 1953.]