94. *Mesomorphism and Polymorphism of Some* p-*Alkoxybenzoic and* p-*Alkoxycinnamic Acids.*

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The seven alkoxybenzoic acids which had previously been observed to give turbid melts (J., 1929, 2660; 1935, 1874) have now been examined in polarised light, together with three further members of the *p*-alkoxybenzoic acid series and eight homologous

p-alkoxycinnamic acids. The types of mesomorphic form are described, and the transition temperatures have been found, with respect both to the mesomorphism and to polymorphism which occurs in the solids. The variation of the mesomorphism in the two homologous series is discussed, and compared with that shown by the cholesteryl esters. *p*-Propoxybenzoic acid has the simplest structure of any substance in which a mesomorphic form has been observed. The mesomorphism must be due to the association of the acid in doubled molecules, which must therefore have a strictly linear structure.

THE occurrence of mesomorphism in some *p*-alkoxybenzoic acids was recently reported (J., 1929, 2660; 1935, 1874), the phenomenon having been detected from the formation of a cloudy melt clearing at a definite upper transition temperature in each case. We have now amplified these observations in two respects: an extended series of both *p*-alkoxybenzoic and *p*-alkoxycinnamic acids has been prepared; and the substances have been examined in detail in polarised light. The nature of the phenomenon has been confirmed and the types of mesomorphic form are now recorded. The various transition temperatures have been determined, including several relating to polymorphism of the solids.

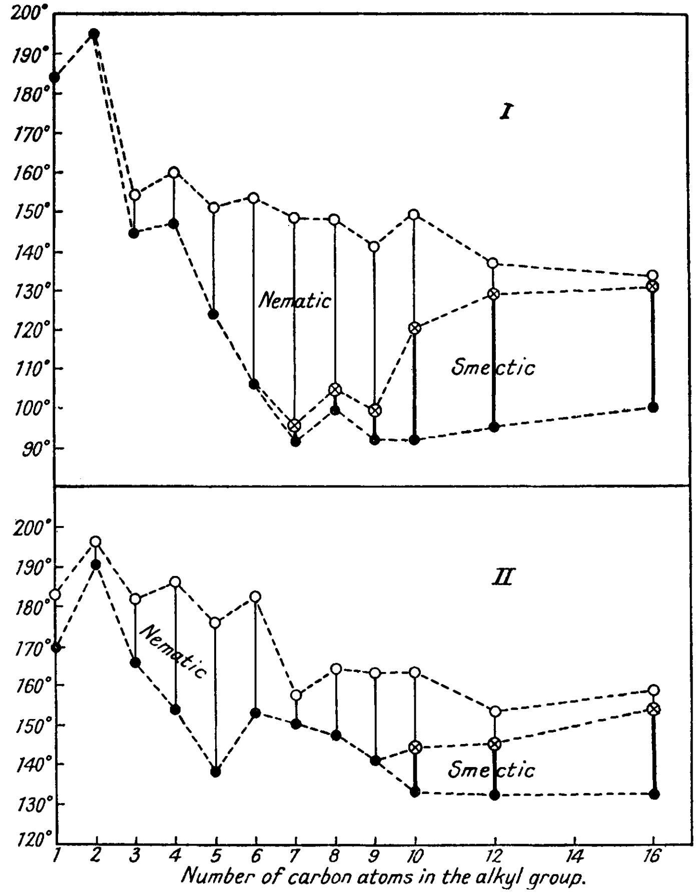
As regards the solids, polymorphism is found in only one of the cinnamic acids examined, namely, p-*hexyloxycinnamic acid*, the second form of which is monotropic. Six of the benzoic acids are polymorphic. *p*-Propoxy-, *p*-heptyloxy-, and p-*decyloxy*-benzoic acids are dimorphic, the second form being enantiotropic; p-*nonyloxy*- and p-*dodecyloxy-benzoic acids* are dimorphic, the second form being monotropic; and *p*-octyloxybenzoic acid shows trimorphism in the solid state, one form being monotropic, the others enantiotropic.

In the substituted cinnamic acid series the *p*-methoxy-, -ethoxy-, -propoxy-, and -butoxy-acids had been examined by Stoermer (*Ber.*, 1911, **44**, 637) and Stoermer and Wodarg (*Ber.*, 1928, **61**, 2323), who showed that mesomorphism occurs in the *trans*-acids but not in the *cis*-isomerides, into which they are converted by ultra-violet light. These authors had difficulty in preparing *p*-cetyloxycinnamic acid, which they describe as melting at 200—202° with decomposition and with no sign of mesomorphism. Using our usual method of preparation, we have isolated this acid and find that it melts at 132°, above which it exists in both smectic and nematic forms and becomes amorphous at 158°. These facts disprove the contention of Stoermer and Wodarg that mesomorphism is suppressed by extending the alkyl chain to cetyl. We have not ourselves prepared and examined the *cis*-isomerides of our acids, as there can be no doubt of the validity of the view that such substances cannot give rise to mesomorphs. It was, however, noticed that a specimen of cetyloxycinnamic acid, after prolonged exposure of a thin film of the solid to daylight, melted without yielding any mesomorphic form, and a similar observation was made with two other of the cinnamic acids. It seems possible that some conversion into the *cis*-isomerides may have taken place under these conditions.

The occurrence and range of existence of the mesomorphic forms in these two series of acids are represented graphically in the figure. The general trend in the two series is similar, and the chief points of difference may be regarded as arising from the relatively high temperatures at which some of the acids melt. Thus the range of existence of the mesomorphic forms is generally wider in the benzoic acid series, but this is clearly an extension further downwards in the temperature scale in the one set: the relatively high melting points of the cinnamic acids cut off, as it were, the lower region of possible existence of mesomorphic forms of these substances. In the same way the fact that *p*-methoxy- and -ethoxy-benzoic acids give no mesomorphic form may be attributed to the higher melting points (184° and 195°) of the solids in these two acids, and this is definitely confirmed by the observation that a nematic liquid is at once produced when a mixture of the two acids is melted.

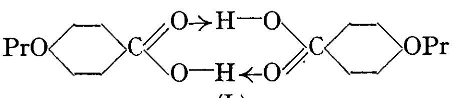
In his important paper on the mesomorphic state, Friedel (*Ann. Physique*, 1922, **18**, 273) discussed the variation of the mesomorphism in the homologous series of cholesteryl esters of the saturated fatty acids, of which he examined ten. In this series he found that the first four (formate to butyrate) gave a nematic cholesteric form, which in the formate and acetate was monotropic. The esters from the acids of 8, 9, 10, 12, and 14 carbon atoms (octoate to myristate) existed in both nematic and smectic meso-forms, the temperature range of the smectic form increasing as the series was ascended, whilst that of the nematic form diminished. The stearate, however, gave only a smectic form, and this was monotropic. Friedel concluded that the nematic form occurs when the cholesterol is the dominant part of the structure, but the smectic form when the fatty acid becomes more important. No other series was then available for comparison.

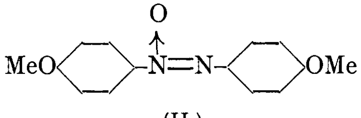
The two new series represented in the figure reveal similar tendencies. In each series the nematic form is found in the lower members, its range of existence increasing as the alkyl group grows, particularly up to amyl and hexyl. At a later point in the series, but earlier in the benzoic than in the cinnamic acid series, for the reasons mentioned above, a smectic form appears and becomes increasingly important at the expense of the nematic form. The decyloxycinnamic acid is the first to give the two enantiotropic meso-forms, but a monotropic smectic form appears in the preceding nonyloxycinnamic acid. Here, then, as in the series of cholesteryl esters, we have the smectic form developing the more as the long alkyl chain, with its greater freedom of rotation and bending, becomes relatively more important in the structure.



Melting points and liquid transition temperatures of : I, p-*alkoxybenzoic acids ;* II, p-*alkoxycinnamic acids.* ● = *solid–liquid transition point ;* ○ = *point of transition from nematic into isotropic liquid ;* ⊗ = *point of transition from smectic into nematic form.*

A point of special interest is the fact that *p*-propoxybenzoic acid has the simplest molecular structure yet found to yield a mesomorphic form. Most of the best known mesomorphic substances have at least two aromatic nuclei linked together and *p*-substituted. The existence of the mesomorphic form of this simple monosubstituted benzoic acid can only be explained on the assumption that it is the doubled molecules of the acid which are concerned. When these are formulated as suggested by Sidgwick (*Ann. Reports*, 1933, **30**, 115; compare Latimer and Rodebush, *J. Amer. Chem. Soc.*, 1920, **42**, 1419) and as confirmed for the case of formic acid by Pauling and Brockway (*Proc. Nat. Acad. Sci.*, 1934, **20**, 336) the molecule (I) is seen to be of similar size and shape to that of a typical nematic substance such as azoxyanisole (II).


(I.)


(II.)

Further support to this conception is afforded by the fact that the methyl ester of propoxybenzoic acid, which we have examined, has a low melting point (15°; compare Cohen and Dudley, J., 1910, **97**, 1732) but shows no sign of mesomorphism. This was to be expected, as the ester will have no tendency to association. In view of the work of Vorländer on the structural features necessary for the occurrence of double refraction in a liquid, the nematic melt from *p*-propoxybenzoic acid must be regarded as conclusive evidence that the arrangement of the two benzene nuclei in the double molecule is strictly linear. Vorländer himself observed that the methyl and ethyl esters of *p*-methoxycinnamic acid melt to isotropic liquids: he also reported, on the other hand, that anisic acid can be made to show double refraction in the liquid state by adding certain other acids to the melt (*Ber.*, 1906, **39**, 803; 1907, **40**, 1966). He does not appear, however, to have provided the explanation of these facts.

EXPERIMENTAL.

Preparation of the Alkoxy-benzoic and -cinnamic Acids.—These acids were prepared in all cases from the respective hydroxy-acid as described previously (Jones, J., 1935, 1874) with the addition of alcohol to the reaction mixture, subsequently removed by evaporation before the acid was isolated by precipitation. The cinnamic acids were recrystallised at least twice and the benzoic acids thrice from glacial acetic acid. The acids previously described in the benzoic series were *p*-methoxy- to *p*-octyloxy-, inclusive, and *p*-cetyloxybenzoic acid. In the cinnamic acid series the *p*-methoxy-acid is well known and the *p*-ethoxy-, *p*-*n*-propoxy-, *p*-*n*-butoxy-, and *p*-*iso*butoxy-acids were described by Stoermer and Wodarg (*loc. cit.*).

Examination of the Substances in Polarised Light.—Each specimen was melted on a microscope slide and examined between crossed Nicols under the microscope while it cooled, the experiment being repeated a number of times. In some cases rapid cooling caused the transitory appearance of a labile liquid or solid form. In order to test whether each form was monotropic or enantiotropic, a simple device for heating the specimen on the microscope stage was used. This consisted of a stout copper strip having a flat box-cavity at one end, into which the microscope slide could be inserted, with small observation holes above and below to allow light to pass through both strip and specimen for purposes of observation. The outside of the strip was thermally insulated with thin asbestos sheet except at the end opposite to that containing the specimen. This exposed end projected over the edge of the microscope stage and was heated by means of a micro-burner as required. This device made it easy to study each transition in both directions and so to determine whether it was enantiotropic or not. Temperatures could not be determined with this heater, but an indication was usually obtained of the relative ranges of stability of the successive phases.

Observations of Transition Temperatures.—Measurements of the solid–liquid and liquid–liquid transition temperatures were made as before by observing the substance in a melting-point capillary heated in a well-stirred paraffin bath. The transition from smectic to nematic form involved a visible change of opacity and a great increase in fluidity: if the material had not been closely packed into the capillary, the transition in question was marked by the flowing of the viscous drops adhering to the walls of the tube. The change was also viewed in polarised light by means of polaroid discs. Temperatures have been corrected for exposed stem and should be subject to an error of not more than 1°. (In the previous paper, J., 1935, 1874, the temperature data for the first two acids were corrected, the remainder uncorrected: they have all now been redetermined.)

With only small amounts of the substances available, no attempt could be made to determine the solid–solid transition temperatures by observing arrests in cooling curves, but the following method was adopted. The substance was melted on a small strip of microscope slide (1 cm. × 3 cm.) and covered with a piece of cover-slip. Any solid–solid transformation could be seen with the naked eye as a wave of change in opacity which passed across the specimen. The specimen so mounted was lowered by means of a thread into a test-tube serving as an inner air-bath surrounded by the heated oil-bath. The bulb of a thermometer was next to the specimen, and the upper end of the test-tube was closed with a cotton-wool plug. The temperature of the bath was now slowly raised, and the specimen from time to time suddenly removed, placed on a cold slab, and examined to see if any solid–solid transformation occurred. The actual transition temperature could thus be determined to about ± 1° by finding two adjacent temperatures between which the observable transition just ceased to be detected.

Series of p-*Alkoxybenzoic Acids.*—p-*Propoxybenzoic acid* (amorphous–154°–nematic–145°–solid I–116°–solid II). The nematic form appears first in spherical drops and resembles that of *p*-methoxycinnamic acid in general character. It is highly mobile and shows high colours between crossed Nicols. Well-defined nuclei and threads are visible. Solid I forms large clear plates showing high double refraction. Solid II appears as numerous crystal sheets with parallel edges and a straight extinction. All three transitions are enantiotropic.

p-n-*Butoxybenzoic acid* (amorphous–160°–nematic–147°–solid). The nematic liquid gives low interference colours. Both changes are enantiotropic.

p-n-*Amyloxybenzoic acid* (amorphous–151°–nematic–124°–solid). This substance gives fine nematic plates with nuclei, and more colour than the preceding. The solid has an extinction which is straight to the cleavage lines. Both changes are enantiotropic.

p-n-*Hexyloxybenzoic acid* (amorphous–153°–nematic–106°–solid). The nematic form shows fine plates with nuclei and threads, and, like the propoxy-acid, it produces very high colours together with a rapid variation with temperature. The solid forms large plates with a high double refraction.

p-n-*Heptyloxybenzoic acid* (amorphous–148°–nematic–95°–smectic–92°–solid II–89°–solid III. Solid I monotropic). The nematic form, besides the usual plates with nuclei showing high colours which change somewhat rapidly with fall of temperature, tends on reheating to appear in homogeneous plates. Before the liquid crystallises there is visible a change to a mottled and viscous smectic form showing the characteristic " oily streaks," this change being reversible. Further cooling yields solid I in large, clear plates of high colour. This is a monotropic form, passing over into solid II, which is enantiotropic but of narrow temperature range. Finally, solid III is observed. There are thus four enantiotropic and one monotropic forms of this substance.

p-n-*Octyloxybenzoic acid* (amorphous–148°–nematic–104°–smectic–100°–solid II–72°–solid III. Solid I monotropic). This substance closely resembles the heptyloxy-acid in its polymorphism, except that the temperature ranges of stability of both smectic liquid and solid II are wider. Solid I is only observable when the melt is rapidly cooled. All the changes are enantiotropic except those involving solid I.

p-n-*Nonyloxybenzoic acid* (amorphous–141°–nematic–99°–smectic–92°–solid II. Solid I monotropic). In this *acid* (Found: C, 72·0; H, 9·3. $C_{16}H_{24}O_3$ requires C, 72·7; H, 9·2%), the nematic and smectic forms are well defined and are succeeded in rapid cooling by a labile solid I which passes over into the stable solid II.

p-n-*Decyloxybenzoic acid* (amorphous–149°–nematic–120°–smectic–92°–solid I–84°–solid II). The polymorphism of this *acid* (Found: C, 72·9; H, 9·3. $C_{17}H_{26}O_3$ requires C, 73·3; H, 9·4%) is similar to that of the preceding acid except that both solid forms are here enantiotropic. Solid I appears in small, clear plates which pass over at 84° into feathery crystals of solid II. All the transitions are therefore reversible.

p-n-*Dodecyloxybenzoic acid* (amorphous–137°–nematic–129°–smectic–95°–solid II. Solid I monotropic). The change from nematic to smectic liquid in this *acid* (Found: C, 74·1; H, 9·9. $C_{19}H_{30}O_3$ requires C, 74·6; H, 9·8%) is very clearly defined, and oily streaks are easily observable in the latter. The monotropic solid I appears as small plates showing high interference colours, which pass over into the arborescent crystals of solid II showing a high double refraction.

p-*Cetyloxybenzoic acid* (amorphous–133°–nematic–131°–smectic–100°–solid). The liquid on cooling yields a nematic form with high colours and very clearly defined plates with nuclei. At a somewhat lower temperature, however, the liquid is viscous and shows oily streaks. The change from nematic to smectic form is here not easy to see, no sharp phase boundary being visible crossing the field of view, but once the nature of the liquid at 132° and about 110° had been ascertained, it was possible to locate it. Careful tests showed that the nematic form is of very narrow range of stability but that both changes are definitely enantiotropic. The existence of two liquid forms could, in this instance, very easily have been overlooked, as in the case of cholesteryl stearate, where the liquid–solid transition is almost impossible to detect and was regarded as absent by Lehmann (Friedel, *loc. cit.*). All the changes are here enantiotropic.

Series of p-*Alkoxycinnamic Acids.*—The properties of *p*-methoxycinnamic acid are well known, and those of *p*-ethoxy-, *p*-*n*-propoxy-, and *p*-*n*-butoxy-cinnamic acids were described by Stoermer and Wodarg (*loc. cit.*).

trans-p-n-*Amyloxycinnamic acid* (amorphous–176°–nematic–138°–solid). The melted *acid* (Found : C, 71·5; H, 7·7. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%) yields fine plates with nuclei which solidify to needles having a straight extinction and a high double refraction.

trans-p-n-*Hexyloxycinnamic acid* (amorphous–182°–nematic–153°–solid II. Solid I monotropic). The nematic form of the *acid* (Found : C, 72·7; H, 8·1. $C_{15}H_{20}O_3$ requires C, 72·5; H, 8·1%) solidifies to a monotropic solid in large plates which are easily kept for some time if chilled, the rate of transformation to the stable form being slow. The nematic form is enantiotropic.

trans-p-n-*Heptyloxycinnamic acid* (amorphous–157°–nematic–150°–solid). The enantiotropic nematic form of the *acid* (Found : C, 73·2; H, 8·4. $C_{16}H_{22}O_3$ requires C, 73·2; H, 8·5%) passes on cooling into needles having an oblique extinction.

trans-p-n-*Octyloxycinnamic acid* (amorphous–164°–nematic–147°–solid). This *substance* (Found : C, 73·7; H, 8·7. $C_{17}H_{24}O_3$ requires C, 73·8; H, 8·8%) also yields only one liquid and one solid form, and the changes are enantiotropic. The solid appears as plates with an oblique extinction.

trans-p-n-*Nonyloxycinnamic acid* (amorphous–163°–nematic–141°–solid. Monotropic smectic form). The highly mobile nematic form of this *acid* (Found : C, 74·4; H, 9·0. $C_{18}H_{26}O_3$ requires C, 74·3; H, 9·1%) appears, as usual, in spherical globules yielding plates with nuclei which readily give homogeneous plates. The high interference colours change considerably as the temperature falls. A well-defined change then occurs to a smectic form, which is, however, monotropic. Finally, large, clear plates of the solid form are produced.

trans-p-n-*Decyloxycinnamic acid* (amorphous–163°–nematic–144°–smectic–133°–solid). The forms of this *acid* (Found : C, 75·0; H, 9·3. $C_{19}H_{28}O_3$ requires C, 75·0; H, 9·3%) are similar to those of the preceding acid, but the changes are now all enantiotropic, and the smectic form has a temperature range of 11°.

trans-p-n-*Dodecyloxycinnamic acid* (amorphous–153°–nematic–145°–smectic–132°–solid). The nematic form (Found : C, 76·1; H, 9·6. $C_{21}H_{32}O_3$ requires C, 76·0; H, 9·6%) closely resembles that of the nonyloxycinnamic acid and, like it, tends to give homogeneous plates. The smectic form is again enantiotropic, but with rather narrow temperature range.

trans-p-*Cetyloxycinnamic acid* (amorphous–158°–nematic–154°–smectic–132°–solid). This substance (Found : C, 77·4; H, 10·3. Calc. for $C_{25}H_{40}O_3$: C, 77·3; H, 10·4%) was prepared by the same method as the other members of the series, and was purified by crystallisation successively from glacial acetic acid and benzene. When heated, it sinters at 125° and melts at 132°. Stoermer and Wodarg (*loc. cit.*), using almost the same method of preparation, obtained a solid of m. p. 200—202°, which gave satisfactory analytical figures but showed no signs of any mesomorphic form. The melt gives a nematic form with fairly high interference colours, and well-defined plates with nuclei. This passes without a sharp boundary change into the smectic form, which is viscous and shows the characteristic oily streaks. The liquid–liquid change is difficult to detect, as in the case of *p*-cetyloxybenzoic acid. The changes are all enantiotropic. A specimen of this substance on a microscope slide heated once or twice and left in daylight for five days was found to melt without giving any mesomorphic phase, and the same result was obtained when the material was scraped off and melted on a fresh slide. Specimens of heptyloxy- and octyloxy-cinnamic acids which had been kept for several months on a slide were also found to melt without passing through any mesomorphic form.

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