539. *Mesomorphism and Polymorphism in Simple Derivatives of* p-*Terphenyl.*

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The molecule of *p*-terphenyl is elongated, and the introduction of simple dipolar substituents at the 4- and 4″-positions may give rise to mesomorphic behaviour. For example, 4-cyano- and 4-methoxy-4″-nitro-*p*-terphenyl and 4-acetamido- and 4-amino-3,4″-dinitro-*p*-terphenyl exhibit nematic mesophases. Other *p*-terphenyl derivatives which, by analogy, might be expected to give mesophases, *e.g.*, 4,4″-dinitro-*p*-terphenyl and 4-acetamido-4″-nitro-*p*-terphenyl, are so high-melting that conditions are unfavourable for the existence of a mesophase. The melting processes of 4-acetamido-3,4″-dinitro-*p*-terphenyl and the amine are complicated by polymorphic changes.

Compounds which exhibit mesomorphic properties vary widely in constitution, but the molecules are always geometrically anisotropic. In general, the molecules contain dipolar groups and polarisable aromatic rings such that the intermolecular attractions are adequate to maintain the parallel arrangement of the molecules after the solid has melted.

In mesomorphic derivatives of benzene, the symmetrical hydrocarbon skeleton must carry two substituents in the *para*-positions and these substituents must be either elongated or of such a nature (*e.g.*, $-CO_2H$) that the molecules dimerise. If strong enough intermolecular attractions operate between such long molecules, mesophases may be obtained on melting the compound, *e.g.*, for *NN*′-di-(*p*-n-alkoxybenzylidene)-*p*-phenylenediamines,[1]

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[1] Gray, Hartley, Ibbotson, and Jones, *J.*, 1955, 4359.

p-azoxyanisole, and *p*-n-propoxybenzoic acid (dimeric). With the elongated molecule of biphenyl, only one suitable substituent in the 4-position is required for the compound to be mesomorphic, *e.g.*, 4-*p*-methoxybenzylideneaminobiphenyl, but again, the substituent functions in two ways, by raising the intermolecular attractions to a suitable level, and by lengthening the molecule appreciably. Suitable 4,4′-disubstituted biphenyls, of course, exhibit pronounced mesomorphic properties, but once more, at least one of the two substituents must be elongated.

We now record the interesting fact that quite simple 4,4″-disubstituted *p*-terphenyls may be mesomorphic. With this long and narrow hydrocarbon molecule, the 4,4″-substituents must be dipolar, but not necessarily of such a complex nature that the length of the molecule is greatly increased. Thus, 4-methoxy-4″-nitro-*p*-terphenyl melts at 210—212°, but gives a nematic mesophase which persists until 259°. Similarly, 4-cyano-4″-nitro-*p*-terphenyl yields a nematic melt at 232°, and the isotropic liquid is obtained only at 275°. On the other hand, 4-chloro-4″-nitro-*p*-terphenyl, m. p. 258°, gives no mesophase. The molecular length is only slightly less than for the nitrile, and the absence of anisotropic properties in the melt must be attributed to the weaker C–Cl dipole moment which contributes less to the intermolecular attractions than the C–CN dipole. For 4,4″-dinitro-*p*-terphenyl,[2] m. p. 272—274·5°, 4-amino-4″-nitro-*p*-terphenyl, m. p. 300—301°, and 4-acetamido-4″-nitro-*p*-terphenyl, m. p. 332—333°, the m. p.s are high, probably owing to intermolecular hydrogen-bonding in the last two instances. For these three compounds, the kinetic energy of the melt must be too great to permit the existence of a parallel molecular arrangement after melting has occurred. No mesophases are therefore observed.

The more elongated molecular structures of Schiff's bases derived from 4-amino-*p*-terphenyl and particularly 4,4″-diamino-*p*-terphenyl with *p*-n-alkoxybenzaldehydes give rise, of course, to extremely thermally stable mesophases.

Two other quite simple derivatives of *p*-terphenyl have, however, been found to show mesomorphic properties. These are 4-acetamido-3,4″-dinitro-*p*-terphenyl and the analogous free amine. The melting phenomena for these compounds are made more complex by the occurrence of solid–solid transitions.

The acetyl compound is dimorphic, and the two crystal forms have different m. p.s. In general, fine, separate, orange-yellow needles, m. p. 230·5—231·5°, are obtained from glacial acetic acid, and spherulites of orange-yellow needles, m. p. 225°, from xylene. The crude material from the preparation, and occasionally the crystallised material, may however shrink and soften at 222—225°, melting finally at 231°, and it is fairly certain that such samples are mixtures of the two solid forms. The melting range for such samples was first attributed to the occurrence of a smectic mesophase, and indeed, when a thin section of the isotropic liquid, mounted between a glass slide and a cover slip, was cooled, a mesophase was observed. This isotropic–mesomorphic transition was found to occur at 228°. The solids obtained on cooling the mesophase behaved in one of two ways, solid II melting at 231° and passing direct into the isotropic liquid, and solid I melting at 225° and giving what appeared to be a smectic mesophase which became isotropic at 228°. These transitions were confirmed when the two dimorphic forms were obtained separate by crystallisation. The mesophase is therefore enantiotropic with respect to solid I, m. p. 225°, and monotropic with respect to solid II, m. p. 230·5—231·5°.

The isotropic liquid always gives the mesophase on cooling, and never crystallises to solid II. The mesophases obtained on different occasions crystallise sharply and within the limits 218—226° and, if the solid is heated immediately, the mesophase is usually observed, *i.e.*, solid I is normally produced. On cooling to room temperature, solid I sometimes changes into solid II, which then gives a normal transition to the isotropic liquid on heating to about 231°. However, the mesophase may crystallise at 226°, above the m. p.

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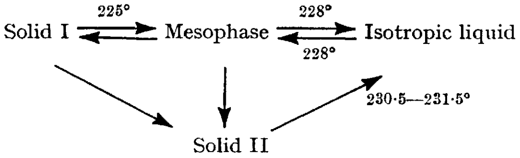
[2] Culling, Gray, and Lewis, *J.*, 1960, 1547.

of solid I. When this occurs, solid II is obtained, and the solid II to isotropic change is observed on raising the temperature. Solid II may therefore arise by solidification of the mesophase or by a polymorphic change of solid I. However, no polymorphic changes of solids I and II, obtained by crystallisation, were found to occur on storing the samples for several weeks.

These observations may be summarised:



Attempts to obtain the solid I–solid II transition temperature by observing a section of the crystalline solid I under the microscope, as it cooled to room temperature, were unsuccessful.

The propyl esters of the 4′-n-alkoxybiphenyl-4-carboxylic acids[3] and their 3′-nitro-derivatives[4] exhibit only smectic mesophases. In the unsubstituted alkoxy-esters, the two dipoles one at each end of the ring system, will operate across the long molecular axis. In the nitro-derivatives, it seems reasonable to assume that the O–CH_2 link in the alkoxy-group will lie *trans* with respect to the nitro-group, and that the C–alkoxy and C–NO_2 dipoles will reinforce one another. There will then be three effective dipoles operating across the long axis of each molecule. The purely smectic characteristics of the above esters have been explained in terms of the distribution of the dipoles, which will enhance the cohesive forces between the sides of neighbouring molecules and favour the adoption of a layer arrangement of the molecules, as required for smectic mesophase formation.

Now the mesophase obtained from the solid form I of 4-acetamido-3,4″-dinitro-*p*-terphenyl adhered to the walls of the capillary tube, and appeared to be smectic, and at first, this was thought to be consistent with the presence in the molecule of the 3-nitro- and the acetamido-dipole moments, which would enhance the intermolecular lateral cohesions. However, since the thermal stability range of the mesophase was only 3°, sections of the anisotropic melt, mounted between glass surfaces, were examined under the microscope to confirm the identity of the mesophase. Thin sections of the mesophase were largely homotropic and exhibited no scintillation effects or turbulence, even when the crystals began to grow. However, when thicker sections are viewed between crossed Nicols, the mesophase is seen to be comprised of a number of highly birefringent areas, each of which shows extinction in four positions at right angles. The molecules appear to be arranged parallel to one another and to the supporting surface, as in the nematic state. These thicker sections were found to exhibit other nematic characteristics such as large numbers of threads, small areas having the centred structure described by Friedel,[5] and intense movement within the melt, particularly when the crystals were growing in the mesophase. The absence of this turbulence in the thin sections is probably accounted for by the more highly orientated nature of the homotropic mesophase, in which the optic axis is uniformly perpendicular to the glass surface. The mesophase is undoubtedly nematic, and it can only be assumed that the anisotropic melt has not time to flow properly in a capillary before it becomes isotropic.

The nematic properties are in fact explicable in terms of molecular structure, if the hydrogen atom on the nitrogen atom of the acetamido-group is hydrogen-bonded to the nitro-group *ortho* to it. The dipoles of the nitro- and acetamido-groups then oppose, and this effect will result in an appreciable reduction in the effective dipole moment acting across the long molecular axis. The system is now seen to be less similar to the biphenyl

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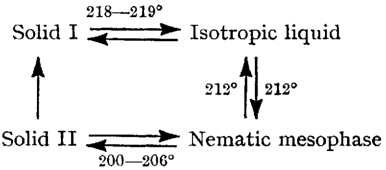
[3] Gray, Hartley, and Jones, *J.*, 1955, 1412.
[4] Gray, Jones, and Marson, *J.*, 1957, 393.
[5] Friedel, *Ann. Phys.*, 1922, **17**, 273.

esters, having only one resultant dipole acting across the long axis of the molecule, and the dipole of the nitro-group in the 4″-position acting in the direction of the long molecular axis. With this distribution of dipole moments, the intermolecular attractions between the sides and planes of the molecules do no appear to be great enough to maintain a stratified arrangement of the parallel molecules when melting occurs. The compound therefore exhibits nematic properties.

4-Amino-3,4″-dinitro-*p*-terphenyl is also nematic. The resultant dipole of the 3-nitro- and amino-groups will act across the long molecular axis, but in the absence of a similar dipole at the other end of the ring system, smectic properties do not arise. It is of interest that this mesomorphism occurs in a free amine, for groups such as OH and NH_2 usually give intermolecular hydrogen-bonding which raises the m. p. of the compound so much that anisotropy is not observed in the melt. However, in this case, the intramolecular hydrogen-bonding between the amino-group and the nitro-group *ortho* to it will reduce the tendency to intermolecular hydrogen-bonding. The low m. p. of 218—219° of the 3,4″-dinitro-amine compared with that of 300—301° for 4-amino-4″-nitro-*p*-terphenyl supports this view. The same arguments may be applied to the acetyl derivatives.

When the isotropic liquid obtained from the amine at 218—219° is cooled, it may give a highly crystalline solid almost immediately, or if the temperature falls to 212°, the nematic mesophase is obtained. If the temperature is raised at once, the nematic mesophase passes back to the isotropic liquid at 212°. On cooling the mesophase, a solid is obtained between 206° and 200° and, if this is heated immediately, it gives the mesophase, which then becomes isotropic. Attempts to obtain the m. p. of this dimorphic form, solid II, were unsuccessful, because in the time taken to reheat the solid sufficiently slowly to obtain an accurate m. p., the solid passed into the other crystal form, solid I, which melted at 218—219° and gave no mesophase. The m. p. of solid II must, however, lie between 206° and 212°. These observations may be summarised:



The change from solid II to solid I is only occasionally visible.

The mesophase is therefore monotropic with respect to solid I and enantiotropic with respect to solid II.

The m. p.s and transition temperatures recorded above and in the experimental section are uncorrected and were obtained by ordinary capillary methods, in order that the results obtained by other workers who may encounter these compounds in the course of synthetic work may be more readily compared with our data (obtained by the use of an exposed thermometer stem from 0°).

EXPERIMENTAL

*4-Amino-4″-nitro-*p*-terphenyl.*—Sodium sulphide nonahydrate (4·82 g.) and sulphur (1·3 g.) were dissolved in boiling water (240 ml.). The hot aqueous sodium polysulphide was added to a solution of 4,4″-dinitro-*p*-terphenyl [2] (2 g.) in pyridine (200 ml.) at about 100°, the addition rate and the temperature being adjusted so that the mixture boiled vigorously throughout the addition. In this way, precipitation of the dinitro-compound is minimised. After the addition, the mixture was refluxed for 5 hr., during which the red nitro-amine separated and any precipitated dinitro-compound passed into solution. The red solid was filtered off from the hot mixture and washed with water and ethanol. Crystallisation from nitrobenzene yielded deep red plates of *4-amino-4″-nitro-*p*-terphenyl* (0·93 g., 51%), m. p. 300—301° (Found: C, 74·6; H, 4·8; N, 9·8. $C_{18}H_{14}N_2O_2$ requires C, 74·5; H, 4·8; N, 9·7%). The *acetyl derivative* was obtained by stirring and heating almost to the b. p. a suspension of the powdered nitro-amine

(3 g.) in acetic anhydride (45 ml.). The bright yellow slurry was cooled. The solid was filtered off, washed with acetic acid, and crystallised from nitrobenzene, giving 4-acetamido-4''-nitro-*p*-terphenyl (3·27 g., 95%), m. p. 332—333° (Found: C, 71·9; H, 5·0; N, 8·6. $C_{20}H_{16}N_2O_3$ requires C, 72·2; H, 4·8; N, 8·5%).

4-*Hydroxy*-4''-*nitro*-p-*terphenyl*.—4-Amino-4''-nitro-*p*-terphenyl (1 g., 1 mol.) was boiled for 15 min. with 5N-sulphuric acid (45 ml.). Acetic acid (60 ml.) was added, and the mixture boiled to dissolve the yellow amine sulphate, which was then obtained in a finely divided form by rapidly cooling and stirring the solution to 0°. Sodium nitrite (1 g., 4 mol.) in water (12·5 ml.) was added at 0° to the stirred suspension, and the temperature was raised to and kept at 20° for 2 hr. The bright yellow suspension of the diazonium sulphate was freed from nitrous acid with sulphamic acid, and cooled to 0° before the gradual addition, with stirring, of 40% aqueous (w/w) sulphuric acid (150 ml.). The mixture was then heated, and the temperature kept at 80° until no coupling reaction was given. The yellow solid was filtered off from the cooled mixture, washed with aqueous sodium hydrogen carbonate, and crystallised from acetic acid. 4-*Hydroxy*-4''-*nitro*-p-*terphenyl* was obtained as bright yellow plates (0·84 g., 84%), m. p. 266—267° (Found: C, 74·3; H, 4·5; N, 4·7. $C_{18}H_{13}NO_3$ requires C, 74·2; H, 4·45; N, 4·8%).

4-*Methoxy*-4''-*nitro*-p-*terphenyl*.—Sodium (0·23 g.) was dissolved in absolute ethyl alcohol (100 ml.). A portion (10 ml., 1 mol.) of this solution (A) and 4-hydroxy-4''-nitro-*p*-terphenyl (0·3 g., 1 mol.) were heated to boiling, and sufficient absolute alcohol was added to dissolve the red sodium salt. To the refluxing solution was then added a portion (1 mol.) of a 10% solution (B) of methyl iodide in absolute ethyl alcohol. The red colour faded after 2 hours' boiling, but reappeared on addition of further quantities (1 mol.) of each of the solutions A and B. Refluxing was continued for 30 min., the same volumes of solutions A and B were again added, and the mixture was boiled for 30 min. The hot mixture was poured into water (120 ml.), and the precipitated *methyl ether* was filtered off, washed with alcohol, and crystallised from acetic acid. The yellow plates of 4-methoxy-4''-nitro-*p*-terphenyl (0·26 g., 83%) (Found: C, 74·9; H, 4·9; N, 4·5. $C_{19}H_{15}NO_3$ requires C, 74·75; H, 4·9; N, 4·6%) had m. p. 210—212°, and exhibited a nematic mesophase which became isotropic at 259°.

4-*Cyano*-4''-*nitro*-p-*terphenyl*.—4-Amino-4''-nitro-*p*-terphenyl (1 g., 1 mol.) was diazotised as described in the preparation of 4-hydroxy-4''-nitro-*p*-terphenyl, and the insoluble amine sulphate was filtered off, washed with a little methanol and then with ether, and air-dried. The amine sulphate was quickly sifted into a stirred solution of potassium nickelocyanide [from solutions of potassium cyanide (0·86 g., 4 mol.) in water (10 ml.) and hydrated nickel sulphate (0·97 g., 1 mol.) in water(10 ml.)] k ept at 50°. Sodium carbonate (0·25 g.) was then added to raise the pH. The temperature was raised slowly to and kept at 100° until no coupling reaction was given. The mixture was cooled, and the dark brown solid filtered off and washed with water and ethanol. The dry solid was sublimed at 240° at 1—2 mm., yielding orange-yellow 4-*cyano*-4''-*nitro*-p-*terphenyl* (0·32 g., 31%), m. p. 232° (Found: C, 76·0; H, 3·9; N, 9·15. $C_{19}H_{12}N_2O_2$ requires C, 76·0; H, 4·0; N, 9·3%). Crystallisation from acetic acid did not raise either the m. p. or the nematic–isotropic transition temperature of 275°.

4-*Chloro*-4''-*nitro*-p-*terphenyl*.—4-Amino-4''-nitro-*p*-terphenyl (0·5 g., 1 mol.) was dissolved by heating it with acetic acid (35 ml.) and 5N-hydrochloric acid (20 ml.), and the solution was cooled quickly, with stirring, to 0°. The finely divided amine hydrochloride was diazotised by adding sodium nitrite (0·24 g., 2 mol.) in water (9 ml.), and stirring for 1 hr. at 0°. Excess of nitrous acid was destroyed with sulphamic acid, and the suspension of the insoluble diazonium chloride was added at 0° to a solution of cuprous chloride (0·94 g., 5·9 mol.) in concentrated hydrochloric acid (4·2 ml.). The mixture was then heated and kept at 100° until no coupling reaction was given; it was then cooled, and the yellow solid was filtered off and washed in turn with concentrated hydrochloric acid, water, and ethanol. The 4-*chloro*-4''-*nitro*-p-*terphenyl* crystallised from benzene in long yellow needles, 0·3 g. (56%), m. p. 258° (Found: C, 70·1; H, 3·9; Cl, 11·7; N, 4·4. $C_{18}H_{12}ClNO_2$ requires C, 69·8; H, 3·9; Cl, 11·5; N, 4·5%).

4-*Acetamido*-3,4''-*dinitro*-p-*terphenyl*.—A stirred suspension of 4-acetamido-4''-nitro-*p*-terphenyl (2 g.) in glacial acetic acid (80 ml.) was heated in an oil-bath at 114°, and a solution of nitric acid (7·2 ml., *d* 1·505) in glacial acetic acid (16 ml.) was added during 1—1·5 min. After a total reaction time of 15 min., a small amount of unchanged material was filtered off from the hot mixture. The bright yellow 4-*acetamido*-3,4''-*dinitro*-p-*terphenyl* (2·1 g., 93%) crystallised when the filtrate was cooled to 15°, and was washed with acetic acid, water, and ethanol. Crystallisation does not greatly improve the quality of the product, which is dimorphic and melts at 230·5—231·5° (from acetic acid) or 225° (from xylene) (Found: C, 63·85; H, 4·3; N, 10·8. $C_{20}H_{15}N_3O_5$ requires C, 63·7; H, 4·0; N, 11·4%). The lower-melting solid exhibits a nematic mesophase which becomes isotropic at 228° (see p. 2700).

4-*Amino*-3,4″-*dinitro*-p-*terphenyl*.—The acetyl derivative (1·2 g.) and concentrated sulphuric acid (12 ml.) were heated to effect dissolution. Water (4 ml.) was cautiously added, the mixture was heated at 125—130° for 30 min., and the solution poured into water. The free base was filtered off and washed with water and 5N-ammonia. The moist product crystallised from pyridine (13 ml.) and water (3 ml.) as red-brown needles and leaflets of 4-*amino*-3,4″-*dinitro*-p-*terphenyl* (0·96 g., 90%), m. p. 216—218°, with softening from 214°. Two crystallisations from pyridine and one from nitrobenzene gave orange crystals, m. p. 218—219°, softening from 216·5° (Found: C, 64·8; H, 4·0; N, 12·2. $C_{18}H_{13}N_3O_4$ requires C, 64·5; H, 3·9; N, 12·5%).

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