

**420.** *Mesomorphism and Chemical Constitution. Part XI.<sup>1</sup> The Preparation and Mesomorphic Properties of Substituted 4-p-n-Alkoxybenzylideneaminobiphenyls.*

By D. J. BYRON, G. W. GRAY, A. IBBOTSON, and B. M. WORRALL.

Certain 4-*p*-n-alkoxybenzylideneamino-halogeno- and -methyl-biphenyls have been prepared and their melting points and mesomorphic transition temperatures recorded. The mesomorphic thermal stabilities of the 2- and the 2'-substituted derivatives are low, and this is explained by the steric effect of the angular substituent. The results suggest that the biphenyl nucleus of a system that is not sterically affected will be more nearly planar in the mesophases than in solution, and that the interplanar angle will be smaller for the smectic than for the nematic mesophase. The trends of the nematic-isotropic transition temperatures along the homologous series of the sterically affected biphenyl derivatives are discussed.

THE effects of substituents on the mesomorphic properties of alkoxyarene-carboxylic acids have been the subject of recent studies.<sup>2-4</sup> The 4'-*n*-alkoxybiphenyl-4-carboxylic acids (I) are particularly suitable parent compounds, because bulky 3'-substituents, *e.g.*, nitro and iodo, do not destroy the mesomorphism.<sup>5,6</sup> However, the interplanar angle,  $\theta$ , for the biphenyl nucleus is not known for the smectic and nematic states of biphenyl derivatives that are not sterically affected, and the simple interpretation<sup>6</sup> of the changes in the mesomorphic thermal stabilities of the octyl ether (I) brought about by different 3'-substituents is made uncertain because changes in  $\theta$  may occur (*a*) when the substituent is changed and (*b*) at the smectic-nematic transition. Likewise, it is difficult to compare the mesomorphic properties of analogous benzene, biphenyl, fluorene, and fluorenone derivatives<sup>7-9</sup> unless assumptions are made about the angle  $\theta$  for the biphenyl system.

As a first step towards understanding the importance of  $\theta$  in relation to the mesomorphic properties of biphenyl compounds, it would be profitable to study mesomorphic biphenyl compounds carrying 2- or 2'-substituents. Only a limited amount of work has been carried out along these lines. Wiegand<sup>10</sup> briefly investigated the effects of di- and tetra-substitution on the mesomorphic properties of 4,4'-di-(*p*-methoxybenzylidene-amino)biphenyl (II). The 2,2',6,6'-tetrachloro- and -tetramethyl-derivatives of compound (II) were not mesomorphic, and this was explained by the non-planarity of the biphenyl nucleus. The 2,2'- and 3,3'-dichloro- and -dimethyl-derivatives of compound

<sup>1</sup> Part X, Gray, *J.*, 1958, 552.

<sup>2</sup> Gray and Jones, *J.*, 1954, 2556.

<sup>3</sup> Gray and Jones, *J.*, 1955, 236.

<sup>4</sup> Gray, Jones, and Marson, *J.*, 1956, 1417.

<sup>5</sup> Gray, Jones, and Marson, *J.*, 1957, 393.

<sup>6</sup> Gray and Worrall, *J.*, 1959, 1545.

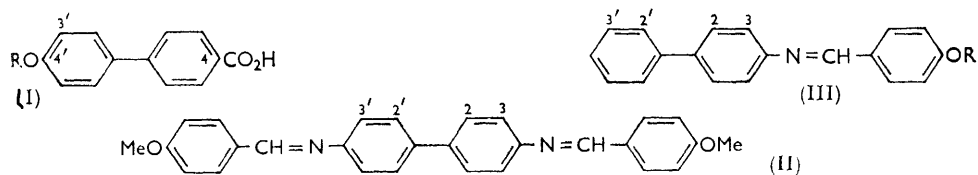
<sup>7</sup> Gray, Hartley, and Jones, *J.*, 1955, 1412.

<sup>8</sup> Gray, Hartley, Ibbotson, and Jones, *J.*, 1955, 4359.

<sup>9</sup> Gray and Ibbotson, *J.*, 1957, 3228.

<sup>10</sup> Wiegand, *Z. Naturforsch.*, 1951, **6b**, 240.

(II) were also studied by Wiegand. He assumed that if the 2,2'-substituents adopted a *trans*-arrangement the molecule would be planar and the compound mesomorphic, but that a *cis*-arrangement would result in twisting of the biphenyl nucleus about the 1,1'-bond and the absence of mesomorphism. The 2,2'-disubstituted derivatives were mesomorphic, and Wiegand concluded that the molecule adopted the planar, *trans*-configuration.



Now, models show that there is a hindrance to rotation about the 1,1'-bond in systems such as 2-chloro-, 2-bromo-, and 2-methyl-biphenyl. Larger, more numerous angular substituents are required before a suitable biphenyl derivative may be resolved. However, the inability to resolve biphenyl derivatives carrying 2-substituents such as chloro, bromo, and methyl does not mean that the molecules are planar, but that they may periodically be planar by rotation about the 1,1'-bond. Rotation about this bond should occur less readily in the mesomorphic state than in solution or in the isotropic liquid, and work was begun by preparing the 4-*p*-n-alkoxybenzylideneaminobiphenyls (III) with 3-, 2-, 2'-, and 3'-methyl substituents. The results suggested that the mesomorphic properties of the 2- and 2'-substituted derivatives were affected by a steric interaction, despite the small substituent involved. The analogous 3-, 2-, 2'-, and 3'-chloro- and -bromo-compounds were therefore prepared. The 3- and 3'-substituted compounds, which are not sterically affected, were included at this stage, in the hope that they might assist in assessing the extent of the increase in  $\theta$  brought about by the angular substituents. As pointed out in a preliminary communication,<sup>11</sup> the 3'-substituted isomers are purely smectic, and the 3-substituted isomers may be anomalous either because a steric effect between the substituent and the benzylideneamino-group is involved or because the molecule adopts the sterically unaffected, but much broader \* *trans*-configuration. Either effect would explain the rather low transition temperatures for the 3-isomers and the absence of smectic properties. For an examination of the effects of fluoro- and iodo-substituents, the 3- and 3'-substituted compounds were not therefore prepared, and it proved impossible to obtain the benzylidene derivatives from 4-amino-2'-fluorobiphenyl in a satisfactorily pure state.

For each of the substituents in a given position (3', 2', 2-, and 3-), four ethers (III; R = n-heptyl to n-decyl), were examined, although with the 2-methyl derivatives a wider range of alkyl groups was studied to show the trend of the transition temperature curve with increasing carbon chain length. In Table I, the m. p.s and mesomorphic transition temperatures of the various compounds are recorded, together with the average decreases [ $\Delta t$  (H—X) smectic and nematic—defined in the footnote below Table I] in mesomorphic thermal stability arising from the introduction of the substituents into the various positions in the parent 4-*p*-n-alkoxybenzylideneaminobiphenyls.<sup>8</sup>

It is clear that the largest decreases in the thermal stabilities of both the smectic and the nematic mesophase are brought about by the 2- and 2'-substituents. With the possible exception of the 3-substituted isomers, for which the molecular breadth of the *trans*-configuration is greater than that of the *cis*-configuration, the breadths of the 3-, 2-, 2'-, and 3'-substituted compounds (for a given substituent) are closely similar, and some other important structural effect must lower the mesomorphic transition temperatures of these 2- and 2'-substituted biphenyl derivatives. It seems probable that this effect

\* The breadth of a molecule is defined as the diameter of the smallest cylinder through which the molecule will pass, flexible alkyl chains being assumed not to interfere.

<sup>11</sup> Gray, "Steric Effects in Conjugated Systems," Butterworths Scientific Publns., London, 1958, p. 160.

is connected with the steric strain imposed on the biphenyl nucleus by the angular substituent.

It is established<sup>2-6</sup> that substitution of a mesomorphic compound decreases the mesomorphic transition temperatures, provided that the substituent broadens the molecule. The increased intermolecular separation decreases the intermolecular attractive forces to an extent outweighing any increase in these attractive forces arising from the polarity and polarisability of the ring-substituent bond. A 2- or 2'-substituent will however exert a second effect, because, if, relative to the sterically unaffected, parent, biphenyl derivative, the interplanar angle,  $\theta$ , is increased, the thickness of the sterically affected molecules will increase the intermolecular separation and cause a further decrease in the mesomorphic transition temperatures. The large  $\Delta t$  (H — X) smectic and nematic values for the 2- and the 2'-isomers in Table I reflect the combined influence of these two factors. To support this interpretation of the large decreases for these isomers, a comparison may be made between the average mesomorphic transition temperatures for the 2- and 2'-methyl derivatives (Table I) and those of the related, but planar, 2-*p*-n-alkoxybenzylideneaminofluorenes<sup>8</sup>—average (C<sub>7</sub>—C<sub>10</sub>) smectic–nematic transition temperature = 166° and average (C<sub>7</sub>—C<sub>10</sub>) nematic–isotropic transition temperature = 186.4°. These much higher transition temperatures suggest strongly that the 2- and 2'-methyl compounds have non-planar molecular structures in the mesomorphic state, and that a steric effect is encountered with one simple angular substituent.

A very striking feature of the results in Table I is the large effect which an iodo-substituent has on the mesomorphic thermal stability, and the very low, monotropic, isotropic–nematic transition temperatures, in some cases occurring well below room temperature, imply that a large steric twist about the 1,1'-bond is achieved with this substituent in

TABLE I.  
4-*p*-n-Alkoxybenzylideneamino-3-, -2-, -2', and -3'-substituted biphenyls.

Substituent	n-Alkyl	Temperature of transition to			Averaged $\Delta t$ (H — X) ¶	
		Smectic	Nematic	Isotropic	Smectic	Nematic
2-Fluoro-	Heptyl	—	88.5°	110°		
	Octyl	(84.5°)	85.5	115	61.3° †	48.7°
	Nonyl	84	92	113		
	Decyl	83.5	100	115		
3-Chloro-	Heptyl	—	(90)	96		
	Octyl	—	86	93.5	—	70
	Nonyl	—	67	91		
	Decyl	—	72	93		
2-Chloro-	Heptyl	—	(45)	64		
	Octyl	(41)	(53.5)	63	113.8 †	109.8
	Nonyl	(43)	(52.5)	66		
	Decyl	(44)	(57.5)	63.5		
2'-Chloro-	Heptyl	—	(52)	72		
	Octyl	—	(59.5)	65.5	118.3 †	102.9
	Nonyl	(34)	(59.5)	77		
	Decyl	(44)	(65)	70		
3'-Chloro-	Heptyl	115	—	136.5		
	Octyl	113	—	139	17	—
	Nonyl	115	—	138.5		
	Decyl	114	—	139.5		
3-Bromo-	Heptyl	—	(82)	91		
	Octyl	—	(85)	96	—	78
	Nonyl	—	59	83.5		
	Decyl	—	63	85		
2-Bromo-	Heptyl	—	(25)	67		
	Octyl	—	(35)	77.5	—	128.2
	Nonyl	—	(35)	66		
	Decyl	—	(40)	60		
2'-Bromo-	Heptyl	—	(36)	68		
	Octyl	—	(45.5)	52	—	117.8
	Nonyl	—	(45)	68		
	Decyl	—	(50)	64		

TABLE 1. (Continued.)

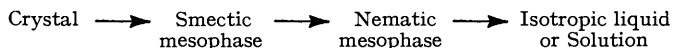
Substituent	n-Alkyl	Temperature of transition to			Averaged $\Delta t$ (H — X) ¶	
		Smectic	Nematic	Isotropic	Smectic	Nematic
3'-Bromo-	Heptyl	(124.5)	—	127	27.9	—
	Octyl	124.5	—	127.5		
	Nonyl	125.5	—	128.5		
	Decyl	124.5	—	129.5		
2-Iodo-	Heptyl	—	(3.5)	69.5	—	147
	Octyl	—	(17.5)	60.5		
	Nonyl	—	(16)	73.5		
	Decyl	—	(22.5)	62.5		
2'-Iodo-	Heptyl	—	(10.5)	79	—	140.8
	Octyl	—	(22)	59.5		
	Nonyl	—	(22.5)	64		
	Decyl	—	(29.5)	61		
3-Methyl	Heptyl	—	79.5	99.5	—	62.2
	Octyl	—	85.5	102		
	Nonyl	—	81	98		
	Decyl	—	85	99.5		
2-Methyl	Heptyl	—	(42)	60	—	112.4
	Octyl	—	(52)	68		
	Nonyl	—	(49)	71		
	Decyl	—	(55)	71		
	Dodecyl	(48.5)	(57)	60		
	Hexadecyl	(57)	(59.5)	67		
2'-Methyl	Octadecyl	(59.5)	(60.5)	72.5	101.1 †	98
	Heptyl	—	(59)	63.5		
	Octyl	(<47)	64	65.5		
	Nonyl	(51)	61	63		
	Decyl	(61.5)	65	68		
3'-Methyl	Heptyl ‡	(93) (111.5)	112	116.5	37.5	45 §
	Octyl ‡	(94) 111	118	121		
	Nonyl ‡	(90) 113.5	—	120		
	Decyl	112.5	—	122		

¶  $\Delta t$  (H — X) smectic or nematic is the difference between the appropriate mesomorphic transition temperature (smectic–nematic or smectic–isotropic; nematic–isotropic) of the 4-*p*-n-alkoxybenzylideneaminobiphenyl and that of the substituted derivative. In the Table averaged  $\Delta t$ (H — X) values are quoted for each substituent in a given position and, unless otherwise stated, these are for four ethers (n-heptyl–n-decyl).

|| Transition temperatures in parenthesis are for monotropic mesophases. † Average decrease for the n-nonyl and n-decyl ethers. ‡ These ethers exhibit two polymesomorphic<sup>5</sup> smectic modifications. § Average decrease for the n-heptyl and n-octyl ethers.

either the 2- or the 2'-position. However, even the 2-fluoro-substituent gives significantly large decreases in smectic and nematic thermal stability. Further, in systems in which a fluoro-substituent does *not* cause a steric effect, decreases in nematic thermal stability ranging between 9° and 26.5° have been observed,<sup>2,6</sup> and on this basis, about one-half at least of the  $\Delta t$  (H — X) nematic value in Table 1 must be caused by the steric interaction of the 2-fluoro-substituent, *i.e.*, by rotation of the unsubstituted phenyl ring further out of the plane of the rest of the molecule than is the case in the parent. Models suggest that the angle,  $\theta$ , for a 2-fluorobiphenyl is probably around 40°, and we may infer that in the nematic mesophase the interplanar angle for the parent is appreciably less than 40°, *i.e.*, intermediate between the planar and the non-planar ( $\theta = 45^\circ$ ) condition for biphenyl itself in the solid state and solution, respectively.

Values for  $\Delta t$  (H — F) smectic of between 0.5° and about 13° have been observed for sterically unaffected systems,<sup>2,6</sup> and therefore some three-quarters at least of the  $\Delta t$  (H — F) smectic value of 61.3° for the 2-fluoro-compounds in Table 1 must be caused by steric interactions of the 2-fluoro-substituent. Probably therefore, the angle,  $\theta$ , for the sterically unaffected 4-*p*-n-alkoxybenzylideneaminobiphenyls is significantly lower in the smectic than in the nematic state. Indeed, the smectic state is an approximation to the solid state, and as we pass through the sequence



the molecular disorder increases. It is not, therefore, unreasonable to propose that the angle,  $\theta$ , for the biphenyl nucleus will also increase in this order, when a compound passes from one of these states to another. The present results suggest that this is so, but as yet give no evidence as to the degree of change of  $\theta$  with change in state.

However, since a given substituent gives rise to such markedly different mesomorphic thermal stabilities dependent upon whether or not it occupies one of the angular positions in the biphenyl nucleus, the following conclusions may be reached:

(1) The molecules of the unsubstituted and substituted compounds do not rotate continuously as units about their major axes in the mesomorphic state.

(2) Introduction of the 2- or the 2'-substituent increases the interplanar angle,  $\theta$ , relative to that in the parent or the 3- or 3'-substituted isomer. In view of this, Wiegand's explanation<sup>10</sup> of the mesomorphic behaviour of 4,4'-di-(*p*-methoxybenzylideneamino)-2,2'-dichloro- and -dimethyl-biphenyl is open to doubt, because the biphenyl ring system appears to be non-planar irrespective of whether the two substituents adopt a *cis*- or a *trans*-arrangement.

(3) Continuous free rotation about the 1,1'-bond of the biphenyl nucleus of either the sterically affected or the sterically unaffected compounds clearly does not occur in the mesomorphic state.

(4) The substituted or unsubstituted biphenyl nucleus in a 4-*p*-n-alkoxybenzylideneaminobiphenyl must therefore adopt some satisfactory interplanar angle,  $\theta$ , such that a balance is achieved between the residual crystal forces in the mesophase (tending to make the system planar) and the steric repulsions between the hydrogen atoms or substituents in the 2- and the 2'-positions (tending to increase  $\theta$ ).

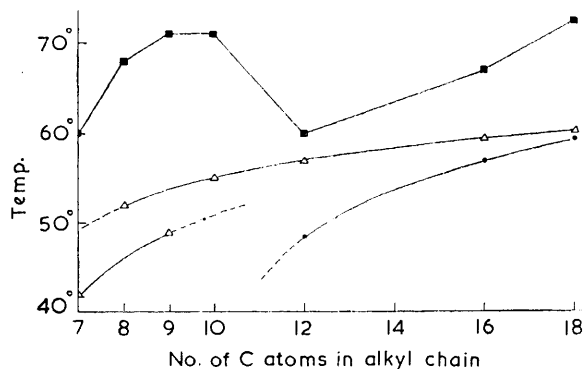
A further point of interest from this study is connected with the trends of the mesomorphic transition temperatures, with increasing alkyl chain length, for certain of the series.

When the mesomorphic transition temperatures for a homologous series of compounds exhibiting smectic and nematic properties are plotted against the number of carbon atoms in the *n*-alkyl group, the following regularities are usually observed. (a) The nematic-isotropic transition temperatures lie on two curves which fall steeply at first and then more gradually as the series is ascended. The uppermost curve corresponds to homologues containing an even number of carbon atoms in the alkyl chain, and *vice versa*. The shapes of these curves are explained in terms of the trends in the intermolecular forces as the series is ascended, the weak and decreasing terminal interactions having an overriding effect and giving a falling curve, the increasing lateral interactions merely reducing the rate of fall of the nematic-isotropic transition line. (b) The smectic-nematic transition temperatures rise rapidly at first, then more gradually, the smectic-nematic curve usually merging smoothly with the nematic-isotropic curves at relatively long chain lengths.

For the derivatives discussed now, only parts (C<sub>7</sub>—C<sub>10</sub>) of homologous series have been studied, but it is apparent that the nematic-isotropic transition lines for the 2- and the 2'-substituted compounds do not conform to the general behaviour outlined under (a) above. As usual, two curves exist, but these appear to rise as the alkyl chain is extended. To verify this, our series of 2-methyl compounds was extended to include the dodecyl, hexadecyl, and octadecyl ethers. The plot of transition temperature against chain length is in the Figure. It is noteworthy that the smectic-nematic curve does not join the nematic-isotropic line even at the octadecyl ether, and this strongly suggests that the lateral intermolecular attractions for these systems are abnormally low. Indeed, this would be expected because of the difficulties of attaining a close, economical, side-by-side packing of the sterically affected molecules. Now the nematic-isotropic transition will be governed by whichever is the weaker—the terminal or the lateral intermolecular attractions. If, in these sterically affected systems, the weak intermolecular lateral attractions exert a dominant effect, then the nematic-isotropic transition line should rise as these attractions grow stronger with increasing alkyl chain length, levelling off as the

decreasing terminal interactions begin to take over as the cause of breakdown of the nematic molecular order. A maximum in the nematic-isotropic transition line would be expected if this interpretation is correct, but it will be reached only at chain lengths considerably greater than octadecyl for the series of 2-methyl compounds under consideration.

Finally, attention is drawn to the nematic-isotropic transition temperature curves for the 4-*p*-*n*-alkoxybenzylideneamino-3-bromo- and -chloro-biphenyls. In each case, the alternation of the transition temperatures gives two transition lines, but, whilst that for the even members falls slightly or remains horizontal with increasing chain length, the line for the odd members rises slightly (1–1.5°). It seems, therefore, that the curve



4-*p*-*n*-Alkoxybenzylideneamino-2-methylbiphenyls. Temp. of transition: solid-isotropic (■), nematic-isotropic (Δ), and smectic-nematic (●).

for the even members has either passed or just attained its maximum, whilst that for the odd members has not. The behaviour of these 3-substituted isomers is in fact intermediate between that of the 2- and the 2'-substituted biphenyl derivatives, and that of a series giving normal, falling nematic-isotropic transition lines. Indeed the decreases in nematic thermal stability brought about by the 3-chloro- and 3-bromo-substituents are much smaller than those brought about by the same substituents in the 2- and the 2'-position, but it has already been noted that these decreases are greater than might have been expected. This has been explained either by the fact that the *trans*-configuration for the 3-substituted monoanils results in a broad, awkwardly shaped molecule or that a steric effect operates in the *cis*-configuration. In either case the intermolecular lateral attractions will be weakened, allowing the explanation of the rising transition lines for the 2- and the 2'-substituted compounds to be applied to the 3-chloro- and 3-bromo-biphenyl derivatives.

Effects of this kind are discussed more fully elsewhere,<sup>12</sup> and have been related to the unusual trends of the mesomorphic transition temperatures of the 2-*p*-*n*-alkoxybenzylideneamino-fluorenones.<sup>8</sup>

#### EXPERIMENTAL

M. p.s are corrected for exposed stem.

*Determination of Transition Temperatures.*—The m. p.s and mesomorphic transition temperatures were determined in our usual way, by using an electrically heated microscope block<sup>13</sup> in conjunction with a projection system.<sup>14</sup> Transition temperatures below room temperature had to be determined by normal capillary methods, the sample being allowed to warm slowly

<sup>12</sup> Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press Inc., London and New York, 1962, Chapter IX, p. 197.

<sup>13</sup> Gray, *Nature*, 1953, **172**, 1137.

<sup>14</sup> Gray and Ibbotson, *Nature*, 1955, **176**, 1160.

in a stirred low-temperature bath. Several of the transition temperatures for the iodo-derivatives which occur just above room temperature were determined by both methods: no differences were then detected.

*Materials.*—The nitro-compounds required for reduction to the substituted 4-aminobiphenyls were obtained in most cases by the Gomberg and/or *N*-acetylnitrosamine reactions. Although the latter method was successful in most cases, 2-, 2'-, and 3'-methyl-4-nitrobiphenyl could be prepared pure only by the Gomberg method. Condensation of a diazo- or *N*-acetylnitrosoamino-compound with nitrobenzene may give three isomers; separation of the required 4-nitro-isomer was generally possible by fractional crystallisation or by fractional distillation followed by crystallisation, the 4-nitrobiphenyl always separating first. With 3'-chloro- and 2'-iodo-4-nitrobiphenyl, the crude mixture of isomers was dissolved in benzene and passed down a column of activated alumina. This did not appear to separate the isomers, but, after removal of the benzene, the product crystallised from ethanol and light petroleum. Pure 2'-chloro- and 2'-bromo-4-nitrobiphenyl could not be obtained by these methods and were prepared by alternative routes.

*N-Acetylnitrosamine Reaction.*—The experimental conditions used were identical with those described<sup>6</sup> for the preparation of methyl 3'-fluoro-4'-n-octyloxybiphenyl-4-carboxylate, the methyl benzoate being replaced by benzene or nitrobenzene (500 ml.) for each 10 g. of acetylamine. The solvents were removed from the reaction mixture, and the residue was crystallised, or it was fractionally distilled or chromatographed and then crystallised from benzene, ethanol, or benzene-light petroleum.

*Gomberg Reaction.*—The amine (0.5 mole) was diazotised in the usual manner, and the solution of the diazonium salt filtered into benzene or nitrobenzene (1 l.), stirred, and maintained at 5°. Over a period (60 min.), 40% aqueous sodium hydroxide was added dropwise to the stirred mixture, at <10°, until about a 2% excess of alkali was present. The emulsion was stirred for 20 hr., during which the colour changed to dark red-brown. The layers were separated, and, after being washed with water, the benzene or nitrobenzene layer was dried, and the solvent was removed. The product was isolated as described above.

Listed in Table 2 are the substituted 4-nitrobiphenyls prepared by the *N*-acetylnitrosamine and the Gomberg reaction. Of these, five were known although the m. p. of 2-chloro-4-nitrobiphenyl could not be raised to the value reported by Mascarelli *et al.* Two of the new compounds, 2-bromo- and 2-iodo-4-nitrobiphenyl, were obtained by *N*-acetylnitrosamine reactions which give rise to a single biphenyl derivative in each case, since benzene was used as the solvent, and their constitutions are not open to doubt. Proofs of constitution for the remaining substituted 4-nitrobiphenyls are given below.

*3-Chloro-4'-nitrobiphenyl.*—This compound was characterised by its unambiguous preparation by deamination of 4-amino-3-chloro-4'-nitrobiphenyl. 4-Acetamido-3-chloro-4'-nitrobiphenyl<sup>15</sup> (14 g.) was heated under reflux for 3 hr. with ethanol (500 ml.) and concentrated hydrochloric acid (250 ml.). Slow dissolution of the acetylamine was followed by separation of the hydrochloride as needles. After cooling, the hydrochloride was filtered off and washed with ethanolic hydrochloric acid. The salt was basified with 2*N*-aqueous ammonia, and the crude nitro-amine crystallised from methanol. The orange needles (9 g., 75%) had m. p. 127—127.5° (Found: C, 50.5; H, 4.4; Cl, 16.5; N, 13.3. C<sub>12</sub>H<sub>9</sub>ClN<sub>2</sub>O<sub>2</sub> requires C, 50.8; H, 4.2; Cl, 16.7; N, 13.2%). The 4-amino-3-chloro-4'-nitrobiphenyl (7.5 g., 0.03 mole) was dissolved in hot 2*N*-aqueous hydrochloric acid (250 ml.) and acetic acid (200 ml.), stirred, and cooled rapidly to 0° to afford the hydrochloride as a fine suspension, and this was diazotised at 0° by dropwise addition of sodium nitrite (2.1 g., 0.0304 mole) in water (10 ml.). The clear solution was added to 30% hypophosphorous acid (132 g., 0.6 mole) and stirred at 0° for 6 hr. Reduction was completed by stirring the mixture at room temperature overnight. The light brown powder was filtered off and crystallised from aqueous methanol (charcoal). The pale yellow plates of 3-chloro-4'-nitrobiphenyl (3 g., 42.5%) had m. p. 92°. Mixed m. p.s with either of the products obtained from the biaryl syntheses showed no depression.

*3-Methyl-4'-nitrobiphenyl.*—This compound was first prepared by the *N*-acetylnitrosamine reaction, which produced an oily mixture of isomeric nitro-compounds. The mixture was reduced and the anils prepared and purified by crystallisation. When it was realised that the isomeric 3-methyl-4-nitrobiphenyl is crystalline and not an oil as stated in the literature,<sup>16</sup> the

<sup>15</sup> Scarborough and Waters, *J.*, 1927, 1137.

<sup>16</sup> Grieve and Hey, *J.*, 1932, 2246.

TABLE 2.  
Substituted 4-nitrobiphenyls.

Subst.	Method	Yield (%)	M. p. Found	Ref.	Analyses
3-Me	1*	10	52—53°	a	Found: C, 72.8; H, 5.1; N, 6.4. C <sub>13</sub> H <sub>11</sub> NO <sub>2</sub> requires C, 73.2; H, 5.2; N, 6.6%.
2-Cl	1	56	70.5	b	Found: C, 61.5; H, 3.5; Cl, 15.3; N, 6.0. Calc. for C <sub>12</sub> H <sub>9</sub> ClNO <sub>2</sub> : C, 61.7; H, 3.45; Cl, 15.2; N, 6.0%.
2-Br	1	34	86	—	Found: C, 52.2; H, 3.0; Br, 28.5; N, 4.9. C <sub>12</sub> H <sub>8</sub> BrNO <sub>2</sub> requires C, 51.8; H, 2.9; Br, 28.8; N, 5.0%.
2-I	1†	21.5	92—93	—	Found: C, 44.0; H, 2.2; I, 39.6; N, 4.4. C <sub>12</sub> H <sub>8</sub> INO <sub>2</sub> requires C, 44.3; H, 2.5; I, 39.0; N, 4.3%.
2-Me	2	2.5	55—56	c	Found: C, 73.1; H, 5.4; N, 6.3%.
2'-I	1‡	5.5	99—101.5	d	Found: C, 44.3; H, 2.5; I, 40.4; N, 4.5%.
2'-Me	2	2	103—104	e	Found: C, 72.9; H, 5.0; N, 6.7%.
3'-Cl	1	5.5	91—92	—	Found: C, 61.4; H, 3.4; Cl, 15.4; N, 5.9%.
	2	2.5	91—92	—	Found: C, 61.5; H, 3.4; Cl, 15.4; N, 5.9%.
3'-Br	1	0.5	93—94	f	Found: C, 52.0; H, 2.8; Br, 28.4; N, 5.0%.
3'-Me	2	0.5	63	—	Found: C, 73.5; H, 5.3; N, 6.7%.

Method: 1, *N*-Acetylnitrosamine reaction. 2, Gomberg reaction.

\* From 3-methyl-4-nitroacetanilide (Cohen and Dakin, *J.*, 1903, **83**, 333) which had been crystallised twice from ethanol and once from benzene. The m. p. of the acetylamine was 120° (Found: C, 55.8; H, 5.3; N, 14.2. Calc. for C<sub>9</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>: C, 55.7; H, 5.15; N, 14.4%). The amine had m. p. 136°. Cohen and Dakin record m. p.s of 103—104° and 133—134° for the acetylamine and the amine, respectively. † From 2-iodo-4-nitroacetanilide (Willgerodt and Arnold, *Ber.*, 1901, **34**, 3343; Elbs and Volk, *J. prakt. Chem.*, 1919, **99**, 273); the m. p. of the acetylamine was 136—138°, compared with that of 128—130° recorded by Elbs and Volk. ‡ From *o*-iodoacetanilide (Doht, *Monatsh.*, 1904, **24**, 956).

(a) Grieve and Hey (*J.*, 1932, 2246) describe this compound as an oil. (b) Mascarelli, Gatti, and Longo (*Gazzetta*, 1933, **63**, 654) give m. p. 73—74°. (c) Bamberger (*Ber.*, 1895, **28**, 403) gives m. p. 56°. (d) Schin-ichi Sako (*Bull. Chem. Soc. Japan*, 1934, **9**, 150) give m. p. 100—101.5°. (e) France, Heilbron, and Hey (*J.*, 1939, 1286) give m. p. 103—104°. (f) Case (*J. Amer. Chem. Soc.*, 1938, **60**, 424) gives m. p. 94—95°.

3-methyl-4'-nitrobiphenyl was made again, this time by the Gomberg reaction. The mixture of nitro-compounds was distilled under reduced pressure, then further fractionated through a short Vigreux column. Three fractions were collected, having b. p. 150—152°, 160—162°, and 162—172°/2—3 mm. After some difficulty, the last of these fractions was obtained solid and, on crystallisation from methanol (twice) and light petroleum (b. p. 40—60°) (twice), a small amount (0.5%) of a compound of m. p. 63° was obtained. Since no reference is made in the literature to 3-methyl-4'-nitrobiphenyl, the material of m. p. 63° was nitrated at 100° for 3.5 hr. with nitric acid (20 ml.; *d* 1.355 at 34°); 3-methyl-4,4'-dinitrobiphenyl separated on cooling as fine, pale straw-coloured needles, m. p. 200—201° (Found: C, 60.6; H, 4.0; N, 10.9. Calc. for C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub>: C, 60.5; H, 3.9; N, 10.85%). Grieve and Hey record the m. p. of this compound as 197°.<sup>16</sup> When the pure 3-methyl-4'-nitrobiphenyl was reduced and converted into the anils, these were found to be identical with those made from the crude mixture of isomeric amines.

3-Methyl-4-nitrobiphenyl is reported<sup>16</sup> as an oil, which on reduction and acetylation gives an acetylamine of m. p. 166°. Grieve and Hey prepared this nitro-compound by nitration of 3-methylbiphenyl, and repeating their procedure indeed gave an oil. Moreover, reduction and acetylation gave the acetylamine, m. p. 166°, reported by Grieve and Hey. However, several crystallisations from benzene raised the m. p. of the acetylamine to 171—172°. The 3-methyl-4-nitrobiphenyl was then prepared by the *N*-acetylnitrosamine reaction from 3-methyl-4-nitroacetanilide, a solid of m. p. 52—53° being obtained after careful crystallisation. On reduction and acetylation, this gave an acetylamine of m. p. 172° after only one crystallisation. Thus it appears that, although the nitration of 3-methylbiphenyl gives largely the 4-nitro-isomer, the product also contains other isomers which produce an oily mixture.

*Substituted 4-Nitro- and 4-Amino-biphenyls Prepared by Other Routes.*—2-Fluoro-4-nitrobiphenyl was obtained by the nitration of 2-fluorobiphenyl<sup>17</sup> by the method of Van Hove.<sup>18</sup> The distillate, consisting of various nitro-isomers, crystallised from ethanol, and on repeated

<sup>17</sup> Schiemann and Roselius, *Ber.*, 1929, **62**, 1809.

<sup>18</sup> Van Hove, *Bull. Classe Sci., Acad. roy. Belg.*, 1923, **32**, 520.



filtration and concentration of the mother liquors, three products were obtained: (a) slightly soluble, long colourless needles of impure 2-fluoro-4-nitrobiphenyl, m. p. 53—76°; (b) bulkier, colourless needles of impure 2-fluoro-4'-nitrobiphenyl, m. p. 46—64°; and (c) pale brown prisms of impure 2-fluoro-2'-nitrobiphenyl. Separation of the 4'- and the 2'-nitro-isomer is facilitated to some extent by their different crystal forms, which permit some degree of mechanical separation. The 2-fluoro-2'-nitrobiphenyl was not required for this work and was not purified further, and it was not found possible to obtain pure 2-fluoro-4'-nitrobiphenyl by crystallisation or chromatography. Three crystallisations of the crude 2-fluoro-4-nitrobiphenyl from ethanol gave long, colourless needles (6 g., 6%), m. p. 81—82°. Van Hove<sup>18</sup> records m. p. 81° for this isomer.

*2-Chloro- and 2-Bromo-4'-nitrobiphenyl.* 2-Acetamido-4'-nitrobiphenyl<sup>19</sup> was hydrolysed to 2-amino-4'-nitrobiphenyl, m. p. 158—159°, which was diazotised and converted into 2-chloro-4'-nitrobiphenyl (59%), as described by Case<sup>20</sup> who obtained m. p. 74—75°. On crystallisation from ethanol, dimorphic forms of this compound are obtained. Slow crystallisation from a dilute solution gave orange-yellow needles, m. p. 74—75°; more rapid crystallisation from a more concentrated solution yielded a buff coloured solid, m. p. 79—80°. The

TABLE 3.  
Substituted 4-acetylaminobiphenyls.

Subst.	M. p.	Ref.	Analyses.
3-Me	172°	a	Found: C, 79.9; H, 6.9; N, 6.0. Calc. for C <sub>15</sub> H <sub>15</sub> NO: C, 80.0; H, 6.7; N, 6.2%.
2-F	157—158	b	Found: C, 73.0; H, 5.4; N, 5.9. Calc. for C <sub>14</sub> H <sub>12</sub> FNO: C, 73.4; H, 5.2; N, 6.1%.
2-Cl	145—146	—	Found: C, 68.2; H, 4.9; Cl, 14.6; N, 5.8. C <sub>14</sub> H <sub>12</sub> ClNO requires C, 68.4; H, 4.9; Cl, 14.5; N, 5.7%.
2-Br	161—162	—	Found: C, 57.9; H, 4.2; Br, 27.5; N, 4.7. C <sub>14</sub> H <sub>12</sub> BrNO requires C, 57.9; H, 4.1; Br, 27.6; N, 4.8%.
2-I	177—178	—	Found: C, 49.8; H, 3.7; I, 37.6; N, 4.0. C <sub>14</sub> H <sub>12</sub> I NO requires C, 49.9; H, 3.7; I, 37.7; N, 4.2%.
2-Me	126	c	Found: C, 80.2; H, 7.0; N, 6.3%.
2'-Cl	161	d	Found: C, 68.2; H, 5.0; Cl, 14.7; N, 5.8%.
2'-Br	156—157	e	Found: C, 58.0; H, 4.2; Br, 27.2; N, 4.7%.
2'-I	161—162	f	Found: C, 49.8; H, 3.8; I, 38.0; N, 4.4%.
2'-Me	143—144	g	Found: C, 80.1; H, 6.6; N, 6.0%.
3'-Cl	183.5—184	—	Found: C, 68.2; H, 4.7; Cl, 14.6; N, 5.9%.
3'-Br	182—183	h	Found: C, 58.3; H, 4.3; Br, 27.3; N, 4.6%.
3'-Me	—*	—	—

(a) Grieve and Hey (*J.*, 1932, 2246) give m. p. 166°. (b) Van Hove (*Bull. Classe Sci., Acad. roy. Belg.* 1923, **32**, 520) gives m. p. 155°. (c) Bamberger (*Ber.*, 1895, **28**, 403) gives m. p. 125°. (d) Harris (*U.S.P.* 2,126,009) gives m. p. 162°. (e) Case (*J. Amer. Chem. Soc.*, 1938, **60**, 424) gives m. p. 155—156°. (f) Schin-ichi Sako (*Bull. Chem. Soc. Japan*, 1935, **10**, 585) gives m. p. 162—163°. (g) France, Heilbron, and Hey (*J.*, 1939, 1286) give m. p. 143—144°. (h) Case (*loc. cit.*) gives m. p. 182—183°.

\* Only a small amount (see above) of 3-methyl-4'-nitrobiphenyl was available for reduction, and this was used to prepare the anils.

corresponding bromo-compound was made by using 48% hydrobromic acid and cuprous bromide; the yield was 58%, and the m. p. 84° (lit.,<sup>19</sup> 82.5°).

*4-Amino-3-chlorobiphenyl.* This was obtained by Scarborough and Waters<sup>21</sup> by hydrolysis of the corresponding acetyl derivative. This method was used in the present work, giving an 85% yield of the amine, m. p. 69.5—70°.

4-Acetamidobiphenyl, obtained in 92—95% yield by the method of Campbell, Anderson, and Gilmore,<sup>22</sup> was chlorinated by dichloramine-τ, rather than by the direct chlorination procedure of Scarborough and Waters.<sup>21</sup> 4-Acetamidobiphenyl (42.2 g., 0.2 mole), dichloramine-τ (24 g., 0.1 mole), acetic acid (750 ml.), and concentrated hydrochloric acid (1.5 ml.) were heated on a steam-bath for 5 hr. Water (250 ml.) was then added to the solution which was left overnight. The acetylamine crystallised as colourless needles and was filtered off, washed with aqueous

<sup>19</sup> Scarborough and Waters, *J.*, 1927, 96.

<sup>20</sup> Case, *J. Amer. Chem. Soc.*, 1943, **65**, 2137.

<sup>21</sup> Scarborough and Waters, *J.*, 1926, 559.

<sup>22</sup> Campbell, Anderson, and Gilmore, *J.*, 1940, 449.

TABLE 4.

4-p-n-Alkoxybenzylideneamino-2-fluorobiphenyls.									
Alkyl	Found (%)				Formula	Required (%)			
	C	H	F			C	H	F	
Heptyl	80.3	7.1			C <sub>26</sub> H <sub>28</sub> FNO	80.2	7.2		
Octyl	80.4	7.5			C <sub>27</sub> H <sub>30</sub> FNO	80.4	7.4		
Nonyl	80.8	7.6			C <sub>28</sub> H <sub>32</sub> FNO	80.6	7.7		
Decyl	80.9	8.0			C <sub>29</sub> H <sub>34</sub> FNO	80.7	7.9		

4-p-n-Alkoxybenzylideneamino-3-chlorobiphenyls.									
Alkyl	Found (%)				Formula	Required (%)			
	C	H	Cl			C	H	Cl	
Heptyl	76.7	6.9	8.7		C <sub>26</sub> H <sub>28</sub> ClNO	76.9	6.9	8.9	
Octyl	77.1	7.1	8.6		C <sub>27</sub> H <sub>30</sub> ClNO	77.2	7.1	8.6	
Nonyl	77.6	7.2	8.2		C <sub>28</sub> H <sub>32</sub> ClNO	77.4	7.4	8.3	
Decyl	77.8	7.4	8.1		C <sub>29</sub> H <sub>34</sub> ClNO	77.7	7.6	8.0	

4-p-n-Alkoxybenzylideneamino-2-, -2'-, and -3'-chlorobiphenyls.									
Alkyl	2-Chloro-Found (%)			2'-Chloro-Found (%)			3'-Chloro-Found (%)		
	C	H	Cl	C	H	Cl	C	H	Cl
Heptyl	77.0	6.9	8.7	76.6	6.6	9.0	77.1	7.1	8.6
Octyl	77.4	7.2	8.5	77.4	6.9	8.6	77.3	7.2	8.5
Nonyl	77.6	7.3	8.1	77.2	7.2	8.5	77.4	7.3	8.5
Decyl	77.8	7.7	7.7	77.5	7.5	8.2	77.4	7.5	8.2

4-p-n-Alkoxybenzylideneamino-3-bromobiphenyls.									
Alkyl	Found (%)				Formula	Required (%)			
	C	H	Br			C	H	Br	
Heptyl	69.5	6.3	17.5		C <sub>26</sub> H <sub>28</sub> BrNO	69.4	6.2	17.8	
Octyl	69.5	6.5	17.5		C <sub>27</sub> H <sub>30</sub> BrNO	69.8	6.5	17.3	
Nonyl	70.3	6.6	17.0		C <sub>28</sub> H <sub>32</sub> BrNO	70.2	6.7	16.8	
Decyl	70.9	7.0	16.7		C <sub>29</sub> H <sub>34</sub> BrNO	70.7	6.9	16.3	

4-p-n-Alkoxybenzylideneamino-2-, -2'-, and -3'-bromobiphenyls.									
Alkyl	2-Bromo-Found (%)			2'-Bromo-Found (%)			3'-Bromo-Found (%)		
	C	H	Br	C	H	Br	C	H	Br
Heptyl	69.5	6.1	17.5	69.6	6.3	17.9	69.8	6.1	17.7
Octyl	69.7	6.3	17.0	69.7	6.4	17.2	70.0	6.7	17.6
Nonyl	70.4	6.8	16.5	70.3	6.6	16.9	69.9	6.7	17.0
Decyl	70.7	7.1	16.2	70.7	6.8	16.0	70.5	6.8	16.5

4-p-n-Alkoxybenzylideneamino-2-, and -2'-iodobiphenyls.										
Alkyl	2-Iodo-Found (%)			2'-Iodo-Found (%)			Formula	Required (%)		
	C	H	I	C	H	I		C	H	I
Heptyl	62.9	5.6	25.4	62.8	5.7	25.6	C <sub>26</sub> H <sub>28</sub> I NO	62.8	5.6	25.6
Octyl	63.6	5.9	24.5	63.2	6.0	25.0	C <sub>27</sub> H <sub>30</sub> I NO	63.4	5.9	24.9
Nonyl	64.3	6.1	24.5	63.8	6.1	23.7	C <sub>28</sub> H <sub>32</sub> I NO	64.0	6.1	24.2
Decyl	64.7	6.3	23.2	64.5	6.5	23.3	C <sub>29</sub> H <sub>34</sub> I NO	64.6	6.3	23.6

4-p-n-Alkoxybenzylideneamino-3-, -2-, -2'-, and -3'-methylbiphenyls.											
Alkyl	3-Methyl Found (%)		2-Methyl Found (%)		2'-Methyl Found (%)		3'-Methyl Found (%)		Formula	Required (%)	
	C	H	C	H	C	H	C	H		C	H
Heptyl	84.0	8.1	84.3	8.0	84.0	8.2	83.9	7.9	C <sub>27</sub> H <sub>31</sub> NO	84.1	8.1
Octyl	84.3	8.4	84.4	8.3	84.3	8.3	84.2	8.3	C <sub>28</sub> H <sub>33</sub> NO	84.2	8.3
Nonyl	84.3	8.6	84.6	8.5	84.5	8.6	84.2	8.6	C <sub>29</sub> H <sub>35</sub> NO	84.3	8.5
Decyl	84.2	8.7	84.4	8.8	84.4	8.8	84.4	8.7	C <sub>30</sub> H <sub>37</sub> NO	84.3	8.7
Dodecyl	—	—	84.6	9.1	—	—	—	—	C <sub>32</sub> H <sub>41</sub> NO	84.4	9.0
Hexadecyl	—	—	84.6	9.8	—	—	—	—	C <sub>36</sub> H <sub>49</sub> NO	84.6	9.6
Octadecyl	—	—	84.8	9.7	—	—	—	—	C <sub>38</sub> H <sub>53</sub> NO	84.6	9.8

acetic acid (75%), and dried. The yield was 67.7%, and the m. p. 146—147°; Scarborough and Waters<sup>21</sup> record the same m. p.

*4-Amino-3-bromobiphenyl.* 4-Acetamidobiphenyl (3 g.) and *N*-bromosuccinimide (3 g.) were heated in chloroform (50 ml.) under reflux for 2 hr., and left overnight. The precipitated succinimide was filtered off. Evaporation of the chloroform gave 4-acetamido-3-bromobiphenyl (1.8 g., 44%), m. p. 161° (from acetic acid). The acetylamine was hydrolysed under reflux in ethanol (50 ml.) and 48% hydrobromic acid (50 ml.) for 1 hr. On removal of some of the ethanol by distillation, the hydrobromide separated. The suspension was cooled, and the hydrobromide filtered off and basified with 2*N*-aqueous ammonia. Crystallisation from light petroleum (b. p. 60—80°) gave the amine, m. p. 66°. Kenyon and Robinson<sup>23</sup> record the above m. p.s for the amine and its acetyl derivative.

*Reduction of Substituted 4-Nitro- to 4-Amino-biphenyls.*—The substituted 4-nitrobiphenyl (2 g., 1 mol.) was heated in ethanol (20 ml.), with stannous chloride (8 g., 4 mol.) and concentrated hydrochloric acid (10 ml.) on a steam-bath for 2 hr., then poured into an excess of 5*N*-aqueous sodium hydroxide. The amine was extracted with carbon tetrachloride, and the extract washed several times with water and dried. Removal of the solvent yielded light brown viscous oils, which were used without purification for the preparation of the anils. With one exception, each of the amines prepared in this way was, however, characterised by the preparation and purification of its acetyl derivative. The results are summarised in Table 3.

*Substituted 4-p-n-Alkoxybenzylideneaminobiphenyls.*—To the substituted 4-aminobiphenyl (0.2 g., 1 mol.) in hot ethanol (15 ml.), the *p*-*n*-alkoxybenzaldehyde<sup>24</sup> (alkyl = *n*-heptyl — *n*-decyl) (1.1 mol.) and a few drops of acetic acid were added. The mixture was heated on a steam-bath for 20 min., more ethanol being added if necessary to dissolve the precipitated anil. The mixture was cooled, and the crystalline product (see Table 4) filtered off, washed with ethanol, and crystallised from ethanol and from benzene–light petroleum (b. p. 40—60°) until the constant m. p.s and mesomorphic transition temperatures recorded in Table 1 were obtained.

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THE UNIVERSITY, HULL.

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<sup>23</sup> Kenyon and Robinson, *J.*, 1926, 3053.

<sup>24</sup> Gray and Jones, *J.*, 1954, 1467.