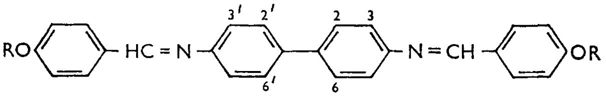
679. *Mesomorphism and Chemical Constitution. Part XIII.*[1] *Di-, Tri-, and Tetra-substituted 4,4′-Di-(*p*-n-alkoxybenzylideneamino)biphenyls*

By D. J. Byron, G. W. Gray, and B. M. Worrall

The effects of di-, tri-, and tetra-substitution on the mesomorphic properties of the 4,4′-di-(*p*-n-alkoxybenzylideneamino)biphenyls have been studied. The decreases in the mesomorphic transition temperatures resulting from the introduction of two or more identical substituents are approximately equal to the sums of the decreases which the single substituents would bring about in the different positions of the biphenyl ring system. Further evidence shows that the mesomorphic transition temperatures are particularly sensitive to substitution which increases twisting about the inter-annular bond of the biphenyl nucleus.

Exceptional cases [2] apart, substitution of the aromatic nucleus of a mesomorphic compound decreases [3] the mesomorphic thermal stabilities. Branching of a terminal alkyl chain exerts a similar effect, again by increasing the intermolecular separation and decreasing the intermolecular attractive forces. The decreases in thermal stability of the mesophases are often large, particularly if the substituent is bulky and weakly dipolar, and if it exerts a steric effect upon neighbouring groups.[1,4] The smectic and nematic thermal stabilities of a compound, and the ranges of temperature over which the mesophases exist, must therefore be considerable, if one is to study the effects of di- and poly-substitution upon the mesomorphic transition temperatures. Only Wiegand [5] has attempted this, by examining the effects of di- and tetra-substitution on the mesomorphic properties of 4,4′-di-(*p*-methoxybenzylideneamino)biphenyl (I; R = Me). The 2,2′,6,6′-tetrachloro- and -tetramethyl-derivatives were not mesomorphic, and this was explained in terms of the non-planar biphenyl ring system. The 2,2′- and 3,3′-dichloro- and -dimethyl-derivatives were mesomorphic and, for the 2,2′-disubstituted derivatives, Wiegand concluded that the molecules must adopt a planar *trans*- and not a non-planar *cis*-conformation.



(I)

Attention should be drawn to three points about Wiegand's work.

(i) The methyl ether (I; R = Me) has such a high nematic–isotropic transition temperature (>345°) that it was not measured, and decreases in transition temperature arising from substitution could not be properly assessed.

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[1] Part XII, S. J. Branch, D. J. Byron, G. W. Gray, A. Ibbotson, and B. M. Worrall, *J.*, **1964, 3279.**

[2] G. W. Gray and B. Jones, *J.*, 1955, 236.

[3] G. W. Gray and B. Jones, *J.*, 1954, 2556; G. W. Gray, B. Jones, and F. Marson, *J.*, **1956, 1417;** 1957, 393; G. W. Gray and B. M. Worrall, *J.*, 1959, 1545.

[4] D. J. Byron, G. W. Gray, A. Ibbotson, and B. M. Worrall, *J.*, **1963, 2246.**

[5] C. Wiegand, *Z. Naturforsch.*, 1951, **6**b, 240.

TABLE 1

Substituted 4,4′-di-(*p*-n-alkoxybenzylideneamino)biphenyls

		Temperature of transition to			Δt(H–X) *	
Substituents	n-Alkyl	Smectic	Nematic	Isotropic	Smectic	Nematic
2,2′-Dichloro-	Heptyl	—	117°	200°	—	160·2°
	Octyl	—	129·5	189		
	Nonyl	—	97·5	178·5		
	Decyl	—	107·5	171·5		
2,3′-Dichloro-	Heptyl	—	69	235	—	126·4
	Octyl	—	79	223·5		
	Nonyl	—	71	212		
	Decyl	—	73·5	204		
2,5-Dichloro-	Heptyl	—	121	225·5	—	134·6
	Octyl	—	117	215·5		
	Nonyl	—	114	204·5		
	Decyl	—	117·5	196		
2,6-Dichloro-	Heptyl	—	107·5	206·5	—	152·9
	Octyl	—	100·5	198		
	Nonyl	—	112	185·5		
	Decyl	—	106	178·5		
3,3′-Dichloro-	Heptyl	—	96	266·5	180·9° †	94·2
	Octyl	88·5°	103	256·5		
	Nonyl	78·5	136·5	245		
	Decyl	88	157·5	235		
2,2′,6-Trichloro-	Heptyl	—	119	133·5	—	222·1
	Octyl	—	108	128		
	Nonyl	—	112	116		
	Decyl	—	(114) ‡	116		
2,2′,6,6′-Tetrachloro-	Heptyl §	—	—	111·5	> 201 ¶	> 253·5 ¶
2,2′-Dibromo-	Heptyl	—	118	171	—	187·6
	Octyl	—	130	160·5		
	Nonyl	—	92	152·5		
	Decyl	—	101·5	145·5		
2,5-Dibromo-	Heptyl	—	134·5	203	—	157·7
	Octyl	—	114·5	192·5		
	Nonyl	—	105·5	179·5		
	Decyl	—	107	174		
2,6-Dibromo-	Heptyl	—	128·5	178	—	179·6
	Octyl	—	113	170·5		
	Nonyl	—	115·5	160		
	Decyl	—	117	153		
3,3′-Dibromo-	Heptyl	—	102·5	248·5	203·9 †	112·4
	Octyl	(80) ‡	96·5	238·5		
	Nonyl	83·5	112·5	226·5		
	Decyl	87·5	135·5	217		
2,2′-Dimethyl-	Heptyl	—	132·5	201	—	160·2
	Octyl	—	130	189·5		
	Nonyl	—	112·5	178·5		
	Decyl	—	104·5	170		
2,3′-Dimethyl-	Heptyl	—	91	234	—	127·1
	Octyl	—	88·5	223·5		
	Nonyl	—	88	211·5		
	Decyl	—	82·5	202·5		
2,5-Dimethyl-	Heptyl	—	118·5	230	—	131·5
	Octyl	—	114	219·5		
	Nonyl	—	113·5	208		
	Decyl	—	114·5	196·5		
3,3′-Dimethyl-	Heptyl	—	125	273	—	90·6
	Octyl	—	107	263		
	Nonyl	—	88	245·5		
	Decyl	—	79·5	236		

* Δt(H–X) smectic or nematic is the difference between the appropriate mesomorphic transition temperature (smectic–nematic; nematic–isotropic) of the 4,4′-di-(*p*-*n*-alkoxybenzylidenamino)biphenyl and that of the substituted derivative. In the Table, averaged Δt(H–X) values are quoted for each set of substituents in the given positions, and unless otherwise stated, these are for the four ethers (n-heptyl to n-decyl). † Averaged decrease for the octyl–decyl ethers. ‡ Transition temperatures in parenthesis are for monotropic mesophases. § Only a small quantity of 2,2′,6,6′-tetrachlorobenzidine was available and this was condensed with *p*-heptoxybenzaldehyde. ¶ Minimum decrease for heptyl ether only.

(ii) It is now known that the introduction of one quite simple 2-substituent into the biphenyl ring system of a mesomorphic compound greatly reduces the mesomorphic thermal stabilities. This is best explained [1,4] in terms of the steric effect of the 2-substituent, and Wiegand's assumption that the *trans*-conformation of a 2,2′-disubstituted derivative of the compound (I; R = Me) is planar in the nematic state is open to considerable doubt.

(iii) No information was obtained about decreases in smectic thermal stability, because the compound (I; R = Me) and its substituted derivatives exhibit only nematic properties.

To obtain more information about the effects of di- and poly-substitution on mesomorphic behaviour, and to meet the above points, we have chosen as the parent compounds a set of four ethers (I; R = n-heptyl, -octyl, -nonyl, and -decyl). These ethers exhibit both smectic and nematic mesophases, and accurate solid–smectic, smectic–nematic, and nematic–isotropic transition temperatures are available for the four compounds.[6] The mesomorphic thermal stabilities are still high, and the mesophases exist over an appreciable range of temperature. These ethers represent better parent compounds than (I; R = Me) from which to obtain information about the effects of di- and poly-substitution on mesomorphic properties. Moreover, the mesomorphic properties of nine monosubstituted derivatives of each of the four ethers (I; R = n-heptyl to n-decyl) are available [1] for comparison. Finally, a more critical judgement of the purity of the compounds under consideration is obtained if four homologues are studied for each substituent, or set of substituents, because quite small amounts of impurity cause deviations from the smooth relationships [7] of the curves obtained on plotting mesomorphic transition temperatures against the number of carbon atoms in the alkyl group.

Difficulties of synthesis limited the number of systems studied, but the results obtained for fifteen series are summarised in Table 1.

A few general comments may be made about the results in Table 1. The averaged decreases in mesomorphic thermal stability are in every case greater than 90°, and the introduction of more than one substituent clearly causes a very pronounced lowering of the mesomorphic transition temperature. As would be expected from earlier studies [1] of monosubstituted derivatives of the four ethers (I; R = n-heptyl to n-decyl), the largest values of Δt(H–X) are observed for systems carrying at least one 2-substituent, which causes twisting about the 1,1′-bond of the biphenyl ring system. In the limiting case, where four of these substituents are present, the 2,2′,6,6′-tetrachloro-derivative of compound (I; R = n-heptyl) is not mesomorphic.

Only with the 3,3′-disubstituted derivatives, in which steric effects are assumed not to operate, are smectic mesophases exhibited. In agreement with the earlier observations on the monosubstituted systems,[1] are the facts that (*a*) two bromo-substituents decrease the mesomorphic thermal stability more than two chloro-substituents, and (*b*) the smectic–nematic and nematic–isotropic transition temperatures of corresponding dimethyl- and dichloro-substituted systems are very closely similar.

3,3′-Disubstituted Derivatives.—Earlier studies of 3-substituted 4-*p*-n-alkoxybenzylideneaminobiphenyls [4] and 4,4′-di-(*p*-n-alkoxybenzylideneamino)biphenyls [1] suggest that the benzylideneamino-group and the 3-substituent are *trans*, so that the molecule adopts a planar conformation in which steric interaction is at a minimum. If this arrangement persists in the 3,3′-disubstituted derivatives of the ethers (I), two possible conformations, (II) and (III), are open to consideration. Of these, we would intuitively favour conformation (III), which is symmetrical about the long axis of the molecule. Furthermore, *X*-ray-crystallographic studies by Toussaint [8] have shown that the chloro-substituents are *trans* in the planar molecule of 3,3′-dichlorobenzidine.

An inspection of the Δt(H–X) values for the 3,3′-disubstituted compounds relative to

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[6] G. W. Gray, J. B. Hartley, A. Ibbotson, and B. Jones, *J.*, 1955, 4359.

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

[8] J. Toussaint, *Acta Cryst.*, 1948, **1**, 43.

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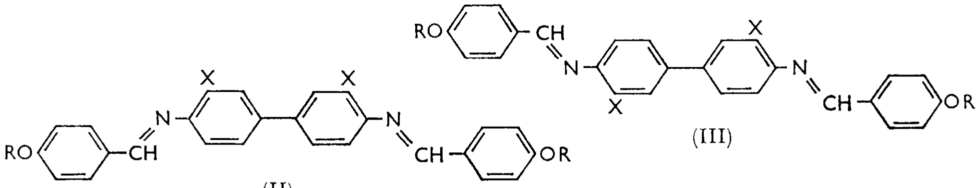
those for the 3-substituted systems helps to decide the probable conformation adopted in the mesomorphic state. Remembering that the orientation of the molecules in the nematic state is such that the parallel, rod-like molecules are free to slide past one another, one might argue that the second chloro-substituent, giving conformation (II), would not greatly affect the separation of the major molecular axes. Indeed, the dipole of the substituent might enhance the cohesive forces between the molecules. If conformation (II) is adopted, a small decrease, or possibly some increase in mesomorphic thermal stability, relative to the 3-substituted systems might be observed. On the other hand, the two chloro-substituents arranged as in conformation (III) should contribute almost equally in reducing the mesomorphic thermal stability. A two-fold decrease in smectic and nematic thermal stability would then be expected for the 3,3′-disubstituted derivatives compared with the 3-substituted derivatives of the ethers (I; R = n-heptyl to n-decyl); Table 2 shows that this is the case. This provides good evidence in favour of conformation (III) for the smectic and nematic states, and provides an interesting example of an additive effect of substitution on mesomorphic thermal stability; other instances of additivity of this kind will be referred to below.



(II)

(III)

The figures in Table 2 show too that Δ*t*(Cl–Br)nematic for the 3,3′-disubstituted compounds is 18·2°, about twice the corresponding values for the 3-substituted analogues (9·6°), and for the 3-substituted 4-*p*-n-alkoxybenzylideneaminobiphenyls (8°).[4] Similarly, Δ*t*(Cl–Br)smectic for the 3,3′-disubstituted compounds (23°) is approximately double the average decrease of this kind observed for other systems (11·25°).

TABLE 2

Averaged Δ*t*(H–X) smectic and nematic values for 3- and 3,3′-substituted derivatives of (I; R = n-heptyl to n-decyl)

Substituents		3-Substitution	3,3′-Disubstitution	Ratio
Chloro-	Smectic	90°	180·9°	2·01
	Nematic	48·4	94·2	1·95
Bromo-	Smectic	111·9	203·9	1·82
	Nematic	58	112·4	1·94
Methyl-	Smectic	110·2	—*	—
	Nematic	48	90·6	1·89

* If a predicted value of 220·4° for Δ*t*(H–Me) smectic is used, the average (C_8—C_{10}) smectic–nematic transition temperature for the 3,3′-dimethyl derivatives would be 92·8°, very close to the average m. p. of 91·5° for these compounds. Clearly, the average transition temperature must be somewhat lower than this, since smectic mesophases are not observed. However, the melts can be supercooled only a few degrees below the m. p. before crystallisation occurs, and there is little opportunity to detect a monotropic smectic mesophase.

Δ*t*(Cl–Br)smectic for the 3-substituted 4,4′-di-(*p*-n-alkoxybenzylideneamino)biphenyls (21·9°) is however almost as high as for the disubstituted compounds. This is difficult to explain, and we can only comment that, even when the benzylideneamino-group and the bromo-substituent are *trans*, the bromo-substituent exerts some steric pressure on the nitrogen. In the monobromo-derivatives, this may cause some bending of one of the benzylideneamino-groups out of the line of the rest of the molecule; the smectic mesophase should be much more sensitive than the nematic mesophase to such an effect. If this bond-bending occurred for conformation (III) for the dibromo-derivatives, the displacement of the two benzylideneamino-groups would be equal and opposite, and the molecule would preserve its linear character. The thermal stability of the smectic mesophase may not then suffer from the effect as in the monosubstituted derivatives.

2,5-*Disubstituted Derivatives.*—No smectic mesophases are exhibited by these compounds, and in the following sections we are solely concerned with nematic properties. The two substituents must be on opposite sides of the molecule, and we can expect that each would decrease the mesomorphic thermal stability, *i.e.*, an additive effect may again arise. The 5-substituent should decrease the nematic thermal stability, as in the 3-substituted derivatives of the ethers (I), by a breadth-increasing effect, and the 2-substituent should exert the same steric and breadth-increasing effects as in the 2-substituted derivatives of the ethers (I). If we then sum the averaged Δt(H–X)nematic values for the 2- and 3-substituted derivatives, the values should compare closely with the observed Δt(H–X)-nematic values for the 2,5-disubstituted derivatives, if the additivity concept is valid. The results in Table 3 show that the agreement is indeed close.

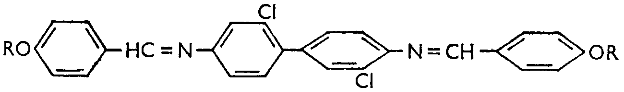
TABLE 3

Averaged values of Δt(H–X)nematic for substituted derivatives of (I; R = n-heptyl to n-decyl)

Substituents	2-Substitution	3-Substitution	Sum	Observed for 2,5-disubstitution
Chloro-	84·1°	48·4°	132·5°	134·6°
Bromo-	99·2	58	157·2	157·7
Methyl-	85·4	48	133·4	131·5

As in all cases, the methyl- and chloro-substituents exert very similar effects on nematic thermal stability. It is again noted that Δt(Cl–Br)nematic is 23·1°, approximately equal to the sum (24·7°) of the Δt(Cl–Br)nematic values for the 2- and 3-halogeno-derivatives of the ethers (I).

2,3′-*Disubstituted Derivatives.*—The position here is more subtle, because the 3′-substituent is in the ring rotated out of the plane of the structure (IV) by the steric effect of the 2-substituent. It is not easy to discuss such a molecule in terms of *cis*- and *trans*-conformations, and it is not possible to assess whether the 3′-substituent projecting upwards from the plane formed by the left-hand side of structure (IV) will have the same effect in decreasing nematic thermal stability as it will when projecting from the side of a 3-chloro-derivative of the ethers (I). If the effect is the same, then the Δt(H–X)nematic values should be the same as for the 2,5-disubstituted derivatives. The observed values, together with the predicted values in parentheses, for the 2,3′-disubstituted derivatives are: chloro, 126·4° (132·5°); methyl, 127·1° (133·4°). The additive nature of the effect of the two substituents seems again to apply, and the greater discrepancy between the observed and calculated values may be attributed to the somewhat smaller effect on the nematic thermal stability of a substituent projecting from the plane of the molecule. It will be noted that the 2,3′-dimethyl- and -dichloro-compounds are of almost the same nematic thermal stability.



(IV)

2,6-*Disubstituted Derivatives.*—As in the 2,5-disubstituted derivatives, the substituents are on opposite sides of the molecule. The 2-substituent will reduce the nematic thermal stability by both breadth-increasing and steric effects, and if the 6-substituent does not further increase the interplanar angle, θ, this should decrease the nematic thermal stability by a breadth-increasing effect. If the additivity of substituent effect applies, the nematic–isotropic transition temperatures of the 2,6-disubstituted and 2,5-disubstituted derivatives should be very close. Reference to the appropriate figures in Table 1 for dichloro- and dibromo-compounds shows that the 2,6-disubstituted compounds have a lower nematic thermal stability by 18—22°. Moreover, Δt(Cl–Br) for these compounds is 26·7° compared with 23·1° for the 2,5-disubstituted compounds. These facts suggest that the interplanar angle for the 2-substituted biphenyl ring system is increased by an additional 6-substituent. Molecular models show that a portion of the strain imposed by a 2-substituent is taken up by bending of bonds. Bond-bending relieves no strain in a symmetrical 2,6-disubstituted biphenyl, and greater rotation about the 1,1′-bond is necessary to relieve the steric pressure. More evidence that introduction of a 6-substituent further increases the interplanar angle is provided by the fact that the intensity and the wavelength of the conjugation band in the ultraviolet spectrum of biphenyl is reduced more for 2,6-dimethylbiphenyl than for 2-methylbiphenyl.[9] A probable explanation of the deviation from the additivity of substituent effect in these 2,6-disubstituted derivatives of the ethers (I) is therefore that the interplanar angle, θ, is significantly greater than in the 2-substituted analogues.

2,2′-*Disubstituted Derivatives*.—The position here is complicated by the possible existence of two conformations. If the *trans*-conformation is adopted, the 2-substituent should lower the nematic–isotropic transition temperature by both breadth-increasing and steric effects, and the 2′-substituent by only the former. However, the interplanar angle may be greater than for a simple 2-substituted biphenyl, as discussed above for the 2,6-isomers, and it might be expected that the nematic–isotropic transition temperature would be about the same as, or slightly higher (since the 2′-substituent projects from the plane of the molecule) than, those of the 2,6-disubstituted derivatives. The nematic thermal stabilities are in fact lower by 7—8°, and Δt(Cl–Br) = 27·6° is even higher than for the 2,6-isomers. This suggests that the interplanar angle, θ, is greater in the 2,2′-disubstituted systems, and this would be explained if the *cis*-conformation were adopted. There is considerable evidence[10] that the *cis*-conformation is favoured in 2,2′-disubstituted biphenyls. Beaven[9] has concluded from ultraviolet absorption spectra that the 2,2′-dihalogenobiphenyls adopt the *cis*-conformation, and Bastiansen[11] has reached the same conclusion from electron-diffraction work on 2,2′-dihalogenobiphenyls. Smare,[12] and Foweather and Hargreaves[13] have demonstrated that, in the crystalline states of 2,2′-dichlorobenzidine and *m*-tolidine hydrochloride, the chloro- and methyl-substituents, respectively, are *cis* to one another. Finally, studies of the dipole moments of 2,2′-dihalogenobiphenyls[14] indicate that the *cis*-conformation is preferred. The low nematic thermal stabilities for the 2,2′-disubstituted derivatives of the ethers (I) at least lend support to these conclusions.

Summarising the position, we may define the order of decreasing nematic thermal stability for the different arrangements of the substituents in disubstituted derivatives of the ethers (I) as 2,3′- > 2,5- > 2,6- > 2,2′-. The order supports the idea that the greater the interplanar angle for the biphenyl nucleus, the lower will be the nematic thermal stability.

2,2′,6-*Trichloro-derivatives*.—Only the 2,2′,6-trichloro-derivatives could be obtained pure, but further evidence for the additivity of substituent effect on nematic thermal stability is given by these compounds. Δt(H–Cl)nematic for the 2,2′-dichloro-derivatives is 160·2°. As a measure of the decrease in nematic stability caused by the 6-substituent, we may take the difference between Δt(H–Cl) for the 2-chloro- and 2,6-dichloro-derivatives = 68·8°. The calculated value for the 2,2′,6-trichloro-derivatives is therefore 229°. This is in quite good agreement with the observed value of Δt(H–Cl)nematic = 222·1°, considering that the enlargement of the angle, θ, on passing from the 2,2′-dichloro- to the 2,2′,6-trichloro-derivatives may not be as great as that on passing from the 2-chloro- to the 2,6-dichloro-derivatives.

2,2′,6,6′-*Tetrachloro-derivatives*.—If we sum Δt(H–Cl)nematic = 222·1° for the 2,2′,6-trichloro-compounds and the difference between Δt(H–Cl)nematic for the 2,2′,6-trichloro- and the 2,2′-dichloro-derivatives = 61·9° (the effect of the 6′-chloro-substituent), we obtain a

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[9] G. H. Beaven, " Steric Effects in Conjugated Systems," Butterworths, London, 1958, p. 22.
[10] Discussion in " Steric Effects in Conjugated Systems," Butterworths, London, 1958, p. 170.
[11] O. Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408; 1950, **4**, 926; 1954, **8**, 1593.
[12] D. L. Smare, *Acta Cryst.*, 1948, **1**, 150.
[13] F. Foweather and A. Hargreaves, *Acta Cryst.*, 1950, **3**, 81.
[14] A. C. Littlejohn and J. W. Smith, *J.*, 1954, 2552; G. H. Beaven and D. M. Hall, *J.*, 1956, 4637.

predicted value of 284° for Δt(H–Cl)nematic for the tetrachloro-derivatives. The predicted, average nematic–isotropic transition temperature would then be 61°. The heptyl ether, m. p. 111·5°, solidified to a glass at 89°, and it is obvious why this type of compound exhibits no mesophase.

The above studies of di-, tri-, and tetra-substituted 4,4'-di-(*p*-n-alkoxybenzylideneamino)biphenyls therefore provide evidence for the additivity of the effects of substituents on nematic thermal stabilities. When deviations from additivity are significant, there is reason to believe that the substituents cause an enlargement of the interplanar angle, θ, for the biphenyl nucleus. This further emphasises how sensitive nematic thermal stabilities are to steric effects. The results do *not* substantiate Wiegand's postulate [5] that 2,2'-disubstituted derivatives of compound (I; R = Me) adopt a planar conformation. Indeed, they confirm our earlier results,[1,4] which show that even 2-substituted derivatives of biphenyl are not planar in the liquid crystalline states, and suggest that the 2,2'-disubstituted systems have an even larger θ value than a 2-substituted analogue, because the *cis*-conformation is preferred.

Little further information on the effects of di- and poly-substitution on smectic thermal stabilities has been obtained, except for the 3,3'-disubstituted derivatives. However, since none of the systems exhibits smectic properties, it is clear that, as for monosubstitution,[1,4] di- and poly-substitution decrease the smectic thermal stabilities of the four ethers (I; R = n-heptyl to n-decyl) more than the nematic thermal stabilities. Thus, in the 2,6-dichloro-compounds, the average value of Δt(H–Cl)smectic must be >206·5°, compared with Δt(H–Cl)nematic = 152·9°.

EXPERIMENTAL

Melting points 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 [15] in conjunction with a projection system.[16]

Materials.—3,3'-Dimethylbenzidine (*o*-tolidine) of AnalaR purity was obtained from British Drug Houses Limited.

3,3'*Dichloro- and* 3,3',5,5'-*Tetrachloro-benzidine.*—*NN'*-Diacetylbenzidine, in glacial acetic acid, was di- and tetra-chlorinated according to the methods given by van Roosmalen.[17] For *NN'*-diacetyl-3,3'-dichlorobenzidine, twice the quantity of glacial acetic acid recommended by van Roosmalen was used. All the *NN'*-diacetylbenzidine then dissolved shortly after the start of the chlorination and a purer product resulted. The *NN'*-diacetyl-3,3'-dichloro- (66%) and -3,3',5,5'-tetrachloro-benzidine (59%) melted at 305—306° and 340—342°, respectively. van Roosmalen [17] records m. p.s of 313° for the dichloro-derivative and of 350° for the tetrachloro-derivative. The deacetylation [17] of these compounds with hot aqueous sulphuric acid afforded 3,3'-dichlorobenzidine (43%), m. p. 128—130°, and 3,3',5,5'-tetrachlorobenzidine (26%), m. p. 224—226°; van Roosmalen [17] reports 133° and 226°, respectively.

Other symmetrically substituted benzidines were obtained from the appropriate substituted nitrobenzenes. The substituted nitrobenzene (0·1 mole) was reduced to the corresponding hydrazobenzene by heating with zinc dust and sodium hydroxide in water, or for 3,3',5,5'-tetrachlorohydrazobenzene and 3,3'-dimethylhydrazobenzene, in aqueous ethanol. The hydrazo-compounds were crystallised from benzene–light petroleum (b. p. 40—60°), dissolved in ether, and rearranged to the corresponding benzidines with concentrated hydrochloric acid, except 3,3',5,5'-tetrachlorohydrazobenzene, which was rearranged by treating a suspension of the hydrazo-compound with hot, concentrated sulphuric acid–water (2 : 1, v/v). The benzidines were crystallised to constant m. p. from ethanol and from benzene–light petroleum (b. p. 40—60°). The relevant experimental methods and results are listed in Table 4.

Unsymmetrically substituted benzidines were obtained from the corresponding substituted azobenzenes. These were reduced and the resulting hydrazobenzenes were rearranged to the required benzidines.

[15] G. W. Gray, *Nature*, 1953, **172**, 1137.

[16] G. W. Gray and A. Ibbotson, *Nature*, 1955, **176**, 1160.

[17] F. L. W. van Roosmalen, *Rec. Trav. chim.*, 1934, **53**, 359.

TABLE 4

Symmetrically substituted hydrazobenzenes and benzidines

	Hydrazobenzenes			Benzidines		
Starting material	Substituents	Yield (%)	M. p.	Substituents	Yield (%)	M. p.
m-Chloronitrobenzene	3,3′-Cl$_2$ [a]	78	90—94° [b]	2,2′-Cl$_2$ [a]	70	165—166° [c]
3,5-Dichloronitrobenzene [d]	3,3′,5,5′-Cl$_4$ [e]	43·5	127—129 [f]	2,2′,6,6′-Cl$_4$ [g]	12·5	210—212 [h]
m-Bromonitrobenzene	3,3′-Br$_2$ [a]	67·5	107—108 [i]	2,2′-Br$_2$ [a]	25	151—152 [j]
o-Bromonitrobenzene	2,2′-Br$_2$ [a]	74	95—97 [k]	3,3′-Br$_2$ [a]	33	131·5—132·5
m-Nitrotoluene	3,3′-Me$_2$ [o]	[m]	—	2,2′-Me$_2$ [a]	33	88—89 [n]

[a] Prepared by the method of H. R. Snyder, C. Weaver, and C. D. Marshall (*J. Amer. Chem. Soc.*, 1949, **71**, 289). [b] A. Laubenheimer (*Ber.*, 1875, **8**, 1624) gives m. p. 94°. [c] A. Laubenheimer (*loc. cit.*) gives m. p. 167°. [d] Chlorination (B. Flürscheim, *J.*, 1908, **93**, 1772) of *p*-nitroaniline gave 2,6-dichloro-4-nitroaniline, which on deamination (R. B. Carlin and W. O. Forshey, *J. Amer. Chem. Soc.*, 1950, **72**, 793) afforded 3,5-dichloronitrobenzene. [e] Prepared by the method of F. L. W. van Roosmalen (ref. 17). [f] Lit.,[17] m. p. 129°. [g] Prepared by the method of R. B. Carlin and W. O. Forshey (*loc. cit.*). [h] The crude product was initially purified by chromatography on a short alumina column and elution with a large volume of benzene. R. B. Carlin and W. O. Forshey (*loc. cit.*) give m. p. 212·5—213·5°. [i] S. Gabriel (*Ber.*, 1876, **9**, 1406) gives m. p. 107—109°. [j] S. Gabriel (*loc. cit.*) gives m. p. 152°. [k] H. R. Snyder, C. Weaver, and C. D. Marshall (*loc. cit.*) give m. p. 97—98°. [l] H. R. Snyder, C. Weaver, and C. D. Marshall (*loc. cit.*) give m. p. 127—129°. [m] Because of its susceptibility to oxidation to the azo-compound on exposure to air this compound was not purified, but was extracted with ether and rearranged directly to the benzidine. [n] (Found: C, 78·9; H, 7·8. Calc. for $C_{14}H_{16}N_2$: C, 79·3; H, 7·55%). P. Jacobsen (*Ber.*, 1895, **28**, 2553) gives m. p. 106—107°. [o] P. Starke, *J. prakt. Chem.*, 1899, **59** (2), 210.

2,3′-*Dimethylazobenzene*.—This was obtained from *m*-nitrotoluene, powdered sodium hydroxide, and *o*-toluidine by the procedure of Mayer and Freitag.[18] Fractional distillation of the red oil gave 2,3′-dimethylazobenzene (31%), b. p. 183—186°/15 mm. Mayer and Freitag [18] record the same b. p.

Other azobenzenes were prepared by the condensation of a substituted aniline with nitrosobenzene or a substituted nitrosobenzene. The appropriate nitrosobenzene (0·1 mole) and the amine (0·125 mole) were separately dissolved in acetic acid (35 ml.) and the solutions mixed. The reaction mixture was heated * on a steam-bath for 15—20 min., during which time the colour changed from green to dark orange-red. In general, if the resulting azo-compound carried no substituent *ortho* to the azo-linkage, the product crystallised from the reaction mixture on cooling. Alternatively, the mixture was added to water (2 l.), the oil extracted with benzene, and the extract washed with water, 2N-aqueous hydrochloric acid, and water. The dried solution was then chromatographed on an activated-alumina column. Benzene was used to elute the required azo-compound, which appeared in the first fractions. With the exception of 2,5-dimethylazobenzene, which is an oil, all the substituted azobenzenes were crystallised to constant m. p. from methanol and from benzene–methanol. Additional information is listed in Table 5.

With the exception of 3,5-dibromoazobenzene, the substituted azobenzenes were reduced as reported [1] earlier for the preparation of 2-methylbenzidine. 3,3′,5-Trichloroazobenzene, initially in suspension, dissolved soon after the start of the reduction.

In the present work, our previous procedure [1] for the rearrangement of hydrazobenzenes was modified as follows. The suspension of the benzidine salt, obtained by filtering the hot reaction mixture containing the hydrazo-compound into concentrated hydrochloric acid, was heated under reflux for 2—3 hr. (24 hr. for the rearrangement of 3,3′,5-trichlorohydrazobenzene) to complete the rearrangement. A volume of the liquid equal to the volume of ethanol present was then distilled off, the suspension cooled, and the salt filtered off. A suspension of the salt in an excess of 2N-aqueous sodium hydroxide was heated on a steam-bath for 1 hr., and the crude amine filtered off from the cooled solution. The pure benzidines were obtained by crystallisation to constant m. p. from benzene–light petroleum (b. p. 40—60°). Table 6 gives further experimental information.

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* Our previous procedure allowed the reactants to stand at room temperature for up to 48 hr. However, the reaction between 2,5-dibromoaniline and nitrosobenzene at room temperature gave a product with a low bromine content. The quicker method of heating the reaction mixture was therefore adopted in the present work, with satisfactory results.

[18] F. Mayer and K. Freitag, *Ber.*, 1921, **54**, 351.

TABLE 5

Unsymmetrically substituted azobenzenes from substituted anilines and nitrosobenzenes

Aniline	Nitrosobenzene	Azobenzene	Time of heating (min.)	Yield (%)	M. p.
2,5-Dichloro-	Unsubst.[a]	2,5-Dichloro-	120	16	63—65°[b]
2,5-Dibromo-[c]	,,	2,5-*Dibromo-*[d]	90	10·5	84—85
2,5-Dimethyl-[e]	,,	2,5-Dimethyl-	90	40	—[f]
2-Chloro-	3-Chloro[g]	2,3′-*Dichloro-*[h]	30	39	51—52
3,5-Dichloro-[i]	Unsubst.	3,5-*Dichloro-*[j]	30	37	94—95
3,5-Dibromo-[k]	,,	3,5-Dibromo-	15	54	100—102[l]
3,5-Dichloro-	3-Chloro	3,3′5-*Trichloro-*[m]	15	46	93—94
3,5-Dibromo-	3-Bromo[n]	3,3′5-*Tribromo-*[o]	60	53	123

[a] A. I. Vogel, " Practical Organic Chemistry," Longmans, London, 3rd edn., 1956, p. 630. [b] T. de Crauw (*Rec. Trav. chim.*, 1931, **50**, 777) gives m. p. 64°. [c] Prepared by nitration (F. M. Jaeger, *Z. Krist.*, 1907, **42**, 442) of *p*-dibromobenzene and reduction with stannous chloride and hydrochloric acid. [d] Found: C, 43·0; H, 2·4; Br, 46·7; N, 8·1. $C_{12}H_8Br_2N_2$ requires C, 42·5; H, 2·4; Br, 47·0; N, 8·25%. [e] From 2,5-dimethylnitrobenzene by reduction with stannous chloride and hydrochloric acid. [f] This compound was an oil and was not analysed. [g] W. J. Migs, S. E. Hoekstra, R. M. Ulmann, and E. Havinga (*Rec. Trav. chim.*, 1958, **77**, 746). [h] Found: C, 57·1; H, 3·4; Cl, 28·2; N, 11·1. $C_{12}H_8Cl_2N_2$ requires C, 57·4; H, 3·2; Cl, 28·2; N, 11·15%. [i] From 3,5-dichloronitrobenzene (see footnote *d* to Table 4) by reduction with stannous chloride and hydrochloric acid. Found: C, 57·2; H, 3·3; Cl, 28·3; N, 11·1%. [k] From *p*-nitroaniline. Direct bromination [A. Claus and R. Wallbaum, *J. prakt. Chem.*, 1897, **56** (2), 61] gave 2,6-dibromo-4-nitroaniline which was deaminated and the product reduced with stannous chloride and hydrochloric acid. [l] J. Burns, H. C. McCombie, and H. A. Scarborough (*J.*, 1928, 2936) give m. p. 104°. [m] Found: C, 50·2; H, 2·5; Cl, 36·8; N, 9·7. $C_{12}H_7Cl_3N_2$ requires C, 50·5; H, 2·5; Cl, 37·3; N, 9·8%. [n] From *m*-bromonitrobenzene using the method of W. J. Migs, S. E. Hoekstra, R. M. Ulmann, and E. Havinga (*loc. cit.*). The product had m. p. 78° in agreement with that reported by R. D. Haworth and A. Lapworth (*J.*, 1921, 768). [o] Found: C, 34·6; H, 1·9; Br, 56·8; N, 6·8. $C_{12}H_7Br_3N_2$ requires C, 34·4; H, 1·7; Br, 57·2; N, 6·7%.

3,3′,5-Tribromohydrazobenzene did not yield a pure benzidine by the above rearrangement procedure. Accordingly, the reduction mixture was filtered, and water was added to the hot filtrate until the hydrazo-compound began to separate. The filtrate was cooled and the 3,3′,5-tribromohydrazobenzene (84%), m. p. 96—98°, was collected. An unsuccessful attempt was then made to rearrange the hydrazo-compound by heating it as a fine suspension in 2 : 1 (v/v) concentrated sulphuric acid–water. The resulting crude amine could not be purified by column chromatography on alumina, and gave impure condensation products with the *p*-n-alkoxybenzaldehydes. The preparation of 2,2′,6-tribromobenzidine was abandoned.

2,6-Dibromobenzidine (50%), m. p. 183—184°, was obtained from 3,5-dibromoazobenzene by treatment with stannous chloride and hydrochloric acid, following the method of Burns, McCombie, and Scarborough,[19] who report m. p. 185° for 2,6-dibromobenzidine.

TABLE 6

Unsymmetrically substituted benzidines from substituted azobenzenes

			Found (%)					Requires (%)			
Benzidine	Yield (%)	M. p.	C	H	Hal	N	Formula	C	H	Hal	N
2,5-Dichloro- ...	55	93—94°[a]	—	—	—	—	—	—	—	—	—
2,5-Dibromo- ...	47	106—107	41·9	3·2	46·8	8·2	$C_{12}H_{10}Br_2N_2$	42·15	2·95	46·7	8·2
2,5-Dimethyl-[b]	22	—	—	—	—	13·2	$C_{14}H_{16}N_2$	—	—	—	13·1
2,3′-Dichloro- ...	38	74—75	56·7	3·7	28·4	10·9	$C_{12}H_{10}Cl_2N_2$	56·95	4·0	28·0	11·1
2,3′-Dimethyl-[c]	29	—	—	—	—	—	—	—	—	—	—
2,6-Dichloro- ...	42	141—142	56·7	4·0	28·3	11·4	$C_{12}H_{10}Cl_2N_2$	56·95	4·0	28·0	11·1
2,2′,6-Trichloro-	17·5	124—125	50·2	3·3	36·9	9·9	$C_{12}H_9Cl_3N_2$	50·1	3·15	37·0	9·75

[a] T. de Crauw (*Rec. Trav. chim.*, 1931, **50**, 777) gives m. p. 95°. [b] Distillation of the crude amine yielded a fraction, b. p. 220—224°/2 mm. This was chromatographed in benzene on alumina to give the pure diamine as a brown gum. The 4,4′-*dibenzylidene derivative* (Found: C, 86·1; H, 6·1; N, 7·5. $C_{28}H_{24}N_2$ requires C, 86·55; H, 6·2; N, 7·2%) had m. p. 145—146°. [c] Distillation of the crude amine yielded a pale yellow glass, b. p. 188—192°/2 mm. The 4,4′-*dibenzylidene derivative* (Found: C, 86·2; H, 6·1; N, 7·2%) had m. p. 117°. F. Mayer and K. Freitag (*Ber.*, 1921, **54**, 351) report b. p. 243—246°/12 mm. for the amine.

Infrared Spectra of the Substituted Benzidines.—The infrared spectra of all the new, substituted benzidines were obtained, and shown to be consistent with the expected structures.

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[19] J. Burns, H. McCombie, and H. A. Scarborough, *J.*, 1928, 2936.

Substituted 4,4′-*Di*-(p-*n-alkoxybenzylideneamino*)*biphenyls*.—The *dianils* were prepared by the general method described [1] previously. 2,2′,6,6′-Tetrachlorobenzidine was condensed with *p*-n-heptoxybenzaldehyde only. Analytical figures are given in Table 7.

Dianils from 3,3′,5,5′-tetrachlorobenzidine could not be prepared by the general method, or by the method [1] used for the 3-substituted benzidines. It was found that 2,4,6-tribromoaniline and anisaldehyde heated at 160° for 60 hr. gave anisic acid, and it was concluded that prolonged

TABLE 7

4,4′-Di-(*p*-n-alkoxybenzylideneamino)dichlorobiphenyls

	2,2′-Dichloro- Found (%)			2,3′-Dichloro- Found (%)				Required (%)		
Alkyl	C	H	Cl	C	H	Cl	Formula	C	H	Cl
Heptyl	72·8	7·6	11·1	72·6	6·9	11·2	$C_{40}H_{46}Cl_2N_2O_2$	73·1	7·1	10·8
Octyl	73·3	7·1	10·9	73·4	7·6	10·7	$C_{42}H_{50}Cl_2N_2O_2$	73·6	7·3	10·4
Nonyl	73·6	7·4	10·1	73·7	7·6	10·4	$C_{44}H_{54}Cl_2N_2O_2$	74·0	7·6	10·0
Decyl	74·1	7·7	9·9	74·2	7·7	10·0	$C_{46}H_{58}Cl_2N_2O_2$	74·5	7·8	9·6

	2,5-Dichloro- Found (%)			2,6-Dichloro- Found (%)			3,3′-Dichloro- Found (%)		
Alkyl	C	H	Cl	Cl	H	Cl	C	H	Cl
Heptyl	72·8	7·4	10·9	73·3	7·0	10·5	73·3	6·7	10·9
Octyl	73·4	7·7	9·9	74·0	7·6	10·9	73·2	7·2	10·4
Nonyl	73·8	7·9	9·5	74·0	7·5	10·3	73·6	7·2	10·1
Decyl	74·6	8·2	9·8	74·5	7·7	10·1	74·4	7·5	9·9

	2,2′-Dibromo- Found (%)			2,5-Dibromo- Found (%)				Required (%)		
Alkyl	C	H	Br	C	H	Br	Formula	C	H	Br
Heptyl	63·9	6·1	22·4	64·2	6·1	21·2	$C_{40}H_{46}Br_2N_2O_2$	64·3	6·2	21·5
Octyl	65·2	6·6	20·4	64·9	6·5	21·0	$C_{42}H_{50}Br_2N_2O_2$	65·1	6·5	20·7
Nonyl	65·6	6·6	20·1	65·8	6·4	20·2	$C_{44}H_{54}Br_2N_2O_2$	65·8	6·7	20·0
Decyl	66·3	7·2	19·3	66·2	6·7	19·7	$C_{46}H_{58}Br_2N_2O_2$	66·5	7·0	19·3

	2,6-Dibromo- Found (%)			3,3′-Dibromo- Found (%)		
Alkyl	C	H	Br	C	H	Br
Heptyl	64·6	6·5	21·2	64·3	6·0	21·0
Octyl	64·9	6·5	21·0	64·9	6·4	20·4
Nonyl	66·0	6·8	20·6	65·5	6·4	19·4
Decyl	66·3	6·9	20·0	66·3	6·8	19·0

4,4′-Di-(*p*-n-alkoxybenzylideneamino)dimethylbiphenyls

	2,2′-Dimethyl Found (%)		2,3′-Dimethyl Found (%)		2,5-Dimethyl Found (%)		3,3′-Dimethyl Found (%)			Required (%)	
Alkyl	C	H	C	H	C	H	C	H	Formula	C	H
Heptyl ...	81·6	8·5	81·4	8·5	81·5	8·9	81·5	8·4	$C_{42}H_{52}N_2O_2$	81·8	8·5
Octyl ...	82·3	8·6	81·6	8·6	81·8	8·5	81·7	8·3	$C_{44}H_{56}N_2O_2$	81·7	8·3
Nonyl ...	82·3	8·8	81·8	8·7	82·0	8·9	82·2	8·9	$C_{46}H_{60}N_2O_2$	82·1	8·9
Decyl ...	82·5	9·2	81·9	8·7	82·6	8·9	82·0	9·3	$C_{48}H_{64}N_2O_2$	82·3	9·1

4,4′-Di-(*p*-n-alkoxybenzylideneamino)-2,2′,6-trichlorobiphenyls

	Found (%)				Required (%)		
Alkyl	C	H	Cl	Formula	C	H	Cl
Heptyl	69·2	6·4	15·8	$C_{40}H_{45}Cl_3N_2O_2$	69·4	6·5	15·4
Octyl	70·0	6·3	14·8	$C_{42}H_{49}Cl_3N_2O_2$	70·0	6·8	14·8
Nonyl	71·0	6·7	14·1	$C_{44}H_{53}Cl_3N_2O_2$	70·6	7·1	14·3
Decyl	71·1	7·4	13·4	$C_{46}H_{57}Cl_3N_2O_2$	71·2	7·4	13·7

4,4′-Di-(*p*-n-heptoxybenzylideneamino)-2,2′,6,6′-tetrachlorobiphenyl

Found (%)				Required (%)		
C	H	Cl	Formula	C	H	Cl
65·8	6·1	19·3	$C_{40}H_{44}Cl_4N_2O_2$	66·1	6·1	19·6

heating of 3,3′,5,5′-tetrachlorobenzidine with the *p*-n-alkoxybenzaldehydes would not give the required products.

The dianils prepared from the crude 2,2′,6-tribromobenzidine were impure. The products exhibited nematic mesophases of roughly the expected thermal stabilities, but the mesomorphic transitions were neither well-defined nor precisely reversible, and the usual alternation of the transition temperatures with alkyl chain length was not observed.

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