The 9,10-Dihydrophenanthrene Structure as a Source of Liquid Crystals: Mesogenic Behaviour and Spectroscopic Properties of 2-Benzylideneamino-9,10-dihydrophenanthrenes

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13 Azomethines have been prepared from 2-amino-9,10-dihydrophenanthrene by reaction with aromatic aldehydes. Those with *p*-alkoxy, *p*-cyano or *p*-phenyl substituents in the aldehydic ring have a nematic mesophase. U.v. spectra, ^1H and ^{13}C n.m.r. spectra, and mass spectra of the series are discussed. Mass spectra show that *ortho*-substituents in the aldehydic ring substantially modify the fragmentation pattern.

It has long been known[1,2] that mono- and bis-azomethines obtained by the reaction of *p*-n-alkoxybenzaldehydes with 4-aminobiphenyl, 2-aminofluorene, 2-aminofluorenone, 2-aminophenanthrene, 4,4'-diaminobiphenyl, 2,7-diaminofluorene, and 2,7-diaminofluorenone show mesomorphic behaviour. At the lower end of the homologous series of alkoxy derivatives only a nematic mesophase is obtained, at the higher end (except for the 2-aminofluorenone series) only a smectic mesophase appears, whereas in the middle range (approximately 5—12 carbon atoms but varying slightly in the different series) both smectic and nematic phases are observed.

The polycyclic part of the structure in the fluorene, fluorenone, and phenanthrene derivatives is flat; it may also be flat in the biphenyl derivatives since biphenyl itself is flat in the crystal,[3] although spectroscopic evidence[4] shows that it is not flat in solution. Substituents in biphenyls, which increase the dihedral angle between the two rings, decrease the nematic thermal stability[5] of mesomorphic biphenyl azomethines; in the extreme case of four *ortho*-substituents (the 2,2',6,6'-tetramethyl and tetrachloro derivatives[5,6]) where the dihedral angle must be *ca.* 90°, mesomorphic behaviour is not shown.

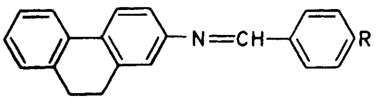
It was of interest to vary the dihedral angle between the two rings of biphenyl by bridging, rather than by the use of substituents, since the conformation can then be expected to approximate to that calculated for a model with normal bond lengths and angles.[7] As part of such an investigation we have prepared monoazomethines from 2-amino-9,10-dihydrophenanthrene,[8] where the dihedral angle is expected[9] to be *ca.* 15°.

Benzylideneanilines exist as stable *E*-isomers at normal temperatures[10-13] but they are not normally planar molecules.[14-16] In benzylideneaniline itself the Ph–C and Ph–N bonds are rotated through *ca.* 10 and 55°, respectively, in the crystal[14] (0 and 52° in the gas phase[17]) and the conformation in solution is probably very similar since there is extensive PhCH=N conjugation but much reduced Ph–N=CH conjugation as revealed in the electronic spectrum.[18-25]

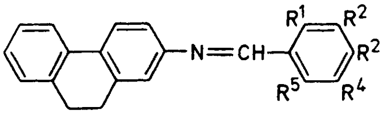
Among the aldehydes used to make the azomethines we have therefore included some with an *ortho*-substituent, since this may be expected to modify the Ph–CH=N dihedral angle and thus perhaps affect the mesomorphic behaviour.

Compounds (1)—(7), with a *para*- but no *ortho*- or *meta*-substituent in the aldehydic ring, have a nematic mesophase. Apart from the *p*-cyano-compound (6) the phase transitions (C ⟶ N and N ⟶ I) are appreciably lower than those for the 4-benzylideneaminobiphenyls with the same substituents but the nematic mesophase temperature range is significantly increased (Table 1). Both these effects are important in relation to the use of liquid crystals in display devices. Where comparison with the phenanthrene series is possible, the dihydrophenanthrene derivatives similarly show lower temperatures for the phase transitions but in most cases the temperature range for the nematic mesophase is larger in the phenanthrenes. A smectic mesophase might have been expected for compound (5) and possibly for compound (4) but was not observed.

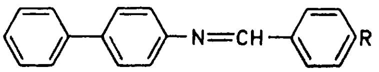
The non-polar bis-methylene bridge in the 9,10-dihydrophenanthrene series both increases molecular thickness and decreases molecular polarisability in comparison with the phenanthrene series. Further, *ortho*- and *meta*-substitution in biphenyl reduces thermal stability of mesophases in the 4,4'-bis-azomethines.[5a] This is also the case in the 4-benzylideneaminobiphenyls;[5b] the effects of 2- or 2'-substituents are particularly marked. The decreases in $T_{N \rightarrow I}$ observed in the present work on passing from the biphenyl to the 9,10-dihydrophenanthrene series are considerably smaller than these and this is consistent with the low dihedral angle of *ca.* 15° for the dihydrophenanthrene system. It is also interesting to note that the effects are small compared with the large decrease in $T_{N \rightarrow I}$ observed on passing from a 4,4'-bis-azomethine to the corresponding 2,2'-dimethyl-4,4'-bis-azomethine; the methyl groups in these compounds probably adopt a *cis*-conformation which will cause the dihedral angle to be much larger than in the, formally, rather similar 9,10-dihydrophenanthrene system. It is not possible on present evidence to separate the molecular broadening and polarisability effects from those produced by the limited twisting of the biphenyl rings in the bridged compounds but work is continuing with other bridged systems.*



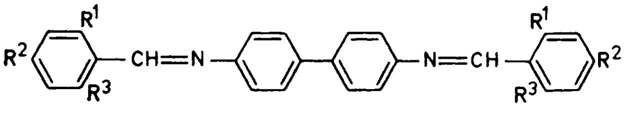
(1) R = OMe
(2) R = OEt
(3) R = $O(CH_2)_3CH_3$
(4) R = $O(CH_2)_5CH_3$
(5) R = $O(CH_2)_7CH_3$
(6) R = CN
(7) R = Ph



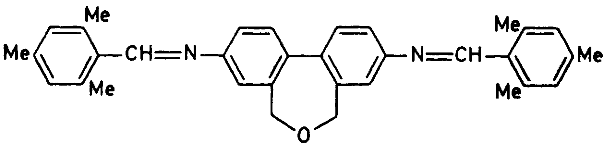
(8) $R^1 = R^2 = R^3 = R^4 = R^5 = H$
(9) $R^2 = R^3 = R^4 = R^5 = H, R^1 = F$
(10) $R^2 = R^3 = R^4 = R^5 = H, R^1 = Me$
(11) $R^2 = R^4 = H, R^1 = R^3 = R^5 = Me$
(12) $R^2 = R^4 = R^5 = H, R^1 = R^3 = OMe$
(13) $R^1 = R^5 = H, R^2 = R^3 = R^4 = OMe$



(14) R = CN
(15) R = Ph



(16) $R^1 = F, R^2 = R^3 = H$
(17) $R^1 = R^2 = R^3 = Me$



(18)

Table 1

Comparison of thermal behaviour of *p*-substituted benzylidene derivatives of 2-amino-9,10-dihydrophenanthrene, 4-aminobiphenyl, and 2-aminophenanthrene

	9,10-Dihydrophenanthrene series			Biphenyl series				Phenanthrene series			
	Temp. of transition to			Temp. of transition to				Temp. of transition to			
p-Substituent	nematic (°C)	isotropic (°C)	Range of nematic mesophase	nematic (°C)	isotropic (°C)	Range of nematic mesophase	Ref.	nematic (°C)	isotropic (°C)	Range of nematic mesophase	Ref.
OMe	118	151	33	161.5	173.5	12	*a*	155	213.5	58.5	*b*
OEt	93.5	162	68.5	146.5	190	43.5	*a*	152.5	217	64.5	*b*
$O(CH_2)_3CH_3$	83	151.5	68.5	147.5	176	28.5	*a*	121.5	204	82.5	*b*
$O(CH_2)_5CH_3$	83.5	141.5	58	146 [c]	168.5	22.5	*a*	113 [e]	194 5	81.5	*b*
$O(CH_2)_7CH_3$	96	137.5	41.4	155.5 [d]	164	8.5	*a*	140 [f]	186.5	46.5	*b*
CN	159	186	27	156.5	217.5	61	*g*				
Ph	181.5	220	38.5	248.5 [h]	253	4.5	*g*				

[a] G. W. Gray, J. B. Hartley, A. Ibbotson, and B. Jones, *J. Chem. Soc.*, 1955, 4359. [b] G. W. Gray, *J. Chem. Soc.*, 1958, 552. [c] Shows transition to smectic mesophase at 132 °C. [d] Shows transition to smectic mesophase at 142.5 °C. [e] Shows transition to a monotropic smectic mesophase at 111 °C. [f] Shows transition to smectic mesophase at 103 °C. [g] This work. [h] 243—245°, D. Vorländer, R. Wilke, U. Haberland, K. Thinius, H. Hempel, and J. Fischer, *Chem. Ber.*, 1938, **71B**, 501.

Of the compounds (8)—(13), which do not have a mesophase, three lack a *para*-substituent in the aldehydic ring (a normal requirement for liquid crystal formation among azomethines) while compounds (11) and (12), although *para*-substituted, are also *ortho*-substituted and presumably the degree of twisting about the C–Ar bond is too great to allow the necessary alignment of molecules. Compound (13) is interesting in that the *p*-methoxy-group is flanked by two *m*-methoxy-groups. The net effect is likely to be that of a large and diffuse substituent at the end of the aldehydic ring, together with a reduced polarisation effect of the *p*-methoxy, owing to its inability, for steric reasons, to take up its most favoured position.

It is of interest that among the biphenyl-4,4'-bis-azomethines, which are particularly favourable structures for showing mesomorphic behaviour, the compounds made from *o*-fluorobenzaldehyde and mesitaldehyde do give a nematic mesophase, although of much lower thermal stability than that of *p*-alkoxy-compounds (Table 2).

Electronic Spectra.—All the compounds show two main bands with maxima at *ca.* 280 nm (Band 1) and *ca.* 345 nm (Band 2) together with intense absorption below 230 nm (Table 3, Figure). Except for compounds (12) and (13) Band 1 is of higher intensity than Band 2. In all the spectra a number of inflections are apparent, indicating a considerable overlapping of bands; this makes the effect of substituents confusing since only the sum of

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* We thank a referee for helpful comments on the thermal stabilities of the mesogens.

effects on different electronic transitions is clearly observed.

Benzylidene in cyclohexane [24] has maxima at 211, 220, 236, 262 ($\varepsilon_{max.}$ 17 000), and 315 nm ($\varepsilon_{max.}$ 7 360; broad maximum). The 262 nm band has been attributed [18-25] to Ph–CH=N conjugation and the 315 nm band to residual conjugation through the whole π system of the non-planar molecule.[20-22, 24-29] The 315 nm band shows strong bathochromic and hyperchromic effects when this conjugation is increased, *e.g.* by protonation at nitrogen,[24] by suitable *para*-substitution,[25, 26] by incorporation of PhN=CH into a planar 3*H*-indole structure,[24, 26] or by replacement of phenyl by β-naphthyl.[29]

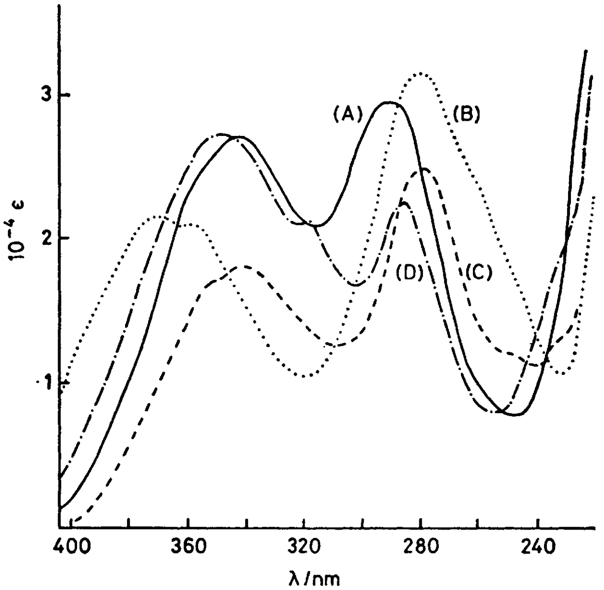
TABLE 2

Transition temperatures for biphenyl-4,4′-bisazomethines

Aldehyde used in preparation	Temp. of transition to nematic (°C)	isotropic (°C)	Ref.
2-Fluorobenzaldehyde	146.5	161.5	*a*
Mesitaldehyde	214.5	260	*a*
4-Methoxybenzaldehyde	266	>390	*b*

[a] This work. [b] G. W. Gray, J. B. Hartley, A. Ibbotson, and B. Jones, *J. Chem. Soc.*, 1955, 4359.

9,10-Dihydrophenanthrene is a highly conjugated substance with absorption maxima in hexane [4] at 263.5 ($\varepsilon_{max.}$ 18 000) and 299.5 nm ($\varepsilon_{max.}$ 4 750). Not surprisingly the 2-benzylideneamino-9,10-dihydrophenanthrenes show increased conjugation compared with benzylideaniline. The longwave band is at 341 nm in compound (8) with $\varepsilon_{max.}$ 18 200 and at 340 nm in compound (11) with $\varepsilon_{max.}$ 19 600. In the other compounds the wavelength is in the range 343—351 nm with stronger absorption in the *p*-substituted compounds (ε *ca.* 26 000), although, exceptionally, compound (6) shows a very large bathochromic shift. The increase in conjugation in the present series is consistent with the replacement of one phenyl by 9,10-dihydrophenanthryl and is not large enough to suggest significant differences in twisting about the Ar–N bond between the present series and benzylideneaniline (*cf.* ref. 26).



U.v. spectra of 2-benzylideneamino-9,10-dihydrophenanthrenes in hexane: (A), compound (1); (B), compound (6); (C), compound (8); (D), compound (12)

The 280 nm band is probably composite, including the 262 nm band of benzylideneaniline, as modified by substituents in the aldehydic ring, and the conjugation band of 9,10-dihydrophenanthrene as modified by the attached nitrogen. It is sensitive to substitution, showing bathochromic shifts of up to 10 nm in the compounds with *p*-alkoxy-groups and of 15 nm for *p*-phenyl substitution [compound (7)], together with increased intensity. *ortho*-Substitution does not have a hypsochromic effect, presumably because the more intense dihydrophenanthrene absorption is dominant.

TABLE 3

U.v. spectra of 2-benzylideneamino-9,10-dihydrophenanthrenes in hexane

Compd.	Shortwave features $\lambda_{inf.}$/nm	$\varepsilon_{inf.}$	Band 1 $\lambda_{max.}$/nm	$\varepsilon_{max.}$	Band 2 $\lambda_{max.}$/nm	$\varepsilon_{max.}$
(1)	(230)	16 100	289	28 800	343	26 400
			(295) [a]	27 700	(355)	23 600
(2)			290	25 500	343	25 250
			(297)	24 600	(358)	21 100
(3)	(230)	15 900	290	27 150	343	26 300
			(295.5)	26 400	(354)	23 700
(6)	(260)	23 400	279	31 100	372	21 300
	(246)	16 600			359	20 900
					(344)	16 450
(7)	(234)	13 400	294	33 900	351	26 900
					(364)	24 200
(8)	(250)	12 200	279	24 500	341	18 200
	(232)	13 250			(353)	17 000
(9)	(259)	15 200	279	24 100	347	19 300
	236	12 600			(356)	18 600
(10)	(231.5)	13 900	281	26 300	345	18 800
(11)	(230) [b]	17 700	284.5	27 700	340	19 600
(12)	(229)	19 900	286	22 050	350	26 700
					(320) [c]	20 500
(13)	(230)	22 200	(296) [d]	20 300	345	25 100
			(276)	14 600	(356)	22 900

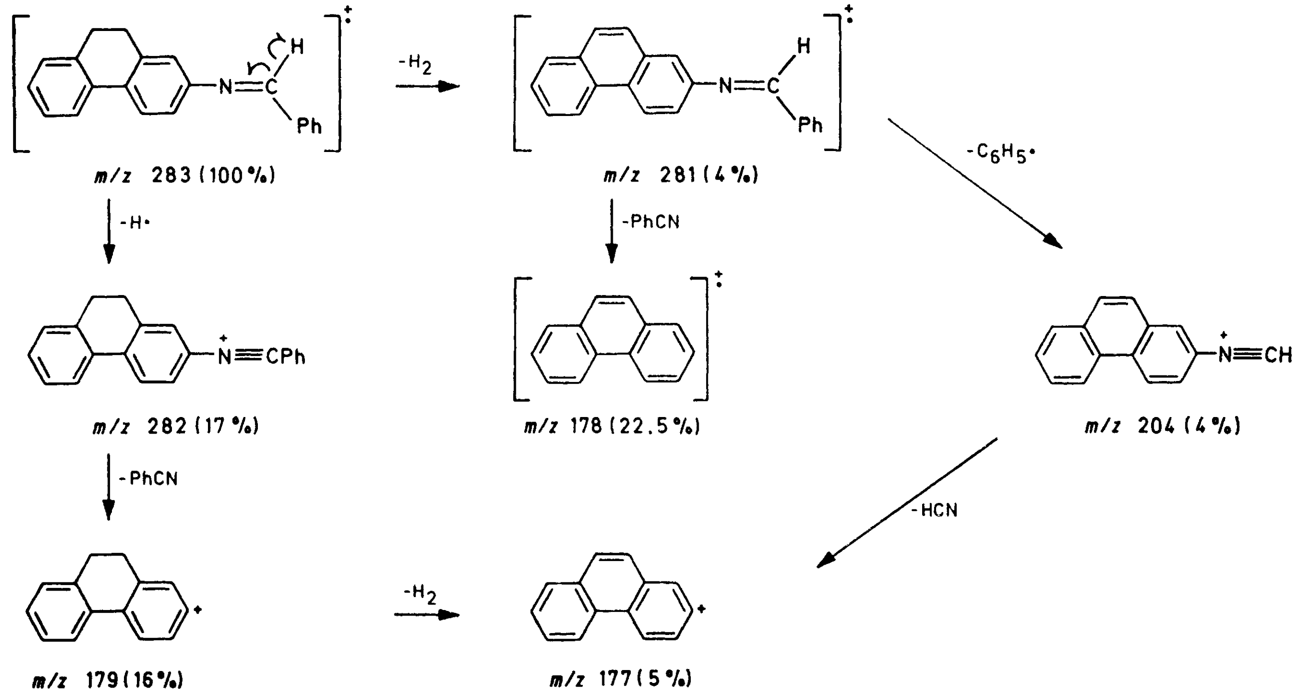
[a] Wavelengths in parentheses denote inflections. [b] Barely discernible. [c] Almost a separate band. [d] Minimum between bands 1 and 2 completely filled.

Twisting about the Ar–N bond allows overlaps of the non-bonded electrons of nitrogen with the π system of dihydrophenanthrene and thus accounts for the appearance of the band at 280 and above instead of at 264 nm.

Thus both bands in the u.v. spectrum support a non-planar conformation in solution for these dihydrophenanthrene azomethines.

The 2,4-dimethoxy-compound (12) shows some reduction in intensity of Band 1 in comparison with the *p*-methoxy-compound (1) and this leads to reversal of intensities of the two bands. In the 3,4,5-trimethoxy-compound (13) a further bathochromic shift of Band 1 and some reduction in intensity leads to the complete filling of the minimum between the two bands.

^{1}H *N.m.r. Spectra.*—Al-Tai *et al.*[30] have studied the effect of substituents in the two phenyl rings on the



SCHEME 1

chemical shift of the aldimine proton in benzylideneanilines. While *para*-substituents in the aldehydic ring exert their normal conjugative effect, *ortho*-substituents have a large steric effect and are deshielding even when they are normally electron releasing. Similar effects are observed in the 2-benzylideneamino-9,10-dihydrophenanthrenes (Table 4). In particular, the four compounds with an *ortho* substituent in the aldehydic ring [(9)—(12)] show strong deshielding of the aldimine proton by an amount which is independent of the size of the *ortho*-group, being in fact larger for one methoxy-group [(12)] than for two methyl groups [(11)] and slightly larger for one fluorine atom [(9)] than for one methyl group [(10)]. (For further discussion of the effect of methoxy, see ref. 30.) The *p*-cyano-group (6) proves to be marginally shielding rather than somewhat deshielding.

TABLE 4

^{1}H and ^{13}C chemical shifts for CH=N in 2-benzylideneamino-9,10-dihydrophenanthrenes (δ values; CDCl$_3$)

Compound	δ (^{1}H)	δ (^{13}C)
(1)	8.42	159.1
(2)	8.42	159.1
(3)	8.42	159.2
(4)	8.45	159.1
(5)	8.45	159.2
(6)	8.51	157.05
(7)	8.56	159.3
(8)	8.525	159.65
(9)	8.83	152.7
(10)	8.81	158.5
(11)	8.83	160.2
(12)	8.87	155.3
(13)	8.43	159.2

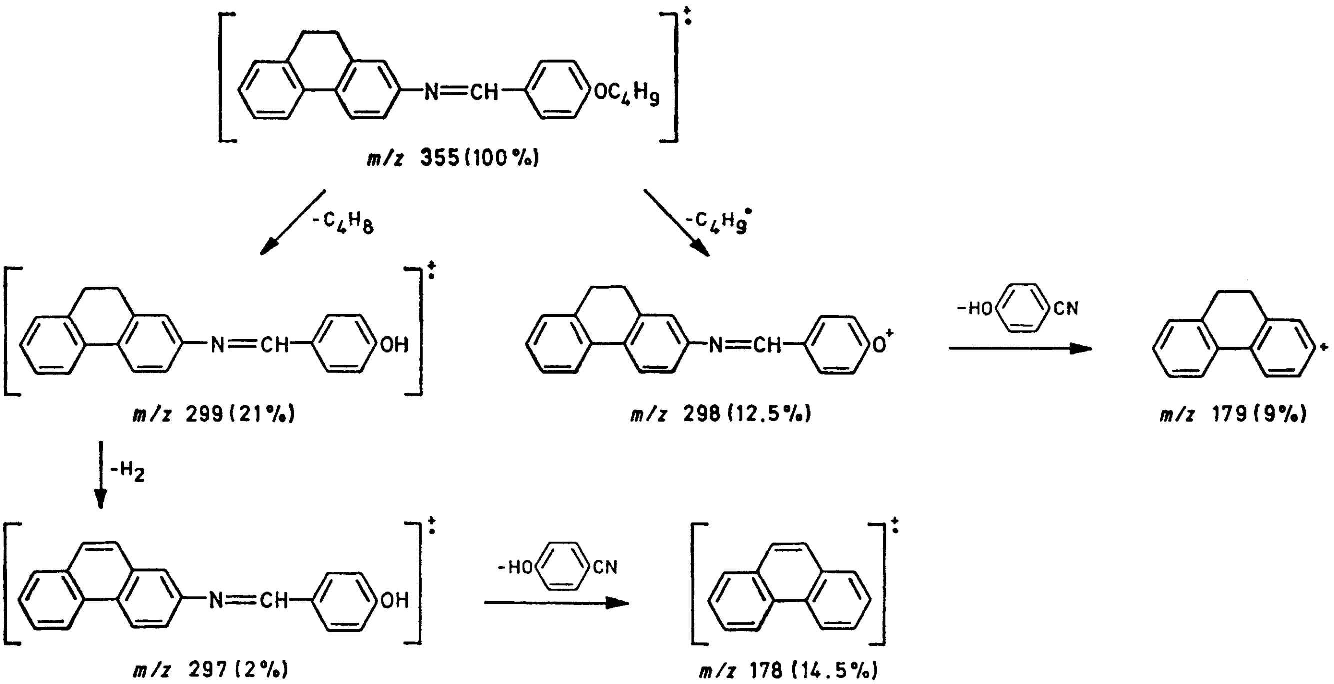
Although the methylene groups at C-9 and -10 are not equivalent, a chemical shift difference could not be detected, even at 220 MHz. The single signal occurred between δ 2.87 and 2.91 and showed no correlation with the nature of the substituents in the aldehydic ring.

^{13}C *N.m.r. Spectra*.—In comparison with compound (8), in which the aldehydic ring is unsubstituted, all the compounds except (11) show *shielding* of the aldimine carbon, irrespective of the nature or position of the substituents. Similar effects have been observed [31] in a

TABLE 5

Some important ions in the mass spectra of 2-benzylideneamino-9,10-dihydrophenanthrenes

	M^+		$[M - H^•]^{+•}$	$[M - H_2]^{+•}$	M^{2+}	*m/z* 179	*m/z* 178	*m/z* 177	$[M - C_nH_{2n+1}^•]^+$		$[M - C_nH_{2n}]^{+•}$		*m/z* 204	Other ions	
Compound	*m/z*	rel.int. (%)	rel.int. (%)	rel.int. (%)	rel.int. (%)	rel.int. (%)	rel.int. (%)	rel.int. (%)	*m/z*	rel.int. (%)	*m/z*	rel.int. (%)	rel.int. (%)	*m/z*	rel.int. (%)
(1)	313	100	16	2	8.5	7	14	4	298	<1			3		
(2)	327	100	5	2	1	6	13	4	298	6	299	3	4		
(3)	355	100	2.5	5		9	14.5	5	298	12.5	299	21	4		
(4)	383	100	1	7		6	9	3	298	9.5	299	21	2.5		
(5)	411	100	3	8		14	16	6	298	18	299	34.5	6		
(6)	308	100	9	7	7	19.5	26	6.5					1		
(7)	359	100	29	14	10	19	27	11					4		
(8)	283	100	17	4	8.5	16	22.5	5					2		
(9)	301	100	13	8	9	23	31	8					1		
(10)	297	100	53	4	14.5	13	33	7	282	6			1.5		
(11)	325	72	39	2	20	10	27	5.5	310	13			2		
(12)	343	46	2	3	6	4	16	5					1	195 149 121	81 100 24
(13)	373	100	5	4.5	6.5	6	7	3	358	2.5			2		



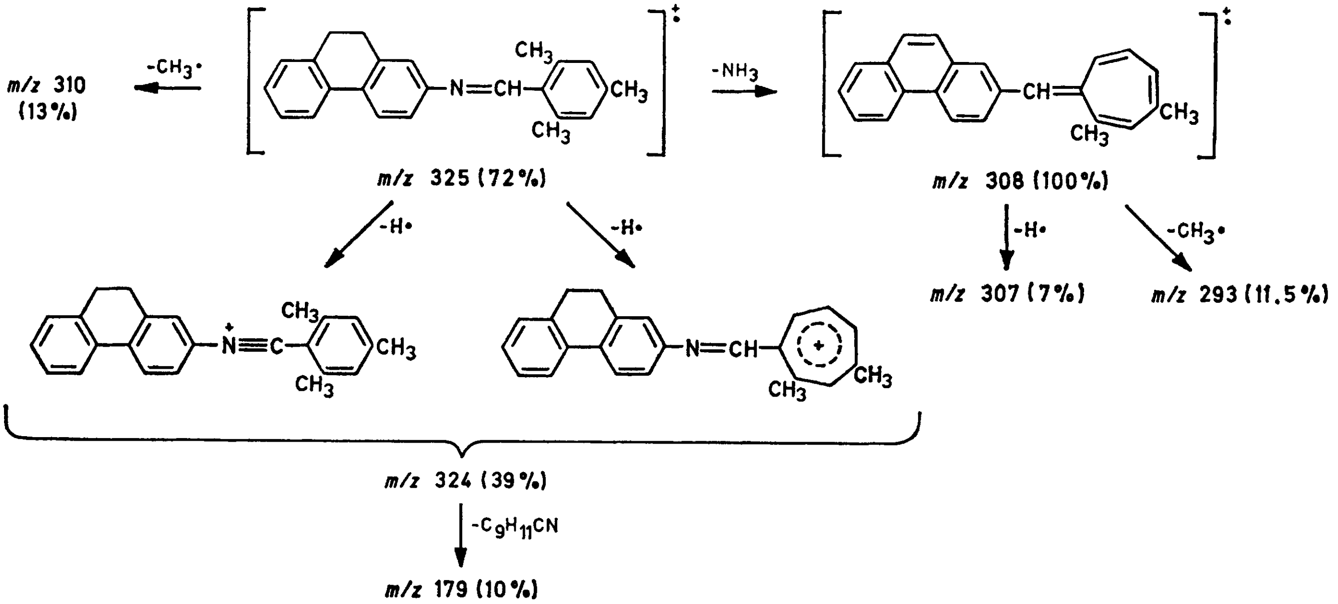
SCHEME 2

TABLE 6

Additional ions in the mass spectra of 2-(*o*-methylbenzylideneamino)-9,10-dihydrophenanthrenes

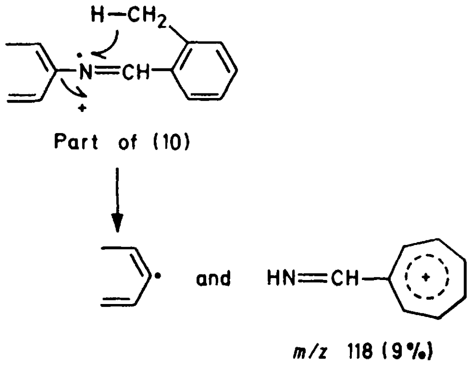
	$[M - NH_2{\bullet}]^{+\,a}$		$[M - NH_3]^{+\bullet}$		$[M - NH_3 - H{\bullet}]^+$		$[M - NH_3 - H_2]^{+\bullet}$		$[M - CH_3NH_2]^{+\bullet}$		$[M - NH_3 - CH_3{\bullet}]^+$		$[M - C_{14}H_{11}{\bullet}]^+$	
Compound	*m/z*	rel.int. (%)	*m/z*	rel.int. (%)	*m/z*	rel.int. (%)	*m/z*	rel.int. (%)	*m/z*	rel.int. (%)	*m/z*	rel.int. (%)	*m/z*	rel.int. (%)
(10)	281	27	280	77	279	26.5	278	7	266	3.5	265	8	118	9
(11)	309	39.5	308	100	307	7	306	3	294	8.5	293	11.5	146	19

[a] Includes the ^{13}C peak for $[M - NH_3]^{+\bullet}$.



SCHEME 3

series of benzylideneanilines with *para*-substituents in the aldehydic ring. Compound (11), with two *ortho*-methyl groups, shows slight deshielding which must be attributed to steric hindrance by the methyl groups, preventing full conjugative interaction between the ring and the carbon–nitrogen double bond. Apart from this the chemical shift of the aldimine carbon does not appear to be sensitive to steric effects.



SCHEME 4

In most of the compounds two signals are observed for the two methylene carbons, one at δ *ca.* 29.04 and the other at δ 29.15—29.20 p.p.m.

Mass Spectra.—The series of 9,10-dihydrophenanthrene-2-azomethines show a common fragmentation pattern which is substantially modified when *o*-methyl or *o*-methoxy groups are present in the aldehydic ring.

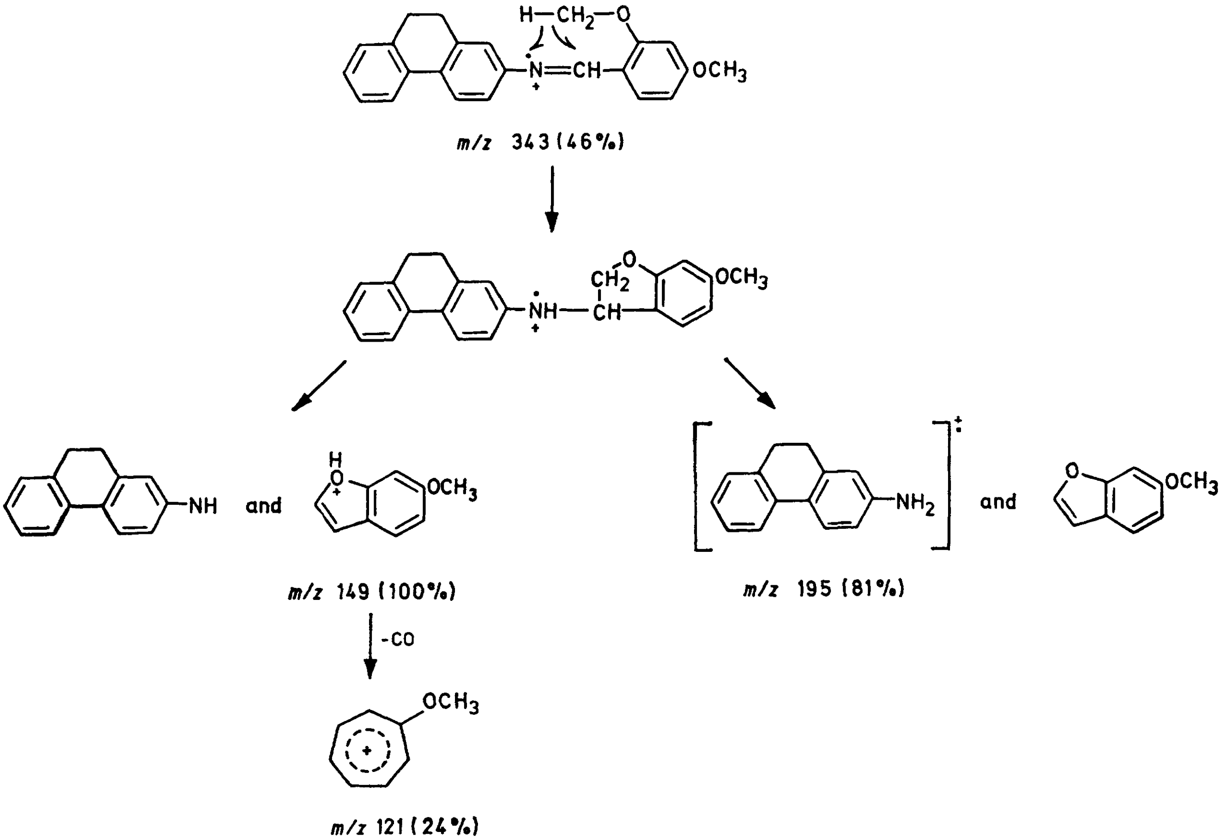
In all the spectra the dihydrophenanthryl cation (*m*/*z* 179), the phenanthrene ion-radical (*m*/*z* 178) and the phenanthryl cation (*m*/*z* 177) are present, the peak at *m*/*z* 178 being the most intense in each case and that at *m*/*z* 177 the least intense (Table 5).

The molecular ion is the base peak for all the compounds except (11) and (12) and, except in the *p*-alkoxy compounds (2)—(5), the doubly charged molecular ion is unusually intense.

Typical fragmentation is illustrated in Scheme 1 for the unsubstituted compound (8); the substituted compounds lose the appropriate substituted benzonitrile. A minor decomposition involves loss of an aryl radical to give the ion at *m*/*z* 204, which is present at low intensity in all the spectra.

Additionally the *p*-alkoxy-compounds (2)—(5) lose an alkene molecule, giving *m*/*z* 299, and an alkyl radical, giving *m*/*z* 298, as shown in Scheme 2.

The two compounds with *o*-methyl groups [(10) and (11)] show a more intense $[M - H\cdot]^+$ peak than the other compounds, presumably owing to loss from the methyl group as well as from the azomethine group (in the mass spectrum of mesitaldehyde $[M - H\cdot]^+$ is the base peak); more strikingly, they show strong peaks



SCHEME 5

resulting from loss of ammonia from the molecular ion and, in the case of compound (11) the $[M - NH_3]^{+\cdot}$ ion-radical becomes the base peak (Tables 5 and 6, Scheme 3). In this compound too, the doubly charged molecular ion is particularly intense (20%).

The first step in ammonia formation is probably transfer of a hydrogen atom from the carbon of the *o*-methyl group to nitrogen. Indeed a subsidiary fragmentation involving homolysis of the phenanthrene–nitrogen bond and rearrangement gives the tropylium-aldimine ion [m/z 118 (9%)] from compound (10) and its dimethyl derivative [m/z 146 (19%)] from compound (11) (Scheme 4). Ammonia formation requires simultaneous C–C bond formation and C–N bond breaking, together with the abstraction of two more hydrogen atoms by the nitrogen. These are thought to come from the reduced part of the 9,10-dihydrophenanthrene since the mass spectrum of the related compound (18), where the biphenyl is bridged by the CH_2–O–CH_2 group instead of by CH_2–CH_2, shows only slight loss of ammonia: the molecular ion of (18) is the base peak and $[M - NH_3]^{+\cdot}$ has an intensity of 9%; the aldimine ion (m/z 146) has an intensity of 25% showing that it is formed readily with either ring system.

In the *o*-methoxy-compound (12) hydrogen transfer from methyl to nitrogen is followed by cyclisation to a dihydrobenzofuran derivative. Heterolysis of the N–C bond generates the protonated benzofuran derivative at m/z 149 as the base peak while a second hydrogen transfer before heterolysis produces the 2-amino-9,10-dihydrophenanthrene ion-radical (m/z 195) at 81% intensity (Scheme 5).

The mass spectrum of 2,4-dimethoxybenzaldehyde also gives the protonated benzofuran ion at m/z 149 but at 60% intensity, the molecular ion (m/z 166) being the base peak.[32] Fractionation of the sample of compound (12) on the mass spectrometer probe before recording the above spectrum removed traces of 2,4-dimethoxybenzaldehyde and 2-amino-9,10-dihydrophenanthrene present as impurities.

EXPERIMENTAL

U.v. spectra were measured in hexane on an SP8-100 Pye–Unicam spectrophotometer. Mass spectra were determined by the P.C.M.U., Harwell, on a VG Micromass ZAB IF mass spectrometer. N.m.r. spectra were measured in $CDCl_3$ solution with tetramethylsilane as internal standard on a JEOL FX90Q Fourier transform spectrometer.

TABLE 7

Analytical data for new compounds

Compd.	M.p. (°C)	Recrystallisation solvent	Formula	Found (%)			Requires (%)		
				C	H	N	C	H	N
(1)	[a]	LP (b. p. 60—80°)	$C_{22}H_{19}NO$	84.1	6.1	4.5	84.3	6.1	4.5
(2)	[a]	LP (b.p. 60—80°)	$C_{23}H_{21}NO$	84.7	6.5	4.2	84.4	6.5	4.3
(3)	[a]	B	$C_{25}H_{25}NO$	84.4	7.1	4.0	84.5	7.1	3.9
(4)	[a]	LP (b.p. 60—80°)	$C_{27}H_{29}NO$	84.2	7.5	3.6	85.5	7.6	3.65
(5)	[a]	LP (b.p. 60—80°)	$C_{29}H_{33}NO$	85.0	8.0	3.4	84.6	8.1	3.4
(6)	[a]	LP (b.p. 100—120°)	$C_{22}H_{16}N_2$	86.0	5.3	9.1	85.7	5.2	9.1
(7)	[a]	B–LP (b.p. 80—100°)	$C_{27}H_{21}N$	90.4	6.0	3.9	90.2	5.9	3.9
(8)	107	LP (b.p. 40—60°)	$C_{21}H_{17}N$	88.6	6.1	4.9	98.0	6.05	4.9
(9)	98	LP (b.p. 40—60°)	$C_{21}H_{16}FN$	83.4	5.3	4.6	83.7	5.4	4.65
(10)	81	LP (b.p. 60—80°)	$C_{22}H_{19}N$	88.8	6.4	4.7	88.8	6.4	4.7
(11)	102	LP (b.p. 60—80°)	$C_{24}H_{23}N$	88.2	7.1	4.2	88.6	7.1	4.3
(12)	117	LP (b.p. 80—100°)	$C_{23}H_{21}NO_2$	80.1	6.2	4.1	80.4	6.2	4.1
(13)	91.5	Hexane	$C_{24}H_{23}NO_3$	77.1	6.2	3.7	77.2	6.2	3.75
(14)	[a]	LP (b.p. 100—120°)	$C_{20}H_{14}N_2$	85.2	5.0	10.0	85.1	5.0	9.9
(16)	[b]	LP (b.p. 80—100°)	$C_{26}H_{18}F_2N_2$	78.5	4.3	7.2	78.8	4.6	7.1
(17)	[b]	T	$C_{32}H_{32}N_2$	86.35	7.0	6.3	86.4	7.3	6.3
(18)	216	T–LP (b.p. 80—100°)	$C_{34}H_{34}N_2O$	83.5	7.0	5.8	83.9	7.0	5.8

Solvents: B, benzene; LP, light petroleum; T, toluene.

[a] See Table 1. [b] See Table 2.

Phase transition temperatures were determined isothermally by differential scanning calorimetry by Dr. M. J. Richardson at the National Physical Laboratory and at Bedford College on a Kofler heating stage mounted on a Kyowa stereomicroscope, using polarisers.

2-Benzylideneamino-9,10-dihydrophenanthrenes.—9,10-Dihydrophenanthrene[33] was nitrated[8] and the 2- and 4-nitro-derivatives were separated. The 2-nitro-derivative was reduced[8] (H_2, Pt, THF) quantitatively and the freshly prepared 2-amino-9,10-dihydrophenanthrene[8] was heated for 5—10 min with the various aldehydes in ethanolic solution containing a few drops of glacial acetic acid. The azomethines were crystallised from hydrocarbon solvents to avoid hydrolysis of labile CH=N groups. Analytical data are given in Table 7.

Other azomethines were prepared similarly from the appropriate aldehydes and amines.

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