166. *Researches on Monolayers. Part I. Molecular Areas and Orientation at Water Surfaces of Aromatic Azo-compounds containing Long Alkyl Chains.*

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A series of twenty-two aromatic azo-compounds containing straight alkyl chains (C_{12}—C_{18}) and, in most cases, one hydroxy-group either *o*- or *p*- to the azo-group, has been examined for unimolecular film-forming properties on water. Condensed films are formed in all cases where a hydroxy-group is present and the alkyl chain has at least 16 carbon atoms, and in many cases where it has 12 carbon atoms. In absence of a hydroxy-group at least two azo-groups appear to be required to give the necessary water attraction for stable films to be formed. The molecules appear to be oriented in the films with the plane of the aromatic nuclei vertical, but the longer axis of this plane is in many cases tilted from the perpendicular at an angle depending on the nature and relative position of the various substituent groups.

A series of long-chain alkyl aromatic azo-compounds has been prepared, and their spreading properties on water have been examined. It is hoped to use these and similar compounds in monolayer reactions to study dye photolysis and the adsorption of dyes by fibres.

A large number of anthraquinone and azo-dyes containing long alkyl chains have been described (see Knight, *J. Soc. Dyers Col.*, 1950, **66**, 34) and several are in commercial use. These, however, are all water-solubilised by sulphonic acid groups. The dyes formed in the " Agfacolour " photographic film during development are also formed from intermediates containing long alkyl chains, incorporated in the emulsion during manufacture. These also contain a water-solubilising group, in some cases a sulphonic group (see, *e.g.*, Adams, " I.G. Farbenindustrie. The Manufacture of Intermediates and ' Colour Formers ' for Agfa Farbenfilm," B.I.O.S. Final Report No. 1605). Water-insoluble long-chain azo-compounds of the type used in the present work do not appear to have been studied previously.

It was expected that alkyl arylazo-compounds, with at least C_{12} chains and containing hydroxy-groups, would be film-forming. The presence of a phenolic group aids film formation; *e.g.*, *p*-alkylphenols, with straight chains of at least 12 carbon atoms, form condensed films (Adam, *Proc. Roy. Soc.*, 1923, *A*, **103**, 676; Adam, Berry, and Turner, *ibid.*, 1928, **117**, 532). The effect of an azo-group on monolayer formation has not been reported. At the outset of the present work three compounds (I, II, III) were prepared to determine whether this group has sufficient water-attraction to assist film formation. It was found that (III) readily forms condensed films, but neither (I) nor (II) does so; thus, a single azo-group has water-attracting properties, but they are less than those of, *e.g.*, the hydroxy-group. It was next found that condensed films are readily formed if the long-chain azo-compound has also a hydroxy-group in the molecule.

The compounds used in the present investigation (I—XXII) have been chosen partly for the availability of the intermediate products and partly for their suitability in showing the effect upon orientation of (*a*) the length of the alkyl chain attached to one of the aromatic nuclei, (*b*) the presence of hydroxy-groups *o*- or *p*- to the azo-group, (*c*) the presence of condensed ring systems in the molecule, and (*d*) the presence of water-attracting groups in the alkyl chain.

The results are shown in the table and Figs. 1—3.

Adam and his co-workers (*loc. cit.*) found that long-chain *p*-alkylphenols in monolayers have a molecular area of about 24 Å^2, consistent with close vertical packing of the benzene rings. The areas of the present compounds lie in the range 30—55 Å^2, and it is evident from a study of scale models that in these monolayers also the molecule is so oriented that the plane of the aromatic nuclei is vertical. The molecules are thus stacked side by side like slices of toast in a rack. Whatever substituent groups may be present, the plane of the rings remains vertical, but the whole molecule may be tilted in this plane at an angle depending on the nature and relative position of the substituent groups.

In illustration, the probable orientations of pairs of molecules of three typical

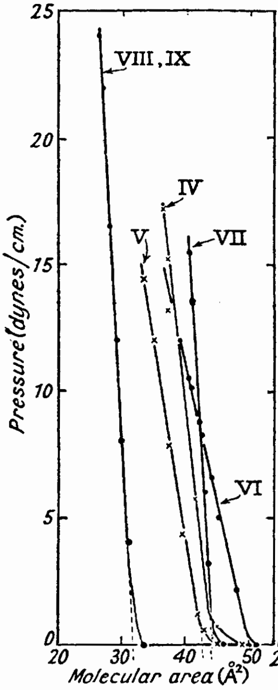


FIG. 1. o-*Hydroxy-azo-compounds.*

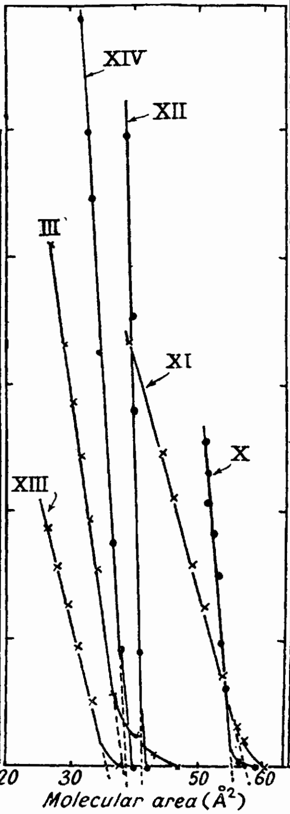


FIG. 2. *Bisazo- and* o-*hydroxyazo-compounds.*

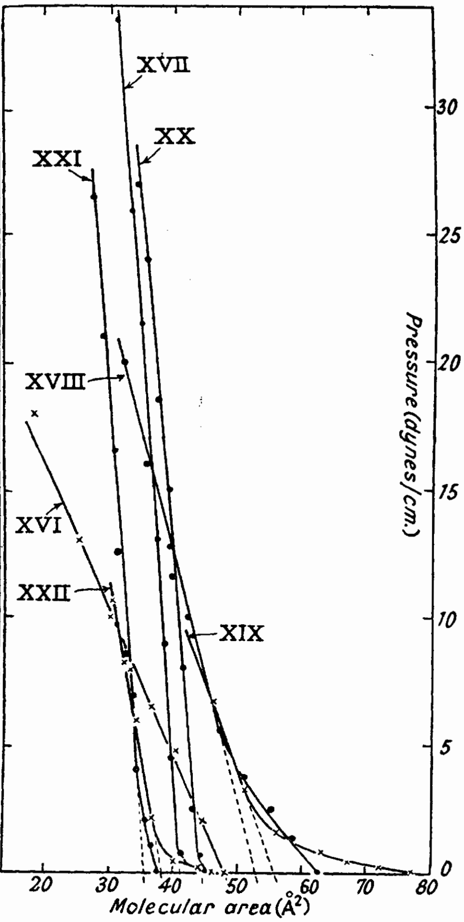
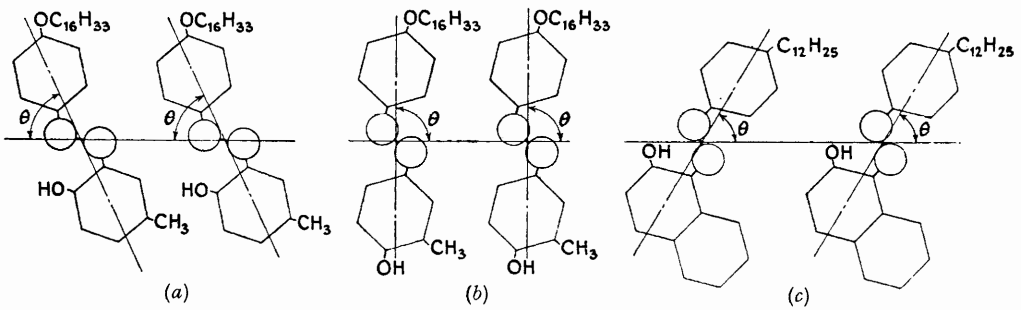


FIG. 3. p-*Hydroxyazo-compounds.*

FIG. 4. *Orientation of typical* o- *and* p-*hydroxyazo-compounds at the water surface.*



(*a*) (XIII, $\theta = 65°$)

(*b*) (XXI, $\theta = 90°$)

(*c*) (V, $\theta = 65°$)

Molecular areas and orientation angles.

No.	Compound		Limiting area (Å²)	Area at zero compression (Å²) *	Probable angle of orientation to water surface
	Azo-compounds without hydroxy-groups.				
I	*p*-Dodecylazobenzene		No film formed		
II	4-Hexadecyloxyazobenzene		No film formed		
III	4′-Hexadecyloxybis(phenylazo)benzene		48	38	90°
	Hydroxyazo-compounds.				
	Diazo-component	Coupling component			
	o-Hydroxyazo-compounds.				
IV	*p*-Dodecylaniline	*p*-Cresol	49	44·5	45°
V	do.	β-Naphthol	45	42·5	60°
VI	do.	3-Phenanthrol	51	50	65°
VII	*p*-Hexadecylaniline	β-Naphthol	46	44·5	60°
VIII	Aniline	*p*-Hexadecylphenol	33	32	90°
IX	do.	*p*-Octadecylphenol	33	32	90°
X	Hexadecyl *m*-aminobenzoate	*p*-Cresol	59	55	80°
XI	do.	β-Naphthol	60	57	55°
XII	Hexadecyl *p*-aminobenzoate	do.	41·5	41	45°
XIII	*p*-Hexadecyloxyaniline	*p*-Cresol	37	35·5	65°
XIV	do.	β-Naphthol	39	38	55°
	p-Hydroxyazo-compounds.				
XV	*p*-Dodecylaniline	*o*-Cresol	No film formed		—
XVI	do.	α-Naphthol	48	48	70°
XVII	do.	α-Anthranol	*ca.* 46	41	90°
XVIII	Hexadecyl *m*-aminobenzoate	*o*-Cresol	63	53	60°
XIX	do.	α-Naphthol	77	55	60°
XX	Hexadecyl *p*-aminobenzoate	*o*-Cresol	45	44	50°
XXI	*p*-Hexadecyloxyaniline	do.	37	36	90°
XXII	do.	α-Naphthol	47	38	90°

* Extrapolated value.

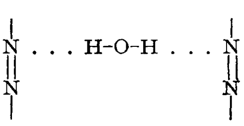
members of the series are shown in Fig. 4, which is drawn to scale from the molecular models.*

The probable angles of orientation given in the last column of the table have all been measured from models; they represent the angle to the water surface of the axis joining the two benzene nuclei on either side of the azo-group (see Fig. 4).

The following observations are made from a survey of the results.

The hydroxy-group attempts to penetrate the water surface as deeply as possible; but in the benzeneazo-β-naphthol series, closest packing is achieved when this group points upwards as shown in Fig. 4(*c*). The azo-group tends to lie below, but close to, the surface. In the compounds having only two benzene nuclei, the azobenzene axis stands vertically to the water surface if the water-attracting groups, *e.g.*, N_2, OH, ·O·, lie along a straight line [Fig. 4(*b*)], but if these groups are not in linear arrangement, the axis is usually tilted in the plane of the nuclei [Fig. 4(*a*)].

The molecules appear to stand about 6 Å apart, measured in a direction at right angles to the plane of the rings. This is consistent with each molecule's being separated from its neighbour by a water molecule, which could join the adjacent azo-groups, as shown in the inset. The compounds with the long-chain alkyl benzoate group in the opposite nucleus to the hydroxy-containing group show evidence of increased tilt due to the water-attraction of the ester group. Thus, the *p*-azobenzoic acid esters are more tilted to the surface than the corresponding ethers or alkylbenzene compounds. The azo-group appears to behave here as a pivot about which the molecular axis may rotate, the strong tendency for the hydroxy-group on one side to plunge



$$N \cdots H{-}O{-}H \cdots N$$

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* For simplicity, the positions of the nitrogen atoms only are shown in full; the benzene rings have been drawn through the centres of the carbon atoms. These molecules are actually closest packed when oriented as shown, but because of the omission of the full carbon and hydrogen atoms this is not immediately obvious.

as far as possible beneath the water surface being partly counteracted by the water-attraction of the ester group at the opposite end of the molecule. This explains why the tilt is greater when the ester group is *p*- to the azo-group than when it is in the *m*-position.

In some instances the molecular area found can only be accounted for by assuming that all the molecules do not stand in the same horizontal plane, some being pushed upwards on compression to allow closer packing. This appears to occur with the *p*-hexadecyl derivatives of phenylazophenol and phenylazo-α-naphthol and with the anthranol compound (XVII) in which the bulky anthranol head has to be accommodated under the water surface.

One observation we are unable to account for is that the area occupied by the *p*-alkylphenylazo-β-naphthol compound (VII) is decreased when the ether-oxygen atom comes between the benzene nucleus and the alkyl chain (XIV).

EXPERIMENTAL

The film balance was of Alexander's design (*Nature*, 1947, **159**, 304), with a trough (30 × 25 × 5 cm.) of Pyrex glass, coated with paraffin wax. The scale deflection was 0·125 cm. per dyne. Distilled water was used as substrate. The surface-active compounds were dissolved in an appropriate solvent (usually benzene) and injected below the surface by an " Agla " micrometer syringe. Measurements were made at room temperature and were reproducible to $\pm$ 1Å^2. Stuart-type molecular models were used in determining the orientation data.

Samples of *p*-dodecylaniline, hexadecyl *m*-aminobenzoate, and *p*-hexadecyloxyaniline were supplied by Imperial Chemical Industries Limited, Dyestuffs Division, and were recrystallised from ethanol before use.

Micro-analyses were by Drs. Weiler and Strauss, Oxford, and Dr. A. C. Syme, Royal Technical College, Glasgow. M. p.s are uncorrected.

p-*Dodecylazobenzene* (I).—This was prepared by Mills's method (*J.*, 1895, **67**, 925) for azobenzene. Nitrosobenzene (10·9 g.) was dissolved in glacial acetic acid (30 c.c.) and then added to *p*-dodecylaniline (13·1 g.) dissolved in the minimum volume of glacial acetic acid. The mixture was kept for several days, with occasional shaking; red crystals of the *azo*-compound separated, having m. p. 72° (from acetic acid) (Found: C, 82·0; H, 9·5; N, 7·9. $C_{24}H_{34}N_2$ requires C, 82·3; H, 9·7; N, 8·0%).

4-*Hexadecyloxyazobenzene* (II).—Benzeneazophenol (2 g.) was dissolved in ethanol (40 c.c.) and refluxed for several hours with hexadecyl iodide (4·1 g.) and sodium (0·27 g.). The *ether* separated, after concentration, as yellow prisms (from benzene) (Found: C, 79·5; H, 9·7; N, 6·8. $C_{28}H_{42}ON_2$ requires C, 79·8; H, 10·0; N, 6·7%).

4′-*Hexadecyloxybis(phenylazo)benzene* (III).—*p*-Aminoazobenzene (1 g.) was diazotised and coupled with phenol (0·48 g.) in dilute aqueous sodium hydroxide. Next morning, the precipitated bisazo-compound was recrystallised from ethanol (orange prisms, m. p. 184°) and refluxed (6 hours) with hexadecyl iodide (1·17 g.) and sodium (0·026 g.) in ethanol. The *ether* was separated by filtration and concentration, and formed orange prisms (from benzene) (Found: C, 77·6; H, 8·9; N, 10·4. $C_{34}H_{46}ON_4$ requires C, 77·8; H, 8·8; N, 10·6%).

Hexadecyl p-*Aminobenzoate.*—*p*-Nitrobenzoyl chloride (9·3 g.) and hexadecyl alcohol (12 g.) were refluxed for 6 hours in dry toluene (40 c.c.), and the solvent was then removed by distillation under reduced pressure. The crude hexadecyl *p*-nitrobenzoate (16 g.) was reduced by refluxing it for 12 hours with ethanol (100 c.c.), concentrated hydrochloric acid (0·6 ml.), water (3 c.c.), and iron dust (15 g.). The product was separated by filtration followed by dilution with water.

Diazotisation.—(i) p-*Dodecylaniline and* p-*hexadecylaniline.* A mixture of the base (0·05 mol.), concentrated hydrochloric acid (16 c.c.), and water (150 c.c.) was stirred for 15 minutes at 50°, then cooled to 0°, and sodium nitrite (3·5 g.), in a little water, slowly stirred in. The suspended hydrochloride dissolved to give a yellowish diazo-solution, which was filtered and used for coupling.

(ii) *Hexadecyl* m- *and* p-*aminobenzoates and* p-*hexadecyloxyaniline.* The amino-compound (0·4 mol.) was well ground with water (15 c.c.) and concentrated hydrochloric acid (6·25 c.c.), and the mixture added to water (45 c.c.). 2N-Sodium nitrite solution (12·5 c.c.) was slowly added. Diazotisation was complete after 30 minutes. The esters were diazotised at 5—10°, and the ether at 15—20°.

1-*Hydroxyanthracene.*—The mixture of anthracene-1- and -2-sulphonic acids, obtained by treating anthracene (50 g.) dissolved in glacial acetic acid (100 c.c.) with 20% oleum (65 g.) at

95° for 5 hours (Battegay and Brandt, *Bull. Soc. chim.*, 1923, **33**, 1667), was separated by fractional crystallisation of the sodium salts from hot water.

p-*Hexadecylaniline.*—Hexadecyl alcohol (1 mol.), aniline (1 mol.), aniline hydrochloride (0·3 mol.), and zinc chloride (0·66 mol.) were heated together at 270° for 10 hours, while the water formed was allowed to distil off, and thereafter for a further 12 hours (Coffey, Haddock, and I.C.I. Ltd., B.P. 468 226). The product, a zinc chloride double salt, was cooled, broken up, and heated for 4 hours with 50% aqueous sodium hydroxide. The oil thus formed was dissolved in ether, washed with dilute hydrochloric acid, then with water, and dried ($CaCl_2$). After the ether had been distilled off, the dry oil was distilled *in vacuo*; it had b. p. 240°/11 mm.

p-*Hexadecyl- and* p-*Octadecyl-phenol.*—Hexadecanoyl or octadecanoyl chloride (0·1 mol.) was refluxed for 5 hours with anisole (0·1 mol.). The ketones thus obtained were subjected to Clemmensen reduction and then demethylated by boiling these products for 24 hours with hydriodic acid (8 mols.); the yield was 25%.

3-*Hydroxyphenanthrene.*—Phenanthrene (50 g.), recrystallised from ethanol, was stirred into concentrated sulphuric acid (32·7 c.c.), the temperature then being raised to 120—125° and kept thereat for 4 hours. The mixture was then cooled to room temperature and carefully stirred into a large volume of cold water. Excess of sodium hydroxide was then added; phenanthrene-2- and -3-sulphonates were slowly precipitated and were separated by the difference in solubility of the barium salts (Fieser, *J. Amer. Chem. Soc.*, 1929, **51**, 2460); the 3-sulphonate was then converted into 3-hydroxyphenanthrene by alkali fusion (Smith, *J.*, 1916, **109**, 568); this formed colourless crystals (from ligroin), m. p. 118—119°.

Azo-compounds from Alkylaniline Derivatives.—These were prepared by slowly stirring the diazonium salt solution, previously neutralised with sodium acetate, into a solution of the calculated quantity of the phenol in ice-cold dilute aqueous sodium hydroxide; the azo-compounds were crystallised from the solvents stated and dried. The *p*-isomers were recrystallised several times to ensure complete removal of any *o*-isomers (checked by chromatography on alumina).

Azo-compounds from Long-chain Alkylphenols.—*p*-Hexadecyl- and *p*-octadecyl-phenol were dissolved in alcoholic sodium hydroxide, for coupling.

Azo-compounds from Hexadecyl m- *and* p-*Aminobenzoates and* p-*Hexadecyloxyaniline.*—The diazo-compounds were coupled with *o*- or *p*-cresol or β-naphthol in aqueous sodium hydroxide solution. To couple diazotised hexadecyl *m*-aminobenzoate with α-naphthol, the latter was dissolved in 75% aqueous ethanol and added carefully to the diazo-solution.

p-*Dodecylaniline* ⟶ p-*cresol* (IV). Owing to the low m. p., some difficulty was experienced in crystallising this *compound*, which, when warmed with acetic acid, tended to form oily globules. These were removed by settling and decantation and by charcoal treatment, to enable the dissolved portion to be crystallised; it gave small orange needles, m. p. *ca.* 35—40° (Found: C, 79·0; H, 9·2; N, 7·1. $C_{25}H_{36}ON_2$ requires C, 78·9; H, 9·5; N, 7·4%).

p-*Dodecylaniline* ⟶ β-*naphthol* (V) formed scarlet needles (from ethanol), m. p. *ca.* 75° (Found: C, 80·5; H, 8·5; N, 6·6. $C_{28}H_{36}ON_2$ requires C, 80·8; H, 8·7; N, 6·7%). p-*Dodecylaniline* ⟶ 3-*hydroxyphenanthrene* (VI) formed crimson needles (from ethanol), m. p. 74° (Found: C, 82·2; H, 8·1; N, 6·0. $C_{32}H_{38}ON_2$ requires C, 82·4; H, 8·15; N, 6·0%). p-*Hexadecylaniline* ⟶ β-*naphthol* (VII) was obtained as orange-red prisms (from glacial acetic acid), m. p. 97—98° (Found: C, 81·1; H, 9·2; N, 6·2. $C_{32}H_{44}ON_2$ requires C, 81·1; H, 9·3; N, 5·95%), and *aniline* ⟶ p-*hexadecylphenol* (VIII) as orange-yellow prisms (from glacial acetic acid and then ethanol), m. p. 84° (Found: N, 6·5. $C_{28}H_{42}ON_2$ requires N, 6·65%). *Aniline* ⟶ p-*octadecylphenol* (IX) formed orange-yellow prisms (from glacial acetic acid and then ethanol), m. p. 87° (Found: C, 80·1; H, 10·1; N, 6·4. $C_{30}H_{46}ON_2$ requires C, 80·0; H, 10·2; N, 6·25%), and *hexadecyl* m-*aminobenzoate* ⟶ p-*cresol* (X) orange prisms (from ethanol), m. p. 82° (Found: C, 74·8; H, 9·1; N, 5·9. $C_{30}H_{44}O_3N_2$ requires C, 75·0; H, 9·2; N, 5·9%). *Hexadecyl* m-*aminobenzoate* ⟶ β-*naphthol* (XI), orange prisms, m. p. 84° (Found: C, 77·0; H, 8·9; N, 5·11. $C_{33}H_{44}O_3N_2$ requires C, 76·8; H, 8·5; N, 5·4%), and the p-*amino*-analogue (XII), orange-red prisms, m. p. 80°. (Found: C, 76·5; H, 8·7; N, 5·6%), were both crystallised from ethanol. p-*Hexadecyloxyaniline* ⟶ p-*cresol* (XIII) formed yellowish-orange needles (from glacial acetic acid and then ethanol), m. p. 67° (Found: C, 77·2; H, 9·8; N, 6·5. $C_{29}H_{44}O_2N_2$ requires C, 77·0; H, 9·75; N, 6·2%), and the β-*naphthol* analogue (XIV) formed dark red prisms (from ethanol), m. p. indef. (Found: C, 78·5; H, 9·1; N, 5·5. $C_{32}H_{44}O_2N_2$ requires C, 78·7; H, 9·0; N, 5·7%). p-*Dodecylaniline* ⟶ o-*cresol* (XV), orange prisms, m. p. 48° (Found: C, 79·0; H, 9·9; N, 7·3. $C_{25}H_{36}O_2N_2$ requires C, 78·9; H, 9·5; N, 7·4%), and its α-*naphthol* analogue (XVI), dark red prisms, m. p. 120° (Found: C, 80·7; H, 8·4; N, 6·5. $C_{28}H_{36}ON_2$ requires C, 80·8; H, 8·7; N, 6·7%), were both crystallised from ethanol. The 1-*hydroxyanthracene* analogue (XVII) formed bluish-red prisms (from glacial acetic acid), m. p. 60° (Found : C, 82·1; H, 8·4; N, 5·9. $C_{32}H_{38}ON_2$ requires C, 82·4; H, 8·2; N, 6·0%). *Hexadecyl* m-*aminobenzoate* ⟶ o-*cresol* (XVIII) formed orange-yellow prisms (from glacial acetic acid), m. p. 103° (Found : C, 74·7; H, 9·1; N, 6·1. $C_{30}H_{44}O_3N_2$ requires C, 75·0; H, 9·2; N, 5·9%), and its α-*naphthol* analogue (XIX), crystallised from ethanol, then purified by alumina chromatography from benzene solution containing 0·5% of ethanol, and finally crystallised from ethanol, formed dark red prisms, m. p. 90° (Found : C, 76·6; H, 8·3; N, 5·6. $C_{33}H_{44}O_3N_2$ requires C, 76·8; H, 8·55; N, 5·4%). *Hexadecyl* p-*aminobenzoate* ⟶ o-*cresol* (XX) crystallised in orange prisms (from glacial acetic acid), m. p. 96° (Found : C, 74·8; H, 9·5; N, 6·0. $C_{30}H_{44}O_3N_2$ requires C, 75·0; H, 9·2; N, 5·9%). p-*Hexadecyloxyaniline* ⟶ o-*cresol* (XXI) formed orange prisms (from glacial acetic acid), m. p. 58° (Found : C, 76·7; H, 10·0; N, 6·1. $C_{29}H_{44}O_2N_2$ requires C, 77·0; H, 9·75; N, 6·2%), and the α-*naphthol* analogue (XXII), purified as (XIX), dark red prisms, m. p. 108° (Found : C, 78·6; H, 8·8; N, 5·6. $C_{32}H_{44}O_2N_2$ requires C, 78·7; H, 9·05; N, 5·75%).

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