728. *Researches on Monolayers. Part III.* The Effect of Mono- and Di-hydric Phenols on Monolayers of Certain Aromatic Compounds.*

By C. H. Giles and E. L. Neustädter.

Azo, hydroxy, and quinone groups in monolayers of aromatic compounds on water form a hydrogen bond with the hydroxy-group in monohydric phenols dissolved in the water phase. The increased water attraction thus imparted, *e.g.*, to the azo-group, may cause an expansion of the film by a change in the angle of tilt of the film molecule. Dihydric phenols in the water act in two ways: (*a*) If there are two suitably placed bonding groups in the monolayer molecule a 1 : 1-molecular complex may be formed, in which each of these groups is bonded with one hydroxy-group in the solute molecule; the two molecules probably stand parallel and side by side; a small increase in film area occurs and the compressibility may decrease. Quinol acts thus on (i) some hydroxyazo-compounds and (ii) benzoquinone and anthraquinone derivatives; with (ii) a quinhydrone-type compound appears to be formed. (*b*) If the solute hydroxy-groups are too far apart for (*a*) to occur, they may form cross-links between monolayer molecules, leading to a considerable increase in film area and compressibility.

A confirmation that the observed effects are caused by hydrogen bonding, and not merely by penetration of the film by bulky solute molecules, is afforded by the absence of significant changes in film area or compressibility when pyridine is used as solute below films of compounds with which it cannot form a hydrogen bond.

The orientation of surface-active azo-compounds in monolayers on water, and on dilute acid and alkali, has been described in Parts I and II (*J.*, 1952, 918, 1864). Many of the most important classes of dye contain the azo-group, which, besides acting as a chromophoric centre in the molecule, is believed to be partly responsible for their adsorption to fibres, by reason of hydrogen-bond formation with suitable groups, *e.g.*, hydroxy-groups in cellulose and the peptide link in protein fibres (see, *e.g.*, Vickerstaff, "The Physical Chemistry of Dyeing," Oliver and Boyd, London and Edinburgh, 1950).

The present paper describes preliminary investigations to determine if such hydrogen-bond formation, both with azo-compounds and other classes of dye, is detectable by experiments on monolayers. Some of the hydroxyazo-compounds already described, and other surface-active bodies containing groups commonly met in dyes and/or fibres, *e.g.*, quinone and imino-groups, have been used, and their bonding properties with hydroxy-compounds, in particular with phenols, have been studied.

Alexander (*Proc. Roy. Soc.*, 1941, *A*, **179**, 470, 486) has examined intra- and inter-molecular hydrogen bonding in monolayers of aliphatic amides and has in one case tentatively suggested a link between two such monolayer molecules through a water molecule. Schulman and Rideal (*ibid.*, 1937, *B*, **122**, 29, 46) have also studied the effect of polyhydric phenols upon protein mono-layers. No systematic study of bonding to fibre substrates by using the monolayer technique, however, appears to have been reported.

For the present research, compounds (VII)—(XIV) (see Table 1) have been prepared, and their film-forming properties on water examined. The action of certain solutes introduced into the aqueous phase has also been studied, by using monolayers of compounds (VII)—(XIV) and of typical azo-compounds (I)—(VI) selected from those described in Parts I and II. The exact choice of structure in compounds (VII)—(XIV) was dictated partly by the need to incorporate the desired groups and partly by the availability of the starting materials.

As solutes in the aqueous phase, phenol itself and also various dihydric phenols and ethylene glycol were used; pyridine was included, to study the effect of a water-soluble molecule which is of similar size to phenol, but has no hydrogen atom free to form an intermolecular bond.

The results are summarised in Tables 1 and 2, and typical curves are shown in Figs. 1—3.

---

* Part II, *J.*, 1952, 1864.

TABLE 1. *Molecular areas and compressibilities of monolayers on aqueous solutions of phenols, etc.*

No.	Compound	θ *	H_2O	Molecular area (Å^2) at zero compression and (in parentheses) compressibility † on : 0·1N-aqueous solutions of §						
				a	*b*	*c*	*d*	*e*	*f*	*g*
	Azo-compounds without hydroxy-groups.									
I	*p*-Dodecylazobenzene	—	No film formed	No film formed	—	—	—	—	—	—
II	4-Hexadecyloxyazobenzene	70° ‡	,,	37 (0·23)	—	—	—	—	—	—
III	4′-Hexadecyloxybis(phenylazo)benzene	90	38 (0·13)	(0·36) 48	—	—	—	37 (0·23)	—	—
	o-*Hydroxyazo-compound.*									
IV	*p*-Dodecylaniline → β-naphthol	60	(0·16) 42·5	(0·42) 102	(0·42) 113	(1·23) 152	(1·33) 198	(0·12) 44	(0·29) 80	(0·38) 110
	p-*Hydroxyazo-compound.*									
V	Hexadecyl *p*-aminobenzoate → *o*-cresol	50	(0·09) 44	(0·40) 51	(0·19) 52	(0·65) 122	(1·23) 175	(0·29) 42	(0·12) 48	(0·30) 50
	oo′-*Dihydroxyazo-compound.*									
VI	*o*-Aminophenol → *p*-hexadecylphenol	80	(0·09) 47	—	(0·14) 51	—	—	—	—	—
VII	*N*-Methylstearamide	—	(0·03) 21	(0·05) 23	(0·08) 29	(0·36) 44	—	—	—	—
VIII	*N*-*n*-Butylstearamide	—	No film formed	—	—	—	—	—	—	No film formed
IX	2-*p*′-Dodecylphenyl-*p*-benzoquinone	80	26 (0·02)	27·5 (0·04)	27 (0)	54 (0·31)	—	—	25 (0)	—
X	2-*p*′-Dodecylphenyl-*p*-quinol	—	(Oxidises)	—	—	—	—	—	—	—
XI	3-*p*-Dodecylanilinomethyl-2-naphthol	90	(0·19) 31	—	(0·18) 31	—	—	—	—	—
XII	1-Stearamidoanthraquinone	60	48 (0·09)	—	(0·05) 55	(0·60) 69	—	—	(0·11) 53	—
XIII	2- ,,	40	42 (0·09)	—	53(0·05)	—	—	—	50 (0·14)	—
XIV	2-Anthraquinonyl stearate	90	33 (0·03)	—	34 (0)	39 (0·16)	—	—	34 (0·01)	—

* θ = Probable angle of orientation on water of longest aromatic axis.

† Expressed as the tangent of the angle to the vertical of the upper portion of the π–A curve (Figs. 1—3).

‡ On phenol solution.

§ *a* = Phenol; *b* = *p*-quinol; *c* = 1 : 5-dihydroxynaphthalene; *d* = sodium 1 : 2 : 4 : 5 : 6 : 8-hexahydroxyanthraquinone-3 : 7-disulphonate; *e* = pyridine; *f* = ethylene glycol; *g* = catechol.

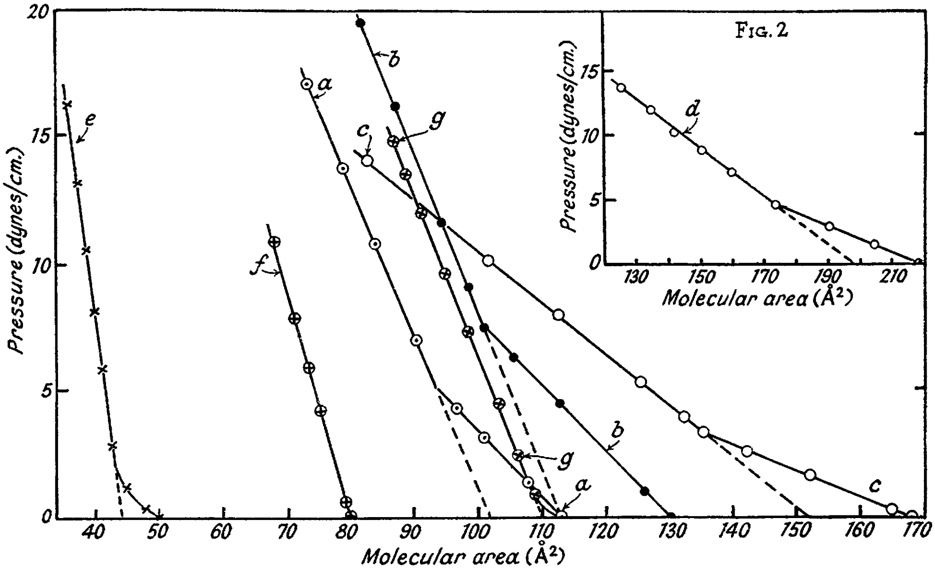
Table 1 gives the data on which most of the conclusions are based; Table 2 shows the areas at which surface pressure is first observed and at which the upper (linear) part of the π–A curve commences.

Monolayers on Water.—Compound (VIII) does not form films. This is undoubtedly owing to a steric effect, the water-attracting "head" group being prevented from penetrating the water surface sufficiently, by reason of the configuration of the hydrocarbon groups on either side (cf. Adam, "The Physics and Chemistry of Surfaces," Oxford Univ. Press, 3rd edn., 1941, Chap. II). (I) and (II) do not form films because the azo-group has insufficient water attraction (see Part I).

Compounds (VII) and (IX)—(XIV) all form stable condensed films. The molecular areas are consistent with orientation of the aromatic nuclei in a vertical plane, but the axis may in some cases be tilted parallel to this plane at an angle determined by the nature and position of the attached groups.

The closest packing of the benzoquinone compound (IX) is achieved when the molecule

FIG. 1. FIG. 2.



FIGS. 1 & 2. *Force–area curves for compound* (IV) *on various substrates.*

(*a*) *Phenol.*
(*b*) *Quinol.*
(*c*) 1 : 5-*Dihydroxynaphthalene.*
(*d*) *Sodium* 1 : 2 : 4 : 5 : 6 : 8-*hexahydroxyanthraquinone*-3 : 7-*disulphonate.*
(*e*) *Pyridine.*
(*f*) *Ethylene glycol.*
(*g*) *Catechol.*

TABLE 2. *Areas* (Å²) *at* (i) *commencement of development of surface pressure and at* (ii) *lowest point of upper* π–A *curve.*

Substrate : *

Com-	H_2O		*a*		*b*		*c*		*d*		*e*		*f*		*g*	
pound	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)
II	—	—	57	32	—	—	—	—	—	—	—	—	—	—	—	—
III	48	35	60	42	—	—	—	—	—	—	48	35	—	—	—	—
IV	45	42	102	94 †	130	100 †	168	135 †	219	174	50	43	80	80	112	107 †
V	45	44	67	44 †	60	47 †	134	98 †	180	172	47	39	52	47	56	48 †
VI	53	46	—	—	52	48	—	—	—	—	—	—	—	—	—	—
VII	23	21	29	22	32	26	53	37 †	—	—	—	—	—	—	—	—
IX	26	26	32	27	31	27	60	51	—	—	—	—	29	25	—	—
XI	31	31	—	—	31	31	—	—	—	—	—	—	—	—	—	—
XII	54	48	—	—	58	55	80	62	—	—	—	—	56	52	—	—
XIII	44	41	—	—	57	53	—	—	—	—	—	—	53	49	—	—
XIV	37	33	—	—	42	34	53	36	—	—	—	—	39	34 †	—	—

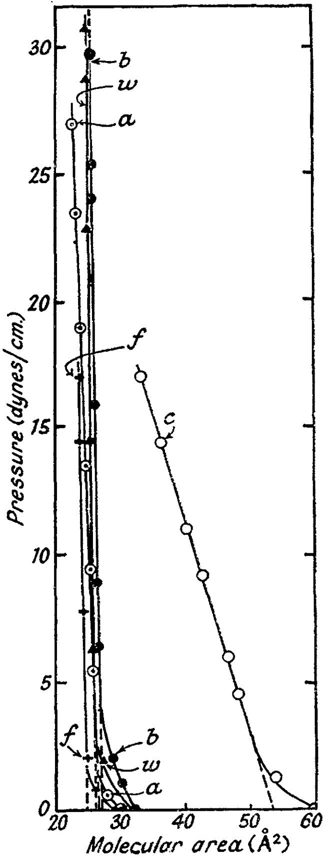
* For key, see table 1.
† Denotes linearity of the lower portion of the π–A curve.

is tilted as shown in Fig. 4. This corresponds to a repeat distance, perpendicular to the plane of the aromatic rings, of 3·5—4 Å, which appears rather too small to accommodate a bridging water molecule, in the manner suggested for the azo-compounds (see Part I).

The quinol derivative (X) is oxidised too readily in the film for reliable measurements to be made. A quinhydrone is probably formed, because when wiped away the film is seen to be dark green.

Compound (XIV) appears to stand with its anthraquinone nucleus vertical, some of the molecules perhaps being forced up a little above the level of the remainder to assist close packing of the quinone groups (Fig. 5). The repeat distance perpendicular to the rings is thus about 4·5 Å. This is greater than the value for (IX). The reason may be that greater separation is necessary to accommodate the $-O-\overset{|}{C}=O$ group, which cannot lie in quite the same plane as the rings.

FIG. 3. *Force–area curves for compound (IX) on various substrates.*



(*a*) *Phenol.* (*f*) *Ethylene glycol.*
(*b*) *Quinol.* (*c*) 1 : 5-*Dihydroxy-naphthalene.*
(*w*) *Water.*

FIG. 4. *Probable orientation of* (IX) *on water* (*θ* = 80°).

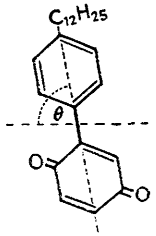


FIG. 5. *Probable orientation of* (XIV) *on water* (*θ* = 90°).

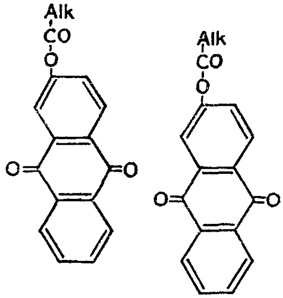


FIG. 6. (XII) (*θ* = 60°).

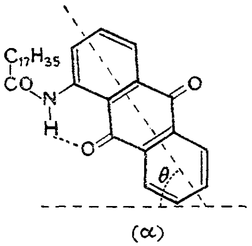
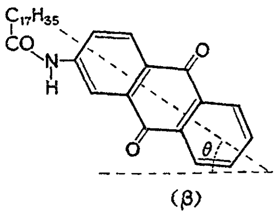


FIG. 7. (XIII) (*θ* = 40°)



Probable orientation of 1- *and* 2-*stearamidoanthraquinone* (XII *and* XIII, *respectively*).

The water-attraction of the amide group in (XII) and (XIII) causes a pronounced tilt (Figs. 6, 7) and the molecules are less closely packed than are those of (XIV).

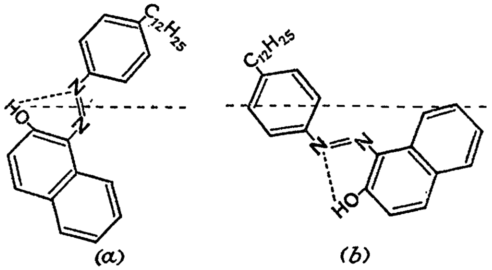
Monolayers on Phenol Solution.—The effect of a hydrogen bond between the phenolic hydroxyl group and an azo-nitrogen atom, combined with the water attraction of the ether oxygen atom, is sufficient to enable a stable film of (II) to be formed on phenol solution. The bond between phenol and the azo-group alone is insufficient to promote film formation, for (I) is not film-forming either on water or on phenol solution.

(VIII) does not form a film on phenol solutions, confirming that steric factors are preventing anchorage to the water surface; otherwise, phenol might be expected to attract the ·CO·NH· group sufficiently to cause monolayer formation.

Phenol causes a large increase in the apparent area of the *o*-hydroxyazo-compound (IV), but only a small increase in that of the *p*-hydroxyazo-compound (V). The *p*-compound is already tilted considerably on water, and any further tilt which might follow a greater solubilising action on the hydroxy, azo, or ester group would have little effect on the apparent molecular area. The observed increase can, in fact, be accounted for by an additional tilt of some 10°. In the case of the *o*-hydroxyazo-compound (IV) the additional attraction of the azo-group for the aqueous phase, imparted by the presence of phenol, must cause a considerable change in tilt. The observed area increase on phenol could be accounted for by a change in tilt of some 90° (Fig. 8), which allows the azo-group to be more exposed to the water phase.

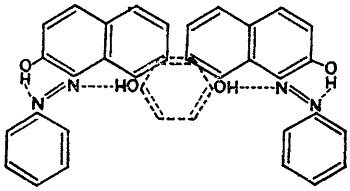
The high compressibility values of the azo-compounds on phenol solution seems to be an indication of the increased solubility of the molecules; monolayers of (VII) and (IX) are almost unaffected in area and compressibility by this solute, suggesting that the film molecules are too closely packed for ready penetration by phenol.

FIG. 8. *Probable orientation of an* o-*hydroxyazo-compound* (IV) *on* (a) *water and* (b) *phenol solution.*



(a) (b)

FIG. 9. *Cross-linking of* (IV) *by quinol.*



Monolayers on Quinol Solution.—Quinol causes considerable increase in area and compressibility of (IV); a small expansion with (V), (VI), (VII), (XII), and (XIII), and no significant expansion of (IX), (XI), and (XIV). The considerable expansion with (IV) is attributable to a cross-linking of the azo-groups in adjacent molecules as shown in Fig. 9.* It is obvious that the increased compressibility of such a film could be accounted for by a "folding" of the cross-linkages, resembling the collapsing of a set of parallel rules.

The smaller expansion of (V), (VI), (XII), and (XIII) must be due to formation of a 1 : 1-molecular complex, because a study of the structure of these molecules shows that each has a pair of groups so placed that they can simultaneously bond with the two hydroxy-groups of quinol. In (V) the azo-group and the *p*-hydroxy-group, and in (VI) one hydroxy-group and one azo-nitrogen atom,† are the effective pairs, and the quinones can similarly react to form quinhydrone-type complexes. The quinol molecule in such a complex must lie flat against the quinone or azo-molecule; thus the film expansion is much less than when cross-bonding occurs (Figs. 10, 11). The compressibility of the quinones (XII, XIII) is slightly reduced by this complex formation, as might be expected, but that of the azo-compounds (V, VI) is somewhat increased and in these, therefore, cross-linkage must occur to a small extent.

Penetration of the film of the benzoquinone compound (IX) by quinol appears to be limited ‡ and no penetration appears to occur with (XIV), presumably because of the tight packing of the film molecules.

---

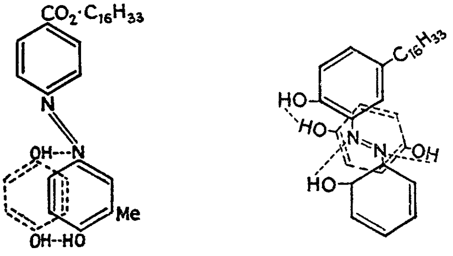
* The $C_{(2)}$-hydroxy-group of the naphthalene nucleus is probably chelated with one azo-nitrogen atom, as shown, leaving one nitrogen atom free to form the intermolecular bond. For clarity, the N····H bonds between quinol and the azo-groups are not shown to scale. The $C_{12}H_{25}$ groups are omitted from Fig. 9.

† Schetty (*Textil-Rundschau*, 1950, **5**, 399) has shown that in *oo′*-dihydroxyazo-compounds only one hydroxy-group is chelated with an azo-nitrogen atom.

‡ That some reaction occurs is shown by the deep green colour of this film when it is wiped off the quinol solution.

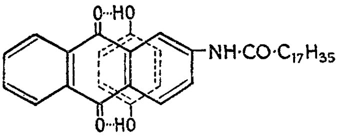
Monolayers on Solutions of Dihydroxy-compounds of Large Molecular Size.—1 : 5-Dihydroxynaphthalene produces a considerable increase in both area and compressibility of films of (IV), (V), (VII), (IX), and (XII). This must be due to cross-linking of two molecules of the film by the dihydroxy-molecule (Fig. 12), but the two hydroxy-groups in the latter are only very slightly further apart * than are those in quinol, so that the much greater increases in the film areas produced by 1 : 5-dihydroxynaphthalene are an indication that the plane of the aromatic rings in these cross-linking compounds lies parallel to the water surface, they may, indeed, float on the surface.

FIG. 10. 1 : 1-*Complex formation of* (*a*) (V) *and* (*b*) (VI) *with quinol.*



(*a*) (*b*)

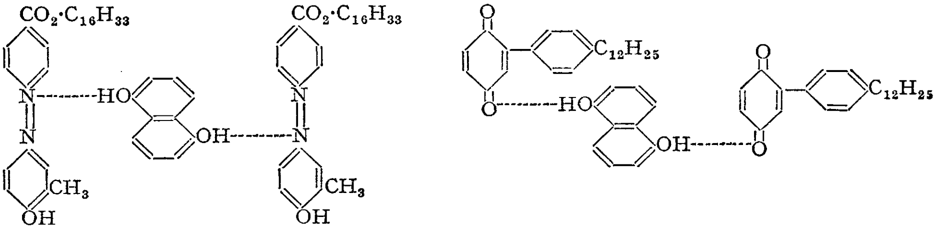
FIG. 11. 1 : 1-*Complex formation of* (XIII) *with quinol.*



A greater expansion should be produced by a water-soluble compound having phenolic hydroxy-groups still more widely separated in the molecule. Sodium 1 : 2 : 4 : 5 : 6 : 8-hexahydroxyanthraquinone-3 : 7-disulphonate was found suitable for trial. As expected, this compound does produce a striking increase in area and compressibility of films of (IV) and (V).

It is noteworthy that the film of (XIV) is so tightly packed and the van der Waals forces between the molecules of the large underwater " head " so great that very few dihydroxy-molecules can penetrate the monolayer. Quinol is without effect and even 1 : 5-dihydroxynaphthalene produces only a small increase in area and compressibility, which may be due to a limited degree of cross-linking. A less likely cause of the small area increase might be 1 : 1-complex formation across the ester group and the most remote quinone group.

FIG. 12. *Cross-linking by* 1 : 5-*dihydroxynaphthalene.*



Monolayers on Pyridine.—The molecule of pyridine is of roughly the same size and shape as that of phenol or quinol, but it has no hydrogen atom free to form a bond. It was thought, therefore, that a study of its action in the aqueous phase below the film might confirm the belief that the effects produced by the hydroxy-compounds are indeed due to hydrogen bonding and not merely to a penetration of the film by unbonded solute molecules. If hydrogen bonding alone is responsible for the increases in the apparent molecular area and compressibility of, *e.g.*, (IV), produced by quinol, then films of this substance on pyridine solution should have the same characteristics as they do on water, because, if the hydroxy-group in (IV) is chelated with one of the nitrogen atoms in the azo-group, there is no group capable of forming a hydrogen bond with pyridine. The data in Table 1 (col. *e*) show that pyridine has, in fact, no significant effect on the area of films of (IV) or of (III). There is a small increase in compressibility.

---

* The distances, centre-to-centre, between the pairs of oxygen atoms are about 6 Å and 6·5 Å in quinol and 1 : 5-dihydroxynaphthalene, respectively.

When present below films of a compound having a free hydroxy-group (*e.g.*, V), pyridine increases the compressibility, but slightly decreases the molecular area. These effects can be attributed to the effect of bonding between the solute and the hydroxy-group in the film molecule. This would cause an increased solubility of the latter, and perhaps some change in its orientation.

Monolayers on Ethylene Glycol.—The molecular areas and compressibility data suggest that this compound is unable to penetrate the films of (IX) and (XIV), but that it probably causes an increased tilt of the molecules of the azo-compounds (IV, V) and the stearamido-anthraquinones (XII, XIII) by increasing the solubility of hydroxy and/or ester groups.

Monolayers on Catechol Solution.—The large increase in compressibility of (IV) and (V) suggests that cross-linking is taking place; this suggestion is supported by the value of the molecular area of (IV), which shows a considerable increase; but the much smaller increase in area of (V) may indicate that re-orientation occurs as well, owing to a change in the relative solubility of the substituent groups in the monolayer molecule, and that this masks the increased film area which would otherwise occur.

N-*Methylstearamide* (VII).—The monolayer of this compound is very slightly increased in area and compressibility by phenol, possibly owing to an enhanced solubility. Quinol has a very much smaller effect on these parameters than would be expected if cross-linkage occurred, and it may be that hydrogen bonding does take place, but the quinol molecules lie parallel with the lines of stearamide molecules, forming a kind of "chain linkage," rather than at right angles to them, as they would do in cross-linking. The larger molecule of 1 : 5-dihydroxynaphthalene causes a much greater increase in area and compressibility. This may be due to some cross-linking at right angles to the lines of stearamide molecules.

Conclusion.—The general conclusion is that hydroxy-groups in a solute beneath the monolayer form hydrogen bonds with azo, quinone, amide, etc., groups in the monolayer molecules, provided that these are not too tightly packed to allow penetration of the solute. If the solute is a monohydric compound, the effect is to increase the attraction of the film-forming substance for water, often with a change in the orientation of the molecules in the layer and an expansion of the film.

Solutes having two hydroxy-groups may use both of them in forming bonds with suitable groups in the monolayer molecule. This they may do in either of two ways: (*a*) they may form cross-links between two monolayer molecules, thus considerably expanding the film and increasing its compressibility, or, (*b*) if two hydroxy-groups in the solute molecule are at a distance apart corresponding with that of two hydrogen-bonding groups in the monolayer molecule, they may form with the latter a 1 : 1-molar complex in which the two molecules are flat-packed side-by-side. The film is then only slightly expanded and its compressibility may be slightly reduced.

That the effects recorded are actually due to hydrogen bonding, and not merely to penetration of the film by bulky solute molecules, is confirmed by the use of pyridine. When this substance is the solute in the aqueous layer below films of substances with which it cannot form a hydrogen bond, no significant changes are observed.

EXPERIMENTAL

The film balance, the general technique used, and the preparation of compounds (I)—(VI) have been described in Parts I and II. The scale deflection of the film balance was 1·0 cm. per dyne.

In the present work, for the aqueous phase, distilled water alone or 0·1N-solutions therein of the water-soluble phenols, etc., in pure form were used. Sodium 1 : 2 : 4 : 5 : 6 : 8-hexahydroxyanthraquinone-3 : 7-disulphonate was an exception; it was a commercial sample of the dye alizarine-cyanine WRS (Bayer) (Colour Index No. 1063); it was readily soluble in water to a dark maroon solution [Found: purity (by $TiCl_3$ titration), 62%, 6 atoms of hydrogen being assumed to be required per mol. of dye]. Paper chromatography showed only traces of coloured impurities; the main impurity was probably sodium chloride.

The conclusions have been checked by the use of Stuart-type molecular models (see Appendix).

N-*Methylstearamide* (VII).—Methylamine hydrochloride (10 g.) was suspended in chloroform (50 c.c.) and to it was added, during 5 minutes, stearoyl chloride (44·5 g.) in chloroform (50 c.c.) at room temperature, with stirring and cooling. *N*-Methylmorpholine (30·7 g.), dissolved in chloroform (50 c.c.), was then added during 30 minutes. After a further hour, the solution was filtered and washed with dilute hydrochloric acid, sodium carbonate, and water successively. After being dried (Na_2SO_4), the chloroform was distilled off, and the residue recrystallised from alcohol; it formed colourless prisms, m. p. 91° (Found: C, 76·7; H, 12·8; N, 4·4. Calc. for $C_{19}H_{39}ON$: C, 76·8; H, 13·1; N, 4·7%).

N-n-*Butylstearamide* (VIII).—Stearoyl chloride (30 g.) was added slowly with cooling (in cold water) to *n*-butylamine (5·9 g.). A solid mass resulted; this was washed with dilute hydrochloric acid to remove any amine and recrystallised from alcohol, followed by ether, giving white needles of the *amide*, m. p. 70° (Found: C, 78·2; H, 13·5; N, 4·3. $C_{21}H_{43}ON$ requires C, 77·9; H, 13·3; N, 4·1%).

2-p′-*Dodecylphenyl*-p-*benzoquinone* (IX).—This was prepared by Kvalnes's method (*J. Amer. Chem. Soc.*, 1934, **56**, 2478), from *p*-dodecylaniline (26·2 g., 1 mol.) which was diazotised as described in Part I. The *quinone* formed pale yellow prisms, m. p. 76°, from acetic acid (Found: C, 81·6; H, 9·2. $C_{24}H_{32}O_2$ requires C, 81·8; H, 9·1%).

2-p′-*Dodecylphenyl*-p-*quinol* (X).—The quinone (IX) was reduced by boiling it under reflux for 2 hours with zinc dust and acetic acid. The red solution became yellow and the *quinol* was then precipitated in water; it formed prisms (from acetic acid), m. p. 80° (Found: C, 81·6; H, 9·4. $C_{24}H_{34}O_2$ requires C, 81·4; H, 9·6%).

3-p-*Dodecylanilinomethyl*-2-*naphthol* (XI).—This was obtained by the reduction of the corresponding keto-compound, prepared by dissolving 3-hydroxy-2-naphthoic acid (5 g.) in a small volume of toluene to which *p*-dodecylaniline (7 g.), dissolved in toluene, and phosphorus trichloride (5 g.) were added. The mixture was heated under reflux for several hours, and the product, m. p. 160°, recrystallised from benzene and then reduced. A solution of lithium aluminium hydride (1 g.) in 30 c.c. of ether was placed in a 3-necked flask fitted with a stirrer, and a solution of the amide (3·3 g.) in ether was added gradually, with stirring, to produce gentle refluxing. On completion of the reaction, water was added cautiously and the mixture was finally poured into ice and water acidified with sulphuric acid. The aqueous layer was extracted with ether, the extract evaporated, and the *product* recrystallised from benzene; it formed prisms, m. p. 114° (Found: C, 83·7; H, 9·2. $C_{29}H_{39}ON$ requires C, 83·5; H, 9·35%).

1- *and* 2-*Stearamidoanthraquinone* (XII, XIII).—1- or 2-Aminoanthraquinone (22·3 g.) and stearoyl chloride (30 g.) were dissolved in nitrobenzene and heated under reflux for 5 hours (Newton and F. Bayer and Co., B.P. 3055/1909). On cooling the solution crystals separated; recrystallisation from pyridine gave yellow needles, m. p. 120° and 182°, respectively (Found: (XIII) C, 78·3; H, 8·7; N, 3·1. (XIV) C, 78·3; H, 9·1; N, 3·0. $C_{32}H_{43}O_3N$ requires C, 78·4; H, 9·0; N, 2·9%).

2-*Anthraquinonyl Stearate* (XIV).—A solution of stearoyl chloride (30 g.) in nitrobenzene was added to a hot solution of 2-hydroxyanthraquinone (22·4 g.) in nitrobenzene. Heating was continued for 30 minutes at 180°. The *product* separated on cooling; and formed prisms, m. p. 85° from ethanol (Found: C, 78·6; H, 8·6. $C_{32}H_{42}O_4$ requires C, 78·4; H, 8·6%).

Appendix.—Determination of Orientation Angles from Molecular Models. Two Stuart-type models of each molecule are placed flat on squared paper, and oriented at different angles to a line representing the water surface, until a position is found satisfying the following requirements:

The two models are just in contact and are each at the same level, and oriented at the same angle, relative to the surface line; and the water-attracting groups are slightly beneath the surface line. It is found in nearly all cases that there is one such position where the repeat distance is a minimum; the corresponding orientation angle is given in the Tables in this paper and in Parts I and II.

We are indebted to Professor P. D. Ritchie for his interest and encouragement, and to Mr. A. Pajackowski for assistance with some of the syntheses. We also thank the Directors of Imperial Chemical Industries Limited, Dyestuffs Division, for financial assistance to one of us (E. L. N.), and for the supply of several intermediates.

Department of Technical Chemistry,
Royal Technical College, Glasgow, C.1

[*Received, March 4th,* 1952.]