342. *Researches on Monolayers. Part II.* The Effect of Acid and Alkali upon Monolayers of Aromatic Azo-compounds containing Long Alkyl Chains.*

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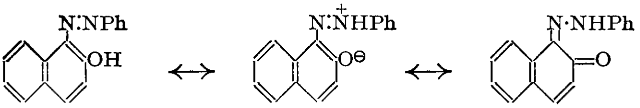
The apparent molecular areas and compressibilities of aromatic hydroxyazo-compounds containing long alkyl chains have been measured in monolayers on dilute acid and alkali. In accordance with published data, the *p*-hydroxy-compounds appear to exist almost completely in the azo-form. The *o*-compounds appear to contain much of the hydrazone form, but the results do not give decisive evidence of the presence or absence of the azo-tautomer in this series, except in one case, where an *oo'*-dihydroxyazo-compound appears to contain the azo-form.

THE determination of molecular areas and orientation of aromatic hydroxyazo-compounds containing long alkyl (C_{12}—C_{18}) chains, in monolayers on water, has been described in Part I.* The work has now been extended by a study of the influence of acid or alkali upon the films, in order to determine whether by this means the presence of a chelate link in *o*-hydroxyazo-compounds or of the quinone hydrazone tautomer in either type of azo-compound could be detected.

The Structure of Hydroxyazo-compounds.—It is well known that many aromatic hydroxyazo-compounds appear to co-exist with the corresponding quinone hydrazone tautomers, but the evidence for the exact formulation of the *o*- and *p*-series is somewhat conflicting (see Sidgwick's "The Organic Chemistry of Nitrogen," Taylor and Baker, Clarendon Press, Chap. XIV). Some authors have claimed that *o*-hydroxyazo-compounds exist only in the quinonoid form, and some state that *p*-compounds are preponderantly in the azo-form. It has also been suggested that resonance of both forms with a third zwitterion configuration may occur in the *o*-hydroxyazo-series (Kuhn, *Naturwiss.*, 1932, **20**, 618), whereby the forms of phenylazo-β-naphthol can be represented thus :



Burawoy and Markowitsch-Burawoy (*J.*, 1936, 36), however, following studies of absorption spectra, stated that the similarity between 2-phenylazo-1-naphthol and its *N*-phenyl derivative, and the difference between these two on the one hand and the corresponding *O*-methyl ether on the other, exclude the interpretation of the structure of the *o*-hydroxyazo-compounds as resonance hybrids.

Chelation of the hydroxy-group with the adjacent azo-group has been detected in water-insoluble *o*-hydroxyazo-compounds when dissolved in organic solvents (Mason, *J. Soc. Dyers Col.*, 1932, **48**, 293; Hendricks, Wulf, Hilbert, and Liddell, *J. Amer. Chem. Soc.*, 1936, **58**, 1991). This fact has usually been considered to account for the insolubility of such compounds in aqueous alkali, but Burawoy (Discussion on paper by Desai and Giles, *J. Soc. Dyers Col.*, 1949, **65**, 639) has pointed out that *o*-nitrophenol, which contains a chelate bond, is nevertheless a stronger acid than the *m*- and the *p*-isomer, and therefore he considers that the insolubility of *o*-hydroxyazo-compounds in alkali is not due to such a bond, but rather to their existence entirely as quinone hydrazones.

Effects of Ionisation in Monolayers.—Ionisation of water-attracting groups in a monolayer, on water, by addition of acid or alkali, as appropriate, *e.g.*, the addition of alkali to the water below a monolayer of a phenol, or of an acid to the water below a monolayer of a base, increases the apparent molecular area of the monolayer compound owing to the mutual electrostatic repulsion of the ions (Adam, "The Physics and Chemistry of Surfaces," Oxford Univ. Press, 3rd edn., 1941, Chap. II). Adam and Miller (*Proc. Roy. Soc.*, 1933,

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* Part I, *J.*, 1952, 918.

A, **142**, 401), for example, found that the molecular areas of long alkyl-chain phenols increased when 2N-sodium carbonate or 2N-sodium hydroxide solutions were used as substrates, for, whereas all the phenols tended to give a molecular area of 24 Å^2 on water, those of *p*-dodecyl- and *p*-hexadecyl-phenol increased to *ca.* 42·5 Å^2 and *ca.* 28·5 Å^2, respectively, on 2N-sodium carbonate solution at 16°. When Adam and Miller's curves are replotted to the scales used in the figures of the present paper, the increases in

FIG. 1. *Areas on* 0·1N-HCl (*abscissæ*).

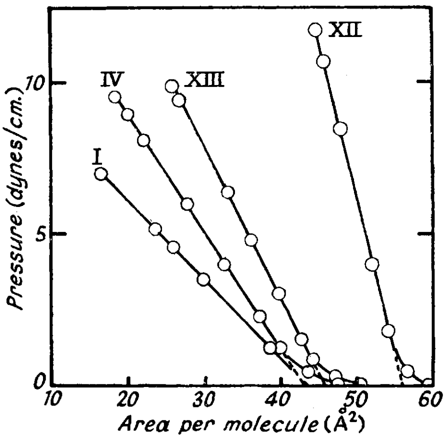


FIG. 2. *Areas on* 0·1N-HCl (*abscissæ*).

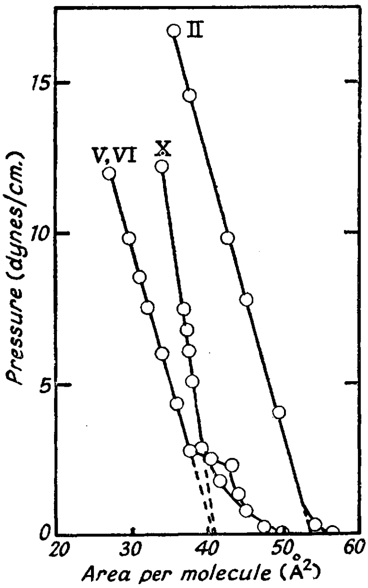


FIG. 3. *Areas on* 0·1N-HCl.

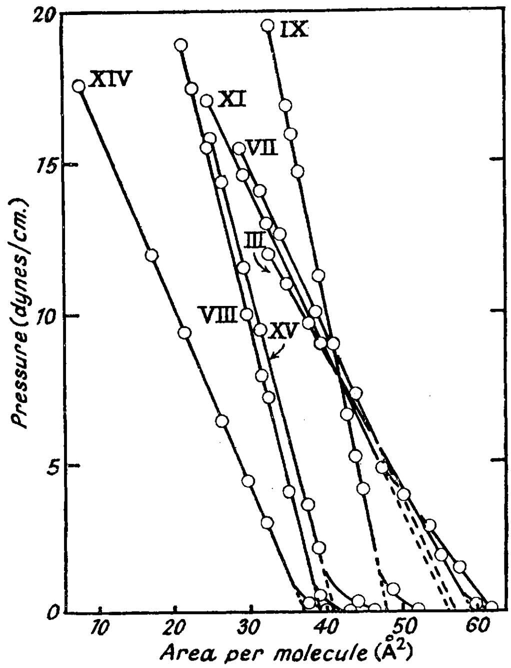
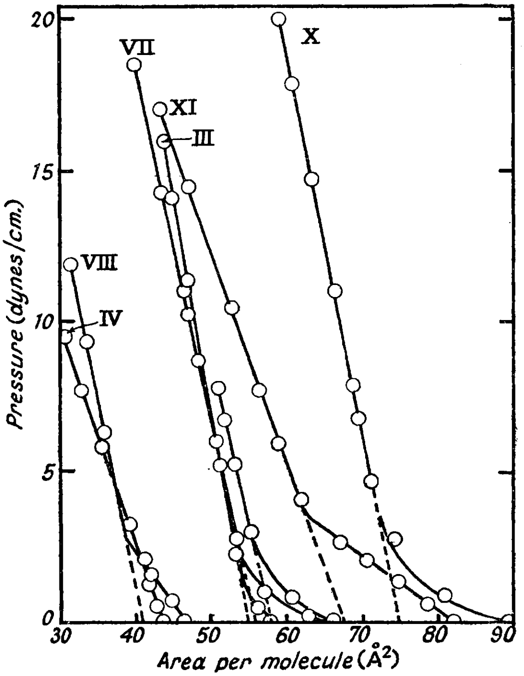


FIG. 4. *Areas on* 0·1N-Na$_2$CO$_3$.

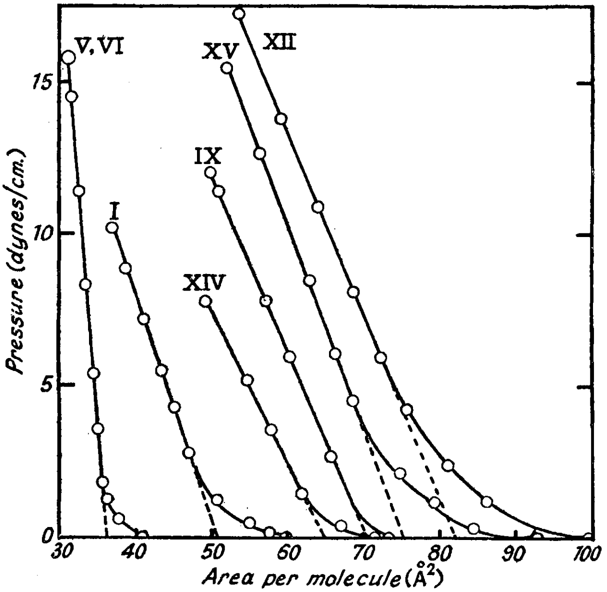


compressibility are *ca.* 0·06 and 0·01, respectively, and these may be attributed to the greater intermolecular distances in the expanded films.

It was thought that an investigation of the behaviour, as monolayers on aqueous acid and alkaline solutions, of the surface-active hydroxyazo-compounds already described by us (Part I, *loc. cit.*) might provide new evidence relating to the configuration of hydroxyazo-compounds in general.

Discussion.—The hydroxy-group of the azo-form would be expected to ionise on alkaline solutions and the imino-group of the quinone form might ionise on acid solutions. Many of the compounds described in Part I have now therefore been examined as monolayers on alkaline and acid solutions. Unbuffered 0·1N-solutions [*][†] of hydrochloric acid and sodium carbonate were used as substrates. Sodium hydroxide was found to be unsuitable [‡] owing to attack by atmospheric carbon dioxide. The pH value of the sodium carbonate solution is close to the probable p*K* values of the compounds examined, and hence if the azo-form is present there may be roughly equal proportions of the ionised and the un-ionised form in the monolayer. Marsden and Schulman (*loc. cit.*) found that under these conditions the apparent molecular areas of certain fatty acids, amines, and esters were at a minimum and increased on either the acid or the alkaline side. As will be seen, the present results demonstrate in most cases a decided increase in molecular area on the alkaline solution, compared with water alone.

FIG. 5. *Areas on* 0·1N-Na_2CO_3.



Although the results show a reasonable consistency throughout the series of compounds tested, yet the interpretations must be considered tentative, based as they are on observation only of changes in compressibility of the films and in the apparent molecular areas. The detailed data are shown in the figures and in the table; in the latter, the film compressibility is expressed by the tangent of the angle (α) to the vertical of the upper part of the force–area curve.

If ionisation takes place at either an –OH or a >NH group we may expect

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[*] For one compound (X) the data in the Table refer to 1·0N-solutions.

[†] Marsden and Schulman (*Trans. Faraday Soc.*, 1938, **34**, 748) and Adam and Miller (*loc. cit.*) noticed certain anomalous effects due to the salts present when buffers were used as substrates.

[‡] Adam and Miller (*loc. cit.*) found that some films tended to collapse on 0·1N-sodium hydroxide, perhaps because of excessive solubility of the monolayer molecules. In the present experiments (II) was found to have an area of *ca.* 150 Å² on 0·1N-sodium hydroxide.

Effect of acid and alkali on compressibilities and apparent molecular areas of hydroxyazo-compounds in monolayers.

	Compound			Apparent molecular area at zero compression (Å²) and compressibility (tan α) § on :						ΔÅ² (%) and Δ tan α			
				Water		0·1N-HCl		0·1N-Na_2CO_3		0·1N-HCl		0·1N-Na_2CO_3	
No.	Diazo-component	Coupling component	θ ¶	Å²	tan α	Å²	tan α	Å²	tan α	ΔÅ² (%)	Δ tan α	ΔÅ² (%)	Δ tan α
	o-Hydroxyazo-compounds.												
I	p-NHPh·$C_{12}H_{25}$	p-C_6H_4Me·OH	45°	44·5	0·11	44	0·97	51	0·33	0	0·86	15	0·22
II	,,	β-$C_{10}H_7$·OH	60	42·5	0·16	53	0·25	58	0·21	24	0·09	36	0·05
III	,,	3-$C_{14}H_9$·OH †	65	50	0·23	59	0·53	55	0·18	18	0·30	10	−0·05
IV	p-NHPh·$C_{16}H_{33}$	β-$C_{10}H_7$·OH	60	44·5	0·05	43	0·65	44	0·33	−4	0·60	−1	0·28
V	NH_2Ph	p-$C_{16}H_{33}$·C_6H_4·OH	90	32	0·07	40	0·27	36	0·09	25	0·20	12	0·02
VI	,,	p-$C_{18}H_{37}$·C_6H_4·OH	90	32	0·07	40	0·27	36	0·09	25	0·20	12	0·02
VII	m-NH_2·C_6H_4·$CO_2C_{16}H_{33}$	β-$C_{10}H_7$·OH	55	57	0·28	57	0·43	56	0·21	0	0·15	−2	−0·07
VIII	p-NH_2·C_6H_4·O·$C_{16}H_{33}$	,,	55	38	0·05	39	0·21	41	0·19	2·5	0·16	8	0·14
	oo′-Dihydroxyazo-compound.												
IX	o-NH_2·C_6H_4·OH	p-$C_{16}H_{33}$·C_6H_4·OH	80	47	0·09	47	0·19	70	0·43	0	0·10	49	0·34
	p-Hydroxyazo-compounds.												
X	p-NHPh·$C_{12}H_{25}$ *	1-$C_{14}H_9$·OH ‡	90(?)	41	0·07	40	0·11	75	0·18	−3	0·04	83	0·11
XI	m-NH_2·C_6H_4·$CO_2C_{16}H_{33}$	o-C_6H_4Me·OH	60	53	0·25	56	0·45	68	0·33	6	0·20	28	0·08
XII	,,	α-$C_{10}H_7$·OH	60	55	0·36	56	0·23	82	0·40	2	−0·13	49	0·04
XIII	p-NH_2·C_6H_4·$CO_2C_{16}H_{33}$	o-C_6H_4Me·OH	50	44	0·09	46	0·51	—	—	5	0·42	—	—
XIV	p-NH_2·C_6H_4·O·$C_{16}H_{33}$	,,	90(?)	36	0·07	37	0·40	65	0·49	2·5	0·33	80	0·42
XV	,,	α-$C_{10}H_7$·OH	90(?)	38	0·18	41	0·25	75	0·36	8	0·07	97	0·18

* The data for this compound were obtained on 1N-solutions of HCl and Na_2CO_3.

† 3-Hydroxyphenanthrene.

‡ 1-Hydroxyanthracene.

§ Where α is the deviation from the vertical of the upper portion of the *F–A* curves in Figs. 1—5.

¶ Where θ is the probable orientation angle on water alone (see Part I).

some or all of the following changes to occur in the monolayer: (*a*) Mutual repulsion of the surface-active ions in the monolayer, leading to an increase in both apparent molecular area and compressibility. (*b*) A change in the balance of forces determining the orientation of the monolayer molecules relatively to the water surface, caused by changes in solubility of the ionisable groups. Thus the –OH group should be reduced in solubility by acid and increased by alkali, and the >NH group should behave in the reverse manner. The molecular orientation might then change, and either a decrease or an increase in molecular cross-section at the water surface would take place, depending, *e.g.*, upon the bulkiness of the under-water "head" group and the orientation of the several substituent groups. Such a change might mask, or be masked by, film expansion due to ionic repulsion, but if so, the latter would still be made evident by an increase in compressibility. (*c*) Partial collapse of the shorter (C_{12}) alkyl chain present in many of the compounds used, if ionic repulsion forces the molecules apart. Its length is so near the minimum required to form solid films that if the "head" groups are mutually repelled the chains may have insufficient cohesion to prevent partial collapse into intermolecular gaps, towards the water surface. If this occurred, the result might be an increase in film area without increase in compressibility. (*d*) In addition, the presence of alkaline solution may cause some degree of hydrolysis of the ester groups in (VII), (XI), (XII), and (XIII). This would lead to a decrease in film area without change in compressibility, because the azo-molecule would be replaced by a long-chain alcohol with a smaller "head" group. The following more detailed discussion of the results shows that most of them can be explained on the basis of one or more of these four effects.

o-*Hydroxyazo-compounds.—On acid.* Compounds (I), (IV), (VII), and (VIII) show little or no increase in molecular area but large increases in compressibility. There is probably ionisation and re-orientation of the molecule. Compound (I), in particular, which has only a benzene ring "head" group and has a very low orentation angle on water, is now able to occupy much less space at the surface because the reduced solubility of the hydroxy-group enables the orientation angle to approach much nearer to 90°. The smallness of the compressibility change of (II) may be due to partial collapse of the alkyl chain as discussed at (*c*) above; (III) has a much larger compressibility increase than (II), perhaps because the larger and more unsymmetrical shape of the under-water "head" leaves greater intermolecular gaps at the surface.

Compounds (V) and (VI) are believed to stand nearly vertically on water and should not therefore change their orientation. They also have C_{16} chains, which would not be expected to collapse, so that the observed increase in area and compressibility must be due largely to ionisation.

On alkali. The area increases of this series, coupled with their mostly rather small increases in compression, could be accounted for by re-orientation due to decreased solubility of an >NH group in the hydrazone tautomer and they are therefore not certain evidence of the presence of an azo-form. The increase of compressibility of (I) would then be due to the greater mobility of the small "head" group, and that of (VIII) to re-orientation caused by the solubility of the ether group increasing relatively to that of the >NH group. Hydrolysis of the ester group in (VII) can account for the decreases in area and compressibility.

The evidence, however, is not decisive enough to exclude the possibility that the hydroxyazo-form is present in this series. If it is present, then the effect of alkali is evidence of an increased solubility of the hydroxy-group, which in that case is not chelated with the adjacent azo-group. In the monolayer, each molecule is in direct contact with water and thus if any azo-tautomer is present, the hydroxy-group may be prevented from bonding with the proximate azo-group by preferential linkages with water.

Compound (IV), which differs from (II) only in having a longer alkyl chain, shows an increase in compressibility but a slight decrease in area. The differences could be explained by a re-orientation of the molecule of (IV) masking the intermolecular repulsion caused by ionisation of the hydroxy-group and a partial collapse of the alkyl chain in (II) interfering with such a change.

The difference here evident in the behaviour of (II) and (IV) is therefore more easily explained by assuming that a hydroxy-form is present, so that on the whole it is not possible to state that *no* hydroxy-form is present in the *o*-hydroxyazo-series.

oo′-*Dihydroxyazo-compound* (IX).—This shows considerable increase in area and compressibility on alkali, evidently due to ionisation, and rather smaller changes on acid. (Even if this compound were wholly in the quinone hydrazone form, one free hydroxy-group would remain).

A study of the structure of (IX) and its orientation at the surface shows that the hydroxy-groups are symmetrically placed in a horizontal line on either side of the azo-group. If, therefore, the compound were *wholly* in the azo-form, the effect of the acid substrate in reducing the solubility of the hydroxy-groups relative to that of the azo-group should cause no change in orientation or in area. The observed changes must therefore be evidence that the compound is *not* wholly an azo-structure.

p-*Hydroxyazo-compounds.—On acid.* These compounds display very small area increases [(X) in fact decreases] and with the exception of the *o*-cresol compounds (XI, XIII, XIV), where re-orientation would be most expected, no appreciable increase in compressibility occurs. It would appear therefore that very little of the quinone hydrazone tautomer is present in this series of compounds.

On alkali. All the compounds examined increase considerably in area, especially (XIV) and (XV), which also increase appreciably in compressibility. The small compressibility change of (XI) and (XII) and their lower degree of expansion are probably due to partial hydrolysis. Compound (X) has a very large and unwieldy under-water "head" and re-orientation of this may account for the smaller change in compressibility compared with (XIV) and (XV), though it has been found difficult to demonstrate the effect on models.

The behaviour of the two *p*-dodecylaniline → cresol compounds may be additional evidence for the preponderance of the hydrazone form in the *o*-hydroxyazo-series. *p*-Dodecylaniline → *o*-cresol, which has the hydroxy-group *p*- to the azo-group, is too soluble to form a film (see Part I). The film-forming properties of the *o*-hydroxy-isomer (from *p*-cresol), however, might be attributed to the absence of a hydroxy-group and the consequent reduced water-solubility, or the reduced solubility might be due to chelation of the azo- and the hydroxy-group.

Conclusion.—The general conclusion is that the water-insoluble *p*-hydroxyazo-compounds appear to exist almost completely in the azo-form, whereas the corresponding *o*-hydroxyazo-compounds contain the hydrazone form. The evidence for the presence of the azo-form in the latter series is equivocal (except possibly in the case of the *oo*′-dihydroxy-azo-compound, where the evidence appears to be positive). This is in general agreement with much of the published information.

Experimental.—The film balance, the general technique used, and the preparation of the azo-compounds (except IX) have been described in Part I. In place of distilled water alone, solutions of hydrochloric acid (0·1N) and sodium carbonate (0·1N) both of analytical reagent quality, in distilled water, were employed as substrates. The molecular area figures are each the mean of at least four successive determinations repeated on fresh films, and were found to be reproducible to ± 1 Å^2. The conclusions have been checked by the use of scale-model molecules.

o-*Aminophenyl* → p-*hexadecylphenol* (IX). *o*-Aminophenol (5·5 g.) was diazotised by Reisenegger's method (*Annalen*, 1884, **221**, 314) and coupled with *p*-hexadecylphenol (16 g.) in aqueous sodium hydroxide; red prisms (from glacial acetic acid and ethanol successively), m. p. 84—85° (Found: C, 76·5; H, 9·3; N, 6·2. $C_{28}H_{42}O_2N_2$ requires C, 76·7; H, 9·6; N, 6·4%).

1-*Hydroxyanthracene.* This compound (α-anthranol), used in the work reported in Part I, was prepared by alkali fusion of the sodium salt of the sulphonic acid.

We thank Professor P. D. Ritchie for his interest and encouragement and the Directors of Imperial Chemical Industries Ltd., Dyestuffs Division, for financial assistance to one of us (E. L. N.) and for the gift of intermediates.

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[*Received, November 7th,* 1951.]