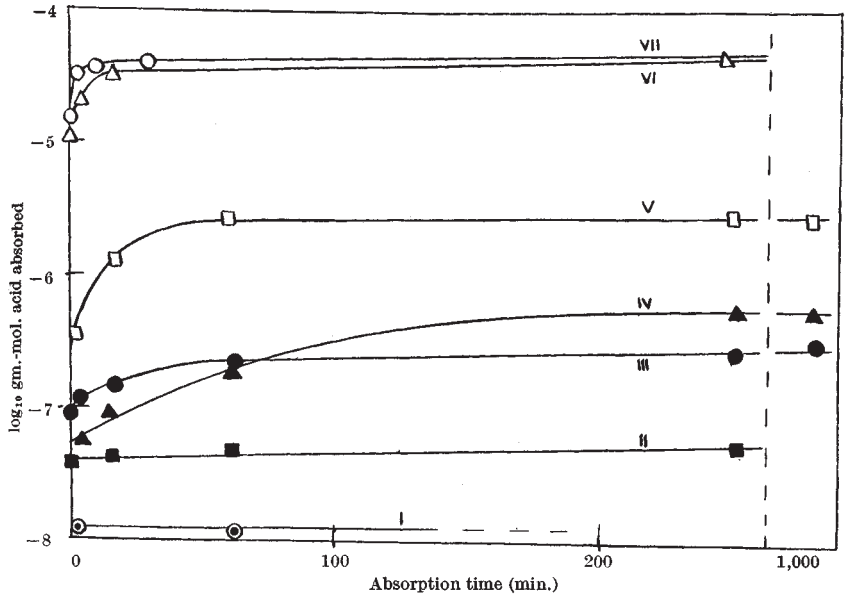

crease using a sulphonic acid-type cation-exchanger and aralkyl-ammonium ions. No comparable results for the anion-exchange reaction appear to have been recorded.

In the case of dyes, the cation-exchange process involves only the diffusion of sodium and hydrogen ions, whereas the acid absorption reaction requires the penetration of the resin by the much larger dye molecules (or dye anions). It seemed possible to postulate, therefore, that some of the dye molecules examined were too large to enter all of the structure of the resin. This hypothesis has been substantiated by studying the absorption of a number of aromatic sulphonic acids of different molecular dimensions. The results obtained using 12·5 ml. of 0·0028 *M* solutions and 1 gm. of air-dry resin at 20° C. are shown in the accompanying diagram. The equilibrium absorptions are given in the table, together with the approximate ionic dimensions.

I Diphenyl - 4 - (2 - azo - 1 - hydroxy - naphthalene - 3 : 6 - disulphonic acid) - 4′ - (2 - azo - 1 - hydroxy - naphthalene - 3 - sulphonic acid). Colour index No. 388.
II 3 : 3′ - Dimethoxydiphenyl - 4 : 4′ - bis - (2 - azo - 8 - amino - 1 - hydroxy-naphthalene-5 : 7-disulphonic acid). Colour index No. 518.
III Naphthalene - 1 - sulphonic acid - 4 - (1 - azo - 2 - hydroxy - naphthalene-6 : 8-disulphonic acid). Colour index No. 185.
IV 2 - Hydroxy - naphthalene - 6 : 8 - disulphonic acid - 1 - azobenzene. Colour index No. 27.
V 2 : 4-Dihydroxy-benzene-1-azobenzene-*p*-sulphonic acid.
VI Naphthalene-2-amino-1-sulphonic acid.
VII Sulphuric acid.

Compound No.	Equilibrium absorption (gm. mol. acid/gm. resin)	Per cent absorption of solute	Approximate largest dimension of ion (A.)
I	0·01 × 10⁻⁶	0·03	30
II	0·05 × 10⁻⁶	0·14	30
III	0·31 × 10⁻⁶	0·9	20
IV	0·45 × 10⁻⁶	1·3	15
V	2·2 × 10⁻⁶	6·3	15
VI	33 × 10⁻⁶	94	10
VII	35 × 10⁻⁶	100	5

All the acids show an initial rapid absorption during the first minute, followed by a slower take-up to an equilibrium value which increases with decreasing molecular size. The large disazo dyes I and II show little increase after the initial rapid absorption, which suggests that this is reaction at the surface, followed, with the smaller molecules, by a slower diffusion into the bulk of the resin. The final equilibrium figure will be modified to some extent by the degree of sulphonation of individual molecules, but the selective diffusion effect must predominate since the more highly sulphonated molecules are less absorbed.

Some of the larger dyes in the form of their sodium salts are associated in solution, but it is not known whether they are equally associated in dilute solutions of their free acids in the absence of inorganic ions. However, since there exists a dynamic equilibrium between single dye molecules and aggregates, the equilibrium figures for the dye absorbed should not be invalidated by this aggregation.

It is thus possible to conclude that the microstructure of anion-exchange resin of the 'De-Acidite' type is such that it is physically impossible for large dye ions to enter and diffuse to all the points of exchange within the granule; as the molecular size of the dye ion is reduced, progressively more of the structure becomes available for absorption, until with simple aromatic sulphonic acids almost all exchange points react. This is consistent with a picture of the resin as an amorphous body containing a network of pores which may vary in size from 10 to 20 A. in diameter, through which all anions must diffuse into the interior of the granule before absorption on the basic exchange points.

The use of exchange resins in the purification and isolation of acid, direct and basic dyes is being investigated, and a complete account will be published elsewhere.

I wish to thank Dr. T. H. Morton for his interest and advice, and the directors of Courtaulds, Ltd., for permission to publish this communication.

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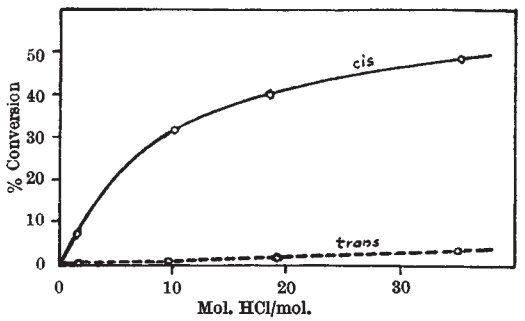
Configuration of Alicyclic Amino-Alcohols

We have extended our investigations[1] on the acyl migration reaction N → O to acyl derivatives of diastereoisomeric alicyclic amino-alcohols[2], such as 2-amino-*cyclo*hexanol[3], with the view of establishing the relative steric positions[4] (that is, configuration) of hydroxyl and acylamido groups.

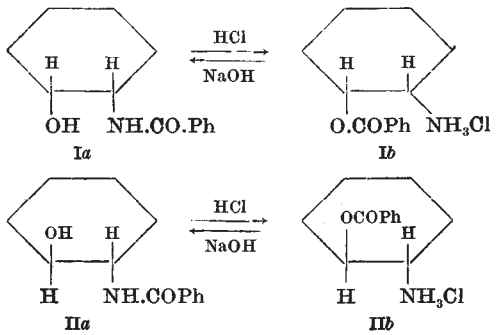
Cis- and *trans*-2-benzamido-*cyclo*hexanol were each treated separately with absolute alcoholic hydrogen chloride at room temperature. The amide, m.p. 189°, previously[5] considered to be II*a*, but recently suggested[6] to be I*a*, gave on action of 2 mol. of hydrochloric acid, O-benzoyl-2-amino-*cyclo*hexanol hydro-

chloride, m.p. 228°, in 9 per cent yield, besides 90 per cent of unchanged amide. Under identical conditions, 2-benzamido-*cyclo*hexanol, m.p. 174°—previously recorded[7] as the *cis* form, but recently postulated[6] to be II*a*—furnished the corresponding O-benzoyl-2-amino-*cyclo*hexanol hydrochloride, m.p. 284°, only to an extent of 0·1–0·2 per cent, while 98 per cent amide was recovered unchanged. Using hydrogen chloride in very great excess at room temperature, 50 per cent of hydrochloride, m.p. 228°, and 4·5 per cent of hydrochloride, m.p. 284°, respectively could be obtained (see graph).



Each amino-ester salt was re-arranged by alkalinization into the amide from which it was prepared; as an acyl shift, O → N never occurs with inversion[8]; consequently the benzoyl shift N → O took place in both cases with retention of configuration.

We interpret this discrepancy in the acyl migration N → O as follows. 2-Benzamido-*cyclo*hexanol, m.p. 189°, undergoing readily acyl migration, is of *cis* configuration (I*a*) as well as the corresponding amino-ester salt, m.p. 228° (I*b*), whereas its diastereoisomer, m.p. 174°, being far less spontaneously convertible into the amino-ester salt, m.p. 284°, possesses *trans*-configuration (II*a*). Our results are in accordance with those of McCasland *et al.*[6] obtained by a quite different way.



Nevertheless, at 100° each diastereoisomeric amide gave, with retention of configuration, the corresponding amino-ester salt, I*b* or II*b* respectively, with an approximate yield of 50 per cent[9]. This can be explained by the well-known flexibility of the *cyclo*hexane ring[10], so that substituents in the *trans* position can approach each other—due to rotation—to the extent required for the acyl migration to take place. The same factor may cause the originally *cis*-placed substituents to move apart. Obviously, an increase of temperature favours such transitions[11]. For similar steric reasons, both the *cis* and *trans* 1.2-*cyclo*hexandiols failed to increase the conductivity of boric acid or to form cyclic acetals[12].

The difference between the stereoisomeric benzamido-*cyclo*hexanols observed in the acyl migration reaction N → O *at room temperature* gives, in our opinion, evidence of their steric structure. Experimental details will be published elsewhere.

We are now extending our investigations to the configuration of diastereoisomeric amino-borneols containing a 'rigid' ring system[13] in order to control the general usefulness of our method for the determination of the configuration of alicyclic amino-alcohols.

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[3] Ralford, L., and Mortensen, F., could not initiate acyl migration of *bis*-acylated 2-amino-*cyclo*hexanol (*J. Amer. Chem. Soc.*, **50**, 1201; 1928).
[4] Attempts to convert amino-*cyclo*hexanol into 1.2-*cyclo*hexandiol of known configuration were unsuccessful: Wilson, N. A. B., and Read, J., *J. Chem. Soc.*, 1270 (1935).
[5] English Patent 454,042 (1936).
[6] McCasland, G. E., *et al.*, *J. Amer. Chem. Soc.*, **71**, 638 (1949), found that benzamido-*cyclo*hexanol, m.p. 189°, can be prepared from its diastereoisomer by tosylation and subsequent detosylation in an analogous manner to the preparation of *cis*-acetyl-*cyclo*hexandiol-1.2 from the *trans* form. cf. Winstein, S., *et al.*, *J. Amer. Chem. Soc.*, **64**, 2796 (1942).
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[8] Welsh, L. H., *J. Amer. Chem. Soc.*, **69**, 128 (1947).
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[11] Bier, G., *Experientia*, **2**, 82 (1946).
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[13] Hückel, W., *loc. cit.*, 71.

Stable Configurations of a Polypeptide Chain

In recent communications in *Nature*, Ambrose and his co-workers proposed a model for the molecular structure of α-keratin based on their measurements with polarized infra-red radiation[1,2]. The same model has already been presented by two of us (S. and M.) in 1947, based on the energy consideration for the intramolecular rotation[3,4].

For some years we have studied the intramolecular rotation from our measurements of the Raman effect, infra-red absorption, dielectric constant, and electron diffraction, and have determined not only the stable configurations of simple molecules with internal rotation axes, but also those of complex ones[5]. We could thus explain, for example, the difference in the elastic properties between polyethylene and poly-*iso*butylene from the difference in their intramolecular potentials[6]. As to a polypeptide chain, two of us determined the following two stable forms of its structural unit by considering the energy change with intramolecular rotational angle about the C—C and the C—N axes: