

## LINEAR ELUTION ADSORPTION CHROMATOGRAPHY

## X. ELECTRONIC AND STERIC EFFECTS IN HETERO-AROMATIC SOLUTES. SEPARATION OF THE DI-AZA-AROMATICS, QUINONES AND RELATED SOLUTES ON ALUMINA

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(Received May 12th, 1964)

## INTRODUCTION

Compound separability in linear elution adsorption chromatography (LEAC) over alumina has been examined previously for a variety of solute types<sup>1-7</sup>. Retention volume (ml/g) for elution by the solvent pentane  $\bar{R}_p$  is related to adsorbent properties (activity function  $\alpha$  and surface volume  $V_a$ ) by means of:

$$\log \bar{R}_p = \log V_a + \alpha S^\circ \quad (1)$$

where  $S^\circ$ , the dimensionless adsorption energy of the solvent from pentane onto calcined alumina, is a function of solute molecular structure only:

$$S^\circ = \sum_i Q^\circ_i + \sum_j q^\circ_j - f(Q^\circ_k) \sum_{i \neq k} Q^\circ_i \quad (1a)$$

The summation  $\sum_i Q^\circ_i$  represents the first order contribution of all solute groups to solute adsorption energy,  $Q^\circ_i$  being the contribution of each group  $i$  to  $S^\circ$ . The summation  $\sum_j q^\circ_j$  takes into account the effect of various intramolecular solute interactions  $j$  (or solute geometry factors) on solute adsorption energy; e.g. solute adsorption energy may be affected either by steric interactions between two adjacent solute groups, or by electronic interactions over longer distances. Finally, the term  $f(Q^\circ_k) \sum_{i \neq k} Q^\circ_i$  corrects for adsorption energy changes which result from the localization of a strongly adsorbing solute group  $k$  on a particular adsorbent site. The effect of the eluent on solute retention volume has been summarized in a recent paper<sup>8</sup> in this series, and seems to be well understood, at least for alumina as adsorbent. The present paper will not be further concerned with the eluent role as such.

The most practical limitation on eqn. (1a) is occasioned by our limited tabulation of  $q^\circ_j$  values for various solute geometries. In principle every new solute necessarily exhibits some unique geometrical relationship among its constituent atoms or groups, and we might expect as many  $q^\circ_j$  values as solutes. In practice the problem is very much simpler, in that many solute geometry relationships have no notice-

able effect on adsorption energy or retention volume. An additional simplification results from our ability to classify some of the important (with respect to adsorption) solute geometry relationships and to relate them to fundamental molecular properties that have been studied in relation to other problems. At the present time there appear to be at least three general contributions of solute geometry *per se* to adsorption energy.

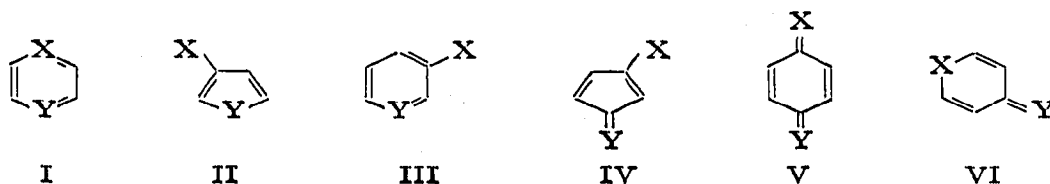
*Electronic interaction* between functional groups in the same molecule can have a profound effect on the adsorption energies of individual solute groups. In the *meta* or *para* substituted derivatives of pyridine<sup>8</sup>, electron withdrawing substituents greatly reduce the adsorption energy of the pyridine nitrogen atom, and electron donating substituents increase its adsorption energy. This effect is reversed in the substituted indoles<sup>6</sup> and phenols<sup>3</sup>, electron withdrawing groups increasing the adsorption energy of the -NH- and -OH groups in these two series of solutes. In all three of these cases, the effect of substituents on adsorption energy can be more easily understood by comparison with the related and well investigated phenomenon of electronic interaction in organic reactions.

*Steric interaction* between neighboring solute groups has long been known to have an important effect on solute adsorption energy. Steric effects can decrease solute adsorption energy by interference of one group with the adsorption of another. One example of this is in the adsorption of the phenyl-arenes<sup>5</sup>; steric interactions can either prevent the optimum planar adsorption of these solutes, or lower the net adsorption energy by creating an energy barrier to adoption of a planar configuration. In either case, solute adsorption energy is decreased. Similarly, bulky substituents adjacent to the nitrogen atom of the pyridine derivatives interfere with the adsorption of the nitrogen atom on strong alumina sites<sup>6</sup>, again with a lowering of solute adsorption energy. In both of these experimental examples, the sterically induced loss in adsorption energy can be quantitatively correlated with the known interatomic distances and non-bonding interatomic potential functions. Steric effects can also affect solute adsorption energy by electronic interaction or bond formation between adjacent solute groups. In the adsorption of the hydroxyanthraquinones on silica<sup>8</sup>, the 1-hydroxy derivatives are less strongly adsorbed than the 2-hydroxy compounds because the hydroxyl can hydrogen bond to one of the keto groups in the 1-derivatives, and this bond must be broken if the hydroxyl group is to interact with an adsorbent site. Finally, in the present and following papers, examples are provided of adjacent solute groups *increasing* solute adsorption energy by virtue of the fact that such groups may be able to simultaneously interact with a single, strong adsorbent site; a similar situation has already been noted in the adsorption of the unsaturated hydrocarbons on silica<sup>9</sup> and discussed theoretically.

*Optimum positioning of the adsorbing groups* within the solute molecule with respect to the topographical arrangement of strong adsorbent sites on the adsorbent surface (for optimum interaction of each adsorbing group with a strong adsorbent site) is also known to substantially affect solute adsorption energy. The previous example of adjacent solute groups interacting with a single adsorbent site is an obvious example of optimum adsorbing group distribution within the solute molecule. A more interesting example is provided by the preferential adsorption on silica of the solute dibenzyl<sup>9</sup>, relative to the fused aromatic hydrocarbons of similar formula. In this case, the two phenyl rings can each interact in an optimum fashion with ad-

jaacent strong adsorbent sites (see particularly, Fig. 10, ref. 7). Similarly, long aromatic hydrocarbons are preferentially adsorbed on alumina<sup>4,5</sup>, relative to shorter, wider isomers, because the longer solutes have a better chance statistically of overlapping two strong adsorbent sites simultaneously. The following paper in this series provides some additional examples in the adsorption of the haloaromatics, and provides a more detailed analysis of this effect for adsorption on alumina.

Major electronic effects have not been observed in the adsorption of the poly-substituted benzenes on alumina<sup>2</sup>, with the exception of the phenols<sup>3</sup>. Theoretically, electronic effects should be most important in solutes such as I-VI, and in such examples of these solute types as have been studied (substituted indoles, II; substituted pyridines, III) large electronic effects are noted. The further experimental



study of this class of compounds seemed worthwhile from the standpoint of better understanding electronic effects in adsorption chromatography. The di-aza-aromatics, compounds with two pyridine-like nitrogens in a single molecule, were attractive in this connection. They include the type I solutes where strong electronic effects could be expected. Several of the di-aza-aromatics were commercially available, and we had already thoroughly studied the factors which determine the adsorption energy of the related pyridine derivatives. Furthermore, it was hoped that their study might resolve certain apparent anomalies<sup>10</sup> in the adsorption chromatographic separation of various *cis* and *trans* azobenzene derivatives. Thus, while *cis*-azobenzene is adsorbed more strongly than *trans*-azobenzene on alumina, the related *p*-bis-(phenylazo)-benzene stereoisomers show the relative adsorption strengths: *cis-trans* > *cis-cis* > *trans-trans*. Similarly, the adsorption strength on silica of the azopyridine stereoisomers reverses in going from the 2,2'-isomer (*trans* > *cis*) to the 3,3'-isomer (*cis* > *trans*).

The substituted fluorenones (type IV) and quinones (type V) also seemed worth studying, for similar reasons. The present communication describes the experimental and theoretical investigation of the separation on alumina of these various classes of compounds, as well as a general analysis of electronic effects in adsorption chromatography.

## EXPERIMENTAL

The retention volume data cited in the present paper were obtained as previously<sup>11</sup>. The chromatographic activities of the adsorbents used are in terms of the revised activity scale<sup>3</sup>. Some difficulty was found in reproducing the  $R^{\circ}$  values for 1,10-phenanthroline and 1-azaindole eluted by dioxan from 3.9% H<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub> (reported previously<sup>3</sup>). In some cases, these solutes did not appear to elute at all under these conditions, whereas previously<sup>3</sup> they were readily eluted. The reason for this anomaly has not yet been resolved.

The eluent strength values ( $\alpha\epsilon^\circ$ ) required in extrapolating values of  $R^\circ$  to  $R_p^-$  were experimentally determined for the binary eluent mixtures as previously<sup>11</sup>, and calculated for the pure eluents. The values used are tabulated in Tables III and IV.

## DISCUSSION

In following sections, the dependence of solute adsorption energy on steric and electronic interactions within certain classes of solute molecules is reviewed and experimentally extended. Almost without exception, a sufficiently complete understanding of these effects is possible so as to permit the quantitative calculation of solute  $S^\circ$  values. The present discussion is intended as an intermediate summary of these results, for ready application to practical separation problems using adsorption chromatography on alumina.

TABLE I

SOLUTE PARAMETERS FOR AZA-AROMATICS, KETO-AROMATICS, FURANS, THIOPHENES AND PYRROLES

<i>Q<sup>o</sup><sub>i</sub> values versus solute geometry</i>						
Group X						
-N=	4.8	4.0	3.8	2.3	0.7	(-0.1)
>C=O	(6.1)	4.7	3.8	3.4*	3.2	3.2*
-O-	1.1	0.3*	0.2	0.0*	0.0*	0.0*
-S-	0.7	0.6	0.6*	0.4*	0.1*	0.0*
-NH-	4.7	4.9	5.1	5.4*	5.6	5.6*

<i>Q<sup>o</sup><sub>i</sub> values for two hetero atoms of ortho grouping</i>			
Group	Exptl. Q <sup>o</sup> <sub>i</sub>	Group	Exptl. Q <sup>o</sup> <sub>i</sub>
	5.5		5.3
	5.5		5.4
	6.5		5.8
	0.7		
	7.4		6.9

\* Estimated values.

Table I summarizes  $Q^\circ_t$  values for five hetero-aromatic groups associated with the various derivatives of pyridine ( $-\text{N}=\text{}$ ), cyclopentadienone ( $-\text{C}=\text{O}$ ), furane ( $-\text{O}-$ ), thiophene ( $-\text{S}-$ ), and pyrrole ( $-\text{NH}-$ ), as a function of the crowding of these groups in different solute geometries. All of these hetero group adsorption energies are seen to vary somewhat with increased crowding by adjacent solute groups: in the first four groups, increased crowding decreases adsorption energy, while in the pyrrole derivatives increased crowding increases adsorption energy. A previous discussion<sup>6</sup> has rationalized these differences in response of the hetero atom adsorption energy to crowding: normally, adsorption of the hetero atom X involves formation of a bond between X and the adsorbent, and increased crowding of X then reduces its adsorption energy; in the case of the pyrroles, the  $-\text{NH}-$  group functions as an acid which neutralizes the basic alumina surface, and increased crowding of the  $-\text{NH}-$  group weakens the strength of the H-N bond, which mildly increases pyrrole acidity and adsorption strength. These  $Q^\circ_t$  values of Table I should provide some insight into the variation of adsorption energy of other solute types with intramolecular crowding of a ring-incorporated hetero group. Substituent groups on an aromatic nucleus, as opposed to the ring-incorporated hetero groups of Table I, show less dependence of adsorption energy on intramolecular crowding<sup>6</sup>; a following paper will discuss these effects in detail. The  $Q^\circ_t$  values of Table I marked by \* are actually estimates rather than experimentally derived values, based on plots of  $Q^\circ_t$  for one group *versus*  $Q^\circ_t$  values for the  $-\text{N}=\text{}$  group. Such plots show a rough correspondence between crowding and  $Q^\circ_t$  values for all of these hetero-aromatic groups. Using the  $Q^\circ_t$  values of Table I for these five hetero-aromatic groups,  $S^\circ$  values for the various benzo derivatives can be calculated from eqn. (1a) with the  $q^\circ_j$  term ignored; the only important solute geometry effect in these molecules is steric crowding of the hetero-aromatic group, and this is taken care of by the  $Q^\circ_t$  values of Table I.

The calculation of  $S^\circ$  values for solutes of the type I-VI must take into account not only the crowding of the groups X and Y, but their electronic interaction. The change in the adsorption energy of the group X as a result of interaction with the non-adjacent group Y may be defined as  $q^\circ_{x,y}$ , and is given by the expression:

$$q^\circ_{x,y} = \underline{A} Q^\circ_x \sigma_y \quad (2)$$

Here,  $\sigma_y$  is the HAMMETT  $\sigma$  value<sup>12</sup> for the substituent Y, a measure of its ability to relay an electronic charge to the position in the solute molecule occupied by the group X.  $Q^\circ_x$  is the adsorption energy of the group X, if it is the localized (strongest adsorbing) solute adsorbing group; if X is delocalized,  $Q^\circ_x$  refers to its  $Q^\circ_t$  value times the function  $f(Q^\circ_y)$ , assuming that the group Y is localized. The parameter  $\underline{A}$  refers to the response of the adsorption energy of X to changes in the charge of X. The calculation of  $q^\circ_{x,y}$  values is straightforward, but sufficiently tedious to be deferred to later sections. We will presently discuss only the more practical consequences of eqn. (2). First, and most important, is the question of whether the  $q^\circ_{x,y}$  values will be large; that is, does electronic interaction between X and Y significantly affect solute adsorption energy? This question is primarily answered by the values of  $\underline{A}$  and  $Q^\circ_x$  involved for the solute type under consideration. Values of  $\underline{A}$  appear to vary between  $\pm 0.1$  to 0.6, and are largest for solutes where the group X behaves as an acid or base upon adsorption (*e.g.* pyridines, phenols, etc.). For

solutes not adsorbing as an acid or base, a value of  $A$  equal  $-0.2$  to  $-0.3$  may generally be assumed.  $\sigma_y$  will generally be less than 1.0, so that for  $q^{\circ}_{x,y}$  to be appreciable (0.1-0.2),  $Q^{\circ}_x$  must be greater than 0.5-1.0, which means that electronic effects will normally be negligible for such solutes as the furan and thiophene derivatives (see Table I), at least as regards the adsorption energy of the hetero-aromatic groups  $-S-$  and  $-O-$ . Similarly, it is believed that electronic effects and  $q^{\circ}_{x,y}$  values for most polysubstituted aromatic hydrocarbons will be small, and this has already been observed<sup>2</sup>.

TABLE II

CALCULATED ADSORPTION ENERGIES  $S^{\circ}$  FOR THE DI-AZA-AROMATICS CONTAINING ONE TO THREE FUSED RINGS

Di-aza-aromatic	$S^{\circ}$ values for $i, j$ di-aza-aromatic				
	$i = 1$	$i = 2$	$i = 3$	$i = 4$	$i = 9$
<b>Di-aza-benzenes</b>					
$j = 2$	8.0 <sup>a</sup>				
3	6.3				
4	5.7 <sup>b</sup>				
<b>Di-aza-naphthalenes</b>					
$j = 2$	7.7 <sup>a, b</sup>				
3	6.8	8.7 <sup>a, b</sup>			
4	6.0				
5	7.0 <sup>b</sup>				
6	8.2	8.5			
7	7.9	8.8			
8	(9.2) <sup>c</sup>				
<b>Di-aza-anthracenes</b>					
$j = 2$	8.4 <sup>a</sup>				
3	7.5	9.4 <sup>a</sup>			
4	6.9				
5	8.3				
6	9.2	9.6			
7	9.1	9.7			
8	8.3				
9	(9.9) <sup>c</sup>	8.4			
10	7.8	8.8			6.5 <sup>b</sup>
<b>Di-aza-phenanthrenes</b>					
$j = 2$	8.4 <sup>a</sup>				
3	7.5	9.4 <sup>a</sup>			
4	6.3	6.9			
5	7.6 <sup>b</sup>	8.2	8.1	10.3 <sup>a, b</sup>	
6	9.0	9.7	9.5		
7	9.2	9.6			
8	8.4				
9	8.0	9.1	8.9	7.4	
10	(9.9) <sup>c</sup>	8.7	8.9	7.3	8.3 <sup>a, b</sup>

<sup>a</sup> *ortho* derivative.

<sup>b</sup> Experimental value.

<sup>c</sup> Estimated  $Q^{\circ}_i$  for two nitrogens intermediate between  $-N=N-$  and those at 1,10-phenanthroline.

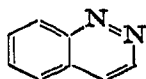
In the di-aza-aromatics and quinones, the combination of terms in eqn. (2) makes  $q^{\circ}_{x,y}$  generally large, so that electronic effects tend to play an important role in determining the separability of various compounds in these two classes.  $A$  is negative for both the  $-N=$  and  $-C=O$  groups, and the  $\sigma_y$  values for these same two groups are positive, so that  $q^{\circ}_{x,y}$  values for the quinones and di-aza-aromatics are always negative. As a result, introduction of a second  $-N=$  group into a mono-aza-aromatic or of a second keto group into a cyclopentadienone derivative to produce either a di-aza-aromatic or quinone, respectively, frequently results in a *net loss* in adsorption energy. Thus, pyrazine is adsorbed much less strongly than pyridine, while fluorenone and anthraquinone are adsorbed to about the same extent. The electronic interaction between X and Y decreases with the distance between the two groups, which means that the di-aza-aromatics or quinones with the hetero-aromatic groups in different rings (*e.g.* 1,5-di-aza-naphthalene, 2,7-naphthoquinone) are generally more strongly adsorbed than the corresponding derivatives with hetero-aromatic groups in the same ring (*e.g.* 1,4-di-aza-naphthalene, 1,4-naphthoquinone). Because of resonance, the *meta* di-aza-aromatics show smaller  $\sigma_y$  values in general, and are more strongly adsorbed. Thus, pyrimidine is predicted to adsorb more strongly than pyrazine.

Whenever the solute groups X and Y are adjacent so as to permit simultaneous adsorption on a single adsorption site,  $S^{\circ}$  is increased markedly. Thus, pyridazine is much more strongly adsorbed than pyrazine, and 1,2-naphthoquinone is more strongly adsorbed than 1,4-naphthoquinone. Table I summarizes some  $Q^{\circ}_t$  values for the combined adsorption energy of two  $-N=$  or  $-C=O$  groups which form adjacent groupings of various types. The two nitrogens in 1,10-phenanthroline are seen to be adsorbed even more strongly than the bonded nitrogen pair of cinnoline or phthalazine, because of the more favorable arrangement of the 1,10-phenanthroline nitrogens for interaction with a single site.

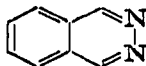
The variation of  $Q^{\circ}_x$  with crowding in the di-aza-aromatics and quinones (as shown in Table I) is in general at least as important as the variation due to electronic and configuration (adjacency of groups) effects. Table II summarizes calculated or measured  $S^{\circ}$  values for all of the one, two and three ring di-aza-aromatics for further illustration of the factors which determine adsorption energy in this series of compounds, as well as for use in estimating the separation of these and similar compound types.

#### THE DI-AZA-AROMATICS AS SOLUTES

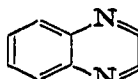
The separation on alumina of the substituted pyridines and higher aromatic analogs (*e.g.* quinolines, acridines) has been studied in great detail<sup>2,6</sup>, and an adequate understanding exists of the factors which determine the adsorption energy of the nitrogen atom in such cases. The di-aza-aromatics, compounds such as cinnoline (VII), phthalazine (VIII), quinoxaline (IX) and 1,5-naphthyridine (X), are closely related to the pyridine derivatives, and should therefore show similar adsorption characteristics. For this reason they were selected for initial study.



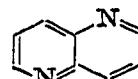
VII



VIII



IX



X

TABLE III  
 ADSORPTION OF THE DI-AZA-AROMATICS ON 3.8% H<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>

Solute	$\log R_p^o$	$\log R_p$	$S^o$	$\Delta \text{expl. } \sigma^b$		$-p$		$\Delta \text{ calc. eqn. (3)}$		
				Expl. eqn. (1)	Calc. eqn. (2)	$r^c$	$z^d$		$r^c$	$z^d$
Pyrazine	0.57 <sup>e</sup>	1.87	5.73	8.68	-2.95	0.76	0.76	2.68	1.47	-3.16
Phenazine	0.81 <sup>f</sup> , 0.29 <sup>g</sup> , -0.39 <sup>h</sup>	2.36	6.50	8.79	-2.29	0.76	0.76	2.13	1.17	-2.51
5:6; 7:8-Dibenzoquinoxaline	0.61 <sup>f</sup>	2.53	6.76	8.37	-1.61	0.57	0.57	1.29	1.00	-1.30
Dibenzo(a, c)phenazine	0.43 <sup>f</sup>	2.67	6.98	7.60	-0.62	0.55	0.55	0.39	0.39	-0.43
1:2; 3:4; 6:7-Tribenzophenazine	0.63 <sup>f</sup>	3.19	7.79							
1,5-Naphthyridine	1.03 <sup>g</sup> , 0.45 <sup>h</sup>	2.70	7.03	8.40	-1.37	0.33 <sup>i</sup>	0.33 <sup>i</sup>	2.24	1.23	-1.15
4,4'-Dipyridyl	0.92 <sup>g</sup> , 0.51 <sup>h</sup>	3.00	7.50	8.90 <sup>i</sup>	-1.40	0.26	0.26	2.69	1.48	-1.08
m-Phenanthroline	1.03 <sup>g</sup> , 0.30 <sup>h</sup>	3.06	7.62	8.15	-0.47	0.17 <sup>j</sup>	0.17 <sup>j</sup>	2.24	0.71	-0.50
Cinnoline	1.24 <sup>h</sup> , 0.01 <sup>k</sup> , -0.24 <sup>m</sup>	3.13	7.70	9.20	-1.50	1.24	1.21	2.68	1.23	-4.80
Benzo(c)cinnoline	-0.05 <sup>k</sup>	3.56	8.37	9.08	-0.75	1.12	1.12	2.24	1.23	-3.89
Phthalazine	1.15 <sup>k</sup> , 0.30 <sup>m</sup>	3.74	8.66	9.64	-0.98	1.14	1.14	2.68	1.47	-4.96
1,10-Phenanthroline	2.03 <sup>h</sup> , 0.64 <sup>m</sup>	4.77	10.27							
cis-Azobenzene	1.11 <sup>l</sup> , 0.43 <sup>g</sup>	2.76	7.12							
trans-Azobenzene	1.03 <sup>n</sup> , -0.28 <sup>o</sup>	1.03	4.42							

<sup>a</sup> Assumes  $Q^o$  values of Table I.

<sup>b</sup> Calculated by the DEWAR-GRISDALE procedure for the corresponding hydrocarbon.

<sup>c</sup> For atom  $n$ .

<sup>d</sup> For atom  $n'$ .

<sup>e</sup> 50% v methylene chloride-pentane eluent ( $\alpha\epsilon^o = 0.207$ ).

<sup>f</sup> 25% v methylene chloride-pentane eluent ( $\alpha\epsilon^o = 0.153$ ).

<sup>g</sup> Benzene eluent ( $\alpha\epsilon^o = 0.209$ ).

<sup>h</sup> Methylene chloride eluent ( $\alpha\epsilon^o = 0.275$ ).

<sup>i</sup> Assumes contribution of -0.8 from non-planarity in solution.

<sup>j</sup> Times 0.7 as in Fig. 2.

<sup>k</sup> 50% v dioxan-pentane eluent ( $\alpha\epsilon^o = 0.361$ ).

<sup>m</sup> Dioxan eluent ( $\alpha\epsilon^o = 0.411$ ).

<sup>n</sup> Pentane eluent ( $\alpha\epsilon^o = 0.000$ ).

<sup>o</sup> Carbon tetrachloride eluent ( $\alpha\epsilon^o = 0.118$ ).



Table III summarizes retention volume data for several of the di-aza-aromatics on 3.8 % H<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>. As in previous studies of the mechanism of adsorption and the quantitative basis of retention volume in LEAC systems, it is useful to compare these experimental  $S^\circ$  data with values calculated by eqn. (1a), using the best adsorption parameters at our disposal. The difference  $\Delta = (S^\circ_{\text{expt.}} - S^\circ_{\text{calc.}})$  can then be interpreted in terms of new effects of the type presently under study. The  $Q^\circ_i$  value of the nitrogen atom in the pyridine derivatives has been shown to vary with the intramolecular crowding by surrounding groups, and Table I summarizes the best values of  $Q^\circ_i$  for the nitrogen atom in various intramolecular configurations. Using these  $Q^\circ_i$  values from Table I and ignoring any  $q^\circ_j$  terms (which were initially unknown, and which lay at the center of the present investigation),  $S^\circ$  values were calculated for the solutes of Table III. For the solute 4,4'-bipyridyl, which is presumed to be non-planar in solution and to adsorb planar it was necessary to estimate the energy barrier to planarity. The previously measured<sup>5</sup> experimental value for biphenyl and related compounds (equal 0.8  $S^\circ$  units for adsorption on 3.8 % H<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>) was assumed applicable.

As expected for the solutes of Table III, we find sizeable values of  $\Delta$  in every case, reflecting strong electronic (and in some cases steric) interaction between the two nitrogen atoms of the di-aza-aromatics. The values of  $\Delta$  are in every case negative; this might have been anticipated from the fact that electron withdrawing substituents on the pyridine ring lower the adsorption energy of the pyridine nitrogen, and the  $-N=$  group is itself electron withdrawing. The values of  $\Delta$  vary widely among these various solutes, and it is important to establish the factors which determine these  $\Delta$  values, and if possible set up a model for their quantitative prediction.

It has been shown<sup>6</sup> that the energy loss  $\Delta$  in the substituted pyridines can be correlated by means of the HAMMETT equation<sup>12</sup>:

$$\Delta = \rho\sigma \quad (3)$$

where  $\rho$  is a parameter for a given organic reaction (the adsorption of a pyridine nitrogen atom on alumina in this case), determined by the response of the reaction to changes in electron density at the reaction site (the pyridine nitrogen atom).  $\sigma$  is a constant for each *meta* or *para* substituent, determined by the electron donating or withdrawing power of the substituent. For the adsorption of the substituted pyridines on alumina,  $\rho$  was measured<sup>6</sup> as  $-2.7$  (converting from kcal to  $S^\circ$  units). We will now attempt to expand the correlation of the substituted pyridine adsorption energies to fit all of the related aza- and di-aza-aromatics.

The HAMMETT equation<sup>12</sup>, eqn. (3), was first derived for *meta* and *para* benzenes and has since been empirically extended to other ring systems as well, although there have been relatively few correlations for non-benzene derivatives. DEWAR AND GRISDALE<sup>13</sup> have recently proposed a general formulation of the HAMMETT equation for application to non-benzene ring systems, and have shown it is possible to calculate  $\sigma$  values for the substituted naphthalenes and biphenyls which are in good agreement with experimental values. Briefly, if  $F$  and  $M$  are substituent parameters (values of these two parameters have been tabulated for a great number of aromatic substituents<sup>13</sup>), then  $\sigma$  in *any* ring system is given by:

$$\sigma = F/r_{ij} + M q_{ij}$$

where  $r_{ij}$  is simply the distance between the ring carbon bearing the substituent ( $j$ ) and the ring carbon adjacent to the reaction center ( $i$ ), and  $q_{ij}$  is a fundamental quantum mechanical property of the molecule (the formal charge created at position  $j$  by introducing a  $-\text{CH}_2-$  group at position  $i$ ). Both  $r_{ij}$  and  $q_{ij}$  turn out to be extremely simple and fast to calculate, so that with given values of  $F$  and  $M$ , the  $\sigma$  values of any substituent in many ring systems are readily obtainable.

Consider next the application of the DEWAR-GRISDALE treatment to the calculation of  $\sigma$  for the pyridine  $-\text{N}=\sigma$  group in various ring systems. Assume as a first approximation that the  $r_{ij}$  and  $q_{ij}$  values of the heteroaromatics are the same as those of the corresponding aromatic hydrocarbons (e.g. equal for naphthalene, quinoline and 1,5-naphthyridine). JAFFÉ<sup>14</sup> has summarized experimental values of  $\sigma$  for various positions of the pyridine and quinoline rings, relative to benzene. Considering only the 3- and 4-positions of these two molecules, best values of  $F$  and  $M$  for the  $-\text{N}=\sigma$  "substituent" can be derived:  $F$  equal 1.04 and  $M$  equal 1.67. Values of  $\sigma$  for the  $-\text{N}=\sigma$  groups in the various molecules of Table III can now be calculated in a straightforward fashion.

The next problem is the calculation of  $\rho$  for these and related solutes. Since the reaction center (i.e. a pyridine type  $-\text{N}=\sigma$  group) is the same in these various solutes, we might initially assume that the values of  $\rho$  are the same. We have seen, however, that  $Q^\circ_i$  for these various groups is a function of solute structure, decreasing with increased intramolecular crowding. The contribution of a substituent group to the adsorption energy of a  $-\text{N}=\sigma$  group, and  $\rho$ , would also be expected to decrease with  $Q^\circ_i$  of the  $-\text{N}=\sigma$  group. Similarly, when one  $-\text{N}=\sigma$  group in a di-aza-aromatic is localized on a strong site (as is generally the case<sup>2</sup>), the adsorption energy of the other  $-\text{N}=\sigma$  group is decreased to the effective value  $f(Q^\circ_n) Q^\circ_{n'}$  where  $Q^\circ_n$  is the value of  $Q^\circ_i$  for the stronger adsorbing nitrogen  $n$ ,  $f(Q^\circ_n)$  is the value of the localization function for  $n$ , and  $Q^\circ_{n'}$  is the value of  $Q^\circ_i$  for the weaker adsorbing nitrogen  $n'$ . As a first approximation, then, we might expect  $\rho$  for localized  $-\text{N}=\sigma$  groups to be given by:

$$\rho = \underline{A} Q^\circ_n \quad (4a)$$

and  $\rho$  for non-localized (delocalized)  $-\text{N}=\sigma$  groups to be given by:

$$\rho = \underline{A} f(Q^\circ_n) Q^\circ_{n'} \quad (4b)$$

where  $\underline{A}$  is a constant for the adsorption on alumina of any  $-\text{N}=\sigma$  group. From the value of  $\rho$  for the substituted pyridines ( $-2.7$ ) and  $Q^\circ_i$  for the pyridine nitrogen group (4.8), we calculate  $\underline{A}$  equal  $-0.56$ .

Consider first the initial four solutes of Table III, which are all derivatives of pyrazine. Values of  $\sigma$  for each nitrogen in the pyrazine derivatives are listed, as calculated by the DEWAR-GRISDALE procedure for the corresponding hydrocarbon derivative, assuming the prior derived values of  $F$  (1.04) and  $M$  (1.67). Values of  $\rho$  from eqns. (4a and 4b) are also listed (assuming  $\underline{A}$  equal  $-0.56$ ). Finally, calculated values of  $\Delta$  are shown, and we see that these agree with the experimental  $\Delta$  values within an average deviation of about  $\pm 0.2 S^\circ$  units. This agreement is certainly within the experimental accuracy of the solute  $S^\circ$  values, considering the necessity of extrapolating  $\underline{R}^\circ$  values to get values of  $\underline{R}_p$ .

Calculation of an  $S^\circ$  value for the fifth solute of Table III, 1:2;3:4;6:7-tribenzophenazine, requires a value of  $Q^\circ_i$  for the more hindered nitrogen atom, which is unavailable. By trial and error calculation of  $S^\circ$  and  $\Delta$  for this solute, we can, however, estimate the best value of  $Q^\circ_i$  for the more hindered nitrogen, equal  $-0.1$ . This appears to be a reasonable value of  $Q^\circ_i$  in that the normal bonding of the nitrogen to the adsorbent<sup>9</sup> is almost completely precluded, and some slight deactivation of the surrounding aromatic carbon atoms by this  $-N=$  group would be expected<sup>2</sup>.

The next three solutes of Table III, beginning with 1,5-naphthyridine, each have the nitrogen atoms contained in different aromatic rings. Before extending the previous treatment to the calculation of  $\Delta$  value for these solutes, it is well to consider some data on the reactivity of the substituted quinolines. Values of  $\sigma$  for substituents in the 6- and 7-positions of quinoline have been reported by BACIOCCHI, ILLUMINATI AND MARINO<sup>15</sup>, while ELDERFIELD AND SIEGEL<sup>16</sup> have reported the  $\sigma$  values of the quinoline nucleus for reaction sites at the 6- and 7- (as well as other positions). These experimental values are for various organic reactions in solution. These various  $\sigma$  values for the effect of a substituent in one ring on a reactive center in the  $\sigma$  other of quinoline are plotted in Fig. 1 *versus* values calculated by the procedure of DEWAR AND GRISDALE as previously. A good correlation is noted, but the slope of the curve is 0.7 rather than the theoretical value of 1.0. This reflects some difference in the way resonance and/or field effects are transmitted across the quinoline ring, relative to a naphthalene ring. Doubtless this property extends to the pyridine ring systems as well, but our initial derivation of  $F$  and  $M$  values for the  $-N=$  group from the pyridine ring system itself has resulted in the cancellation of these differences. For our present purposes it suffices to know that the values of  $\sigma$  we calculate for the interaction of two nitrogens in different fused rings must be multiplied by 0.7 (as in Fig. 1). In the case of 4,4'-dipyridyl in Table III, it is uncertain which basis we should use to calculate values of  $\sigma$ , and we have arbitrarily assumed no correction factor (as

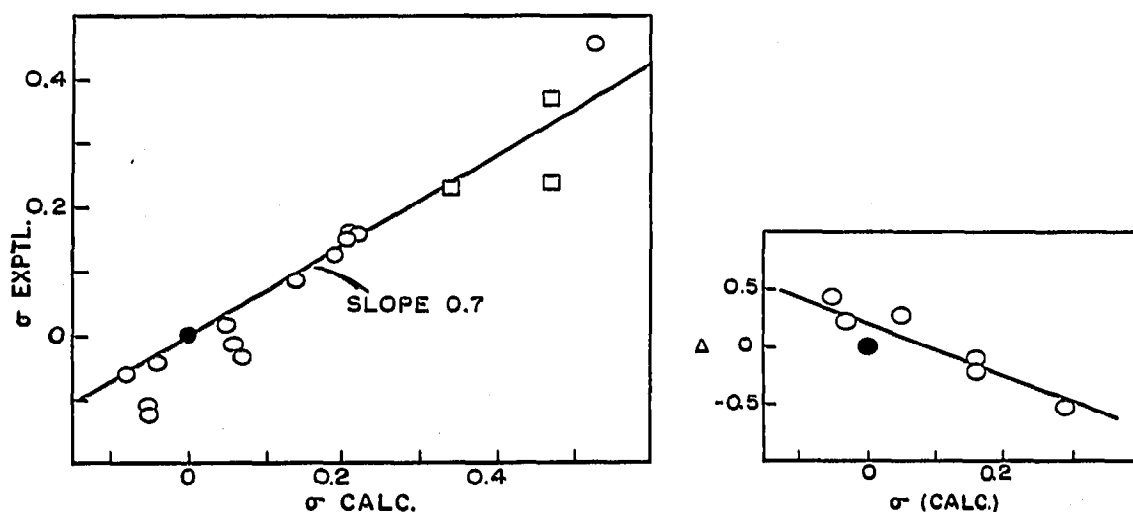


Fig. 1. Experimental  $\sigma$  values for 6- and 7-positions of quinoline *versus* values calculated from the DEWAR-GRISDALE model<sup>13</sup>. O =  $\sigma$  values for substituents in 6- and 7-positions of quinoline with reaction center at the 1-position<sup>15</sup>;  $\square$  =  $\sigma$  values for reaction center at 6- and 7-positions of quinoline<sup>16</sup>.

Fig. 2. Correlation of  $\Delta$  values in 6- and 7-substituted quinolines with  $\sigma$ .

in the pyrazine derivatives). Using values of  $\sigma$  and  $\rho$  calculated in this fashion and shown in Table III, the  $\Delta$  values for 1,5-naphthyridine, 4,4'-dipyridyl and *m*-phenanthroline can be calculated. Again, we see agreement with experimental values which appears within the experimental error of the  $S^\circ$  values themselves ( $\pm 0.2 S^\circ$  units).

As a final example of the interpretation of electronic effects in the adsorption of the aza-aromatics by means of the present model, consider the  $\Delta$  values of the 6- and 7-substituted quinolines which have been reported previously<sup>5,6</sup>. These data are plotted *versus* calculated  $\sigma$  values (corrected by 0.7) in Fig. 2, and the slope (value of  $\rho$ ) of the best (least squares) line through these data is found to be  $-2.20$ . The calculated value of  $\rho$  ( $-0.56 \times 4.0$ ) equals  $-2.24$ . Again, excellent agreement is found between the experimental values of  $\Delta$  for substituted aza-aromatics and values calculated from the DEWAR-GRISDALE model.

To emphasize the significance of the above correlations, it should be pointed out that the treatment followed was derived *entirely* and consistently from theory applicable to (and developed for) classical organic reactions. Thus, starting with  $Q^\circ_i$  values for the nitrogen atom in various configurations (Table I) as measured from unsubstituted mono-aza-aromatics, it has been possible to quantitatively calculate  $S^\circ$  values for the first eight solutes of Table III, the six substituted quinolines of Fig. 2, and the 12 substituted pyridines reported previously<sup>6</sup>. Only one experimental parameter ( $\Delta$ ) has been assumed. To the extent that we can similarly draw on the vast theoretical framework of physical-organic chemistry for other solute types where electronic effects affect adsorption energy, we can tremendously increase our ability to make quantitative calculations of solute adsorption energy (and separability). Because of the success of this treatment in the solute types so far examined, we can apply it to related solutes with considerable confidence. Table II summarizes calculated  $S^\circ$  values for all of the di-aza-aromatics containing 1 to 3 fused aromatic rings. As we will shortly see, the present treatment is inadequate to explain the  $\Delta$  values of *ortho* di-aza-aromatics because of steric effects. The values of  $S^\circ$  for these solute types in Table II were estimated by other means.

It is seen in Table III that values of  $\Delta$  calculated by eqn. (3) for the "*ortho*" di-aza-aromatics (cinnoline and the three following solutes) are significantly more negative than the experimental values (by an average of more than 3  $S^\circ$  units). That is, these solutes are much more strongly adsorbed than predicted by simple electronic considerations. While there is some reason to believe that the DEWAR-GRISDALE treatment may be over-emphasizing the magnitude of electronic effects in the solutes where the nitrogens are bonded to one another, this in itself is an insufficient explanation of the discrepancy between experimental and calculated values. Thus, both TAFT<sup>17</sup> and CHARTON<sup>18</sup> estimate that the non-steric electronic effect in *ortho* and *para* substituted benzenes is of comparable magnitude (the DEWAR-GRISDALE model predicts that the electronic effect in the *ortho* position should be 50-100% higher than in the *para* position), and if this were true,  $S^\circ$  for phthalazine would be predicted equal to about 6.4, whereas the experimental value is 2  $S^\circ$  units greater. Similarly, 1,10-phenanthroline is not subjected to any uncertainty concerning the calculation of the electronic contribution to adsorption energy (the nitrogens are non-adjacent), and the calculated  $S^\circ$  value including electronic interaction ranges from 6 to 7, depending upon the crowding (and  $Q^\circ_i$  values) assumed for the nitrogen atoms. The actual value (10.27) is at least 3  $S^\circ$  units higher. The only explanation that seems to

have merit in explaining the preferential adsorption of the *ortho* di-aza-aromatics is the assumption that both nitrogens in these solutes simultaneously interact with a single site, as pictured in Fig. 3 for the hypothetical adsorption of pyridazine. The well known tendency of 1,10-phenanthroline to chelate with metal salts is a similar phenomenon. As we shall see in the next section of this paper for the quinones, and in the immediately following paper of this series for the halo-aromatics, other solute types also show preferential adsorption of *ortho* type isomers when two adsorbing

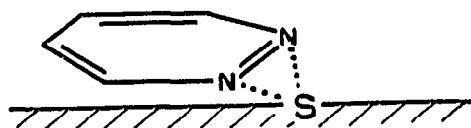


Fig. 3. Hypothetical utilization of same site (S) by both nitrogens in adsorption of pyridazine on alumina.

groups can share an adsorption site. Assuming that this explanation of the preferential adsorption of the *ortho* di-aza-aromatics is correct, it would seem appropriate to consider the two nitrogen atoms in such solutes as constituting a single functional group, from the standpoint of  $S^\circ$  calculations, with all  $q^\circ_j$  or  $\Delta$  terms for this grouping combined into a single  $Q^\circ_i$  value for the two nitrogen atoms. Table I summarizes experimental  $Q^\circ_i$  values for the azo group in the various *ortho* di-aza-aromatics of Table III. Similarly, a value of  $Q^\circ_i$  for the two nitrogens (together) in 1,10-phenanthroline is given, equal 7.4. The very strong adsorption of this latter solute can be attributed to very favorable positioning of the two nitrogen atoms for simultaneous interaction with a single adsorbent site:

We have previously suggested<sup>2</sup> that the adsorption of 2,2'-dipyridyl gives a planar configuration essentially similar to that of 1,10-phenanthroline, rather than with nitrogen atoms lying on opposite sides of the adsorbed molecule. We can now calculate  $S^\circ$  values for each of the two conceivable (planar) configurations of adsorbed 2,2'-dipyridyl with some confidence and hence arrive at the true configuration. For the planar configuration, with nitrogens unopposed, there is no energy barrier to planarity, and we can calculate  $S^\circ$  equal 5.6 by the previous treatment and the data of Table I. For the alternate planar configuration where the nitrogens are equivalent to those in 1,10-phenanthroline, ADRIAN<sup>10</sup> estimates an energy barrier of 2.0 kcal, and we can calculate  $S^\circ$  (for adsorption on 3.8%  $H_2O-Al_2O_3$ ) equal 7.6, in good agreement with the experimental value of 7.5<sup>2</sup>. While the closeness of the calculated and experimental values is fortuitous, this check constitutes good evidence for a 1,10-phenanthroline type configuration in adsorbed 2,2'-dipyridyl.

We can briefly summarize the factors that determine the relative adsorption energy (on alumina) of the di-aza-aromatics. First, the intramolecular crowding of individual nitrogen atoms plays a role as in the case of the mono-aza-aromatics. The more crowded the nitrogens, the lower will be the adsorption energy. Second, the greater the distance between the two nitrogens, as when the nitrogens are in different rings, the greater will be the adsorption energy. The most important exception is when the two nitrogens are linked together in an azo group. Third, di-aza-aromatics where the nitrogens are conjugated with each other as in the 1- and 4-positions of pyrazine will tend to be adsorbed less strongly, relative to unconjugated di-aza-aromatics such as pyrimidine. Finally, whenever the two nitrogens are in a position

favorable to simultaneous bonding with a single adsorbent site, adsorption energy will be much increased.

#### SEPARATION OF THE *cis* AND *trans* FORMS OF THE AZOBENZENES AND RELATED COMPOUNDS ON ALUMINA AND OTHER ADSORBENTS

JACQUES AND KAGAN<sup>10</sup> have recently reviewed the separability on various adsorbents of the *cis* and *trans* isomers of the azobenzene derivatives and related compounds. COOK<sup>20</sup> was the first to note that *cis*-azobenzene is more strongly adsorbed on alumina than the *trans* isomer, and this applies to a large number of the mono- and di-substituted azobenzenes as well (e.g. *m*-methyl, *m*-nitro, *p*-chloro, *p*-bromo, *p*-nitro, etc.). On silica, FREUNDLICH AND ZELLER<sup>21</sup> found the same separation order (*cis* > *trans*), while on charcoal *trans*-azobenzene is the more strongly held isomer. CAMPBELL *et al.*<sup>22</sup> found that on silica the *cis* isomer of 3,3'-azopyridine is more strongly held, while the reverse order holds for the adsorption of *cis* and *trans* 2,2'-azopyridine. Finally, COOK<sup>20</sup> has noted that for adsorption of the *p*-bis-(phenyl-azo)-benzenes, the adsorption strengths are *cis-trans* > *cis-cis* > *trans-trans*. The basis for selectivity in the separation of the *cis* and *trans* azobenzenes has received only brief theoretical attention<sup>21,23</sup>, and no satisfactory explanation has yet been offered for the variation of adsorption order (*cis versus trans*) between different compounds on the metal oxide adsorbents.

FREUNDLICH AND ZELLER<sup>21</sup> explained the reversal in separation order of the azobenzenes between alumina and charcoal in terms of the hydrophilic and hydrophobic character of these two adsorbents, and the preferential solubility of *cis*-azobenzene in water and methanol and of *trans*-azobenzene in petroleum ether. This is not to say, however, that solvent effects are controlling separation order in the azobenzenes; our previous analysis of the role of the eluent<sup>3</sup> clearly contradicts this possibility. KLEMM *et al.*<sup>23</sup> postulated the greater adsorption affinity of *cis*-azobenzene on alumina (in contrast to the preferential adsorption of the *trans* isomer in the stilbenes) as due to the greater ease of forming a bond between the adsorbent and the *n*-electrons of the nitrogens in *cis*-azobenzene. In view of our preceding analysis of the adsorption energies of the di-aza-aromatics, it is instructive to compare the experimental adsorption energies of the azobenzenes with values calculated according to Table I. The experimental  $S^\circ$  values for *cis* and *trans* azobenzene are given in Table III. Before calculating  $S^\circ$  values for these two compounds, the sterically induced non-planarity of *cis*-azobenzene must be taken into account. Proceeding as previously<sup>5</sup>, we calculate that *cis*-azobenzene is adsorbed with the nitrogens in the plane of the adsorbent surface, and the two phenyl groups at an angle of about 60° to the plane of the surface. The energy loss relative to planar adsorption of this compound is calculated at about -1.0  $S^\circ$  units (3.8% H<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>), considering delocalization of the two phenyl rings. *trans*-Azobenzene is believed planar in solution<sup>19</sup>. Using the  $Q^\circ_i$  value for the azo group in benzo(*c*)cinnoline (5.5), we then calculate a value of  $S^\circ$  for *cis*-azobenzene equal to 7.4, which is reasonably close to the experimental value of 7.1 (Table III). Similarly, for *trans*-azobenzene we calculate  $Q^\circ_i$  equal 0.84 for the two azo nitrogens\*,

\* Assumes  $Q^\circ_i$  for each nitrogen atom same as in 3:4-benzacridine (0.7), electronic deactivation of each nitrogen by the other as calculated by the DEWAR-GRISDALE model, and no possibility of simultaneous interaction of both nitrogens with one single site.

and  $S^\circ$  for *trans*-azobenzene equal 4.6, again in reasonable agreement with the experimental value (4.4). The separation of the azobenzene stereoisomers on alumina is thus well explained by the factors which determine the relative adsorption of the pyridines and di-aza-aromatics; this is basically the same explanation as that offered originally by KLEMM *et al.*<sup>23</sup>.

In the case of azobenzenes substituted by *meta* or *para* groups such as methyl or the halogens<sup>20</sup>, these groups can have very little effect on the adsorption energy of either *cis* or *trans* azobenzene, inasmuch as their  $Q^\circ_i$  values are quite small, and the retention of preferential adsorption for the *cis* isomer is therefore to be expected. For the stronger adsorbing nitro group ( $Q^\circ_i$  equal 2.75) this situation becomes less obvious, although since  $S^\circ$  for *cis*-azobenzene exceeds that of *trans*-azobenzene by 2.7 units, it is difficult to see how substitution of one nitro group into azobenzene could lead to a reversal of separation order. The experimental observations of COOK<sup>20</sup> on the separation of the substituted azobenzenes on alumina are thus qualitatively in agreement with our theoretical predictions.

In the case of the *p*-bis-(phenylazo)-benzene derivatives, assumption of adsorption of all isomers in the plane of the adsorbent surface (but with twisting of *cis* phenyl groups as in *cis*-azobenzene) clearly leads to the predicted order: *cis-cis* > *cis-trans* > *trans-trans*. Experimentally, *cis-trans* is held most strongly, and some explanation for this anomaly must be sought. After consideration of several possibilities, involving unique localization phenomena, mutual deactivation of the various nitrogen atoms by electronic interaction, etc., we believe the following explanation is the most likely. KLEMM *et al.*<sup>23</sup> originally postulated, in interpreting the adsorption order of the pyridine derivatives, that these solutes tend to adsorb in a tilted or vertical configuration, with the nitrogen atom closest to the adsorbent surface for optimum interaction with a surface site. This hypothesis has been shown<sup>6</sup> inapplicable to the adsorption of the pyridine derivatives, which appear to adsorb in an essentially planar configuration. In the case of *cis*-azobenzene, however, with twisting of the attached phenyl rings 60° out of the plane of the adsorbent surface, there is a considerable driving force to tilted adsorption as proposed by KLEMM *et al.*<sup>23</sup>. Thus, in the absence of tilting, the nitrogen in *cis*-azobenzene would be required to lie about 1.5 Å more distant from the adsorbent surface than in the case of the nitrogen of a planar aromatic such as pyridine. This would be expected to reduce the adsorption energy of the azo group markedly. At the same time, tilting of the phenyl rings in *cis*-azobenzene would not markedly affect their adsorption energy, which by virtue of twisting and delocalization is already fairly small. If adsorbed *cis*-azobenzene is then tilted so as to maintain the azo group close to the alumina surface, *para* substituents on either of the two phenyl rings must be considerably elevated above the adsorbent surface by a kind of lever effect, with resultant reduction in the adsorption energy of such *para* substituents. In *cis-cis-p*-bis-(phenylazo)-benzene then, it is conceivable that the second (delocalized) *cis* azo linkage adds very little to the adsorption energy of the solute (relative to the adsorption energy of *cis*-azobenzene), and steric strain between the various phenyl groups would similarly prevent any sizeable increment to  $S^\circ$  of this solute from the third phenyl group. We would predict an  $S^\circ$  value for the *cis-cis* isomer about equal to or only slightly larger than that of *cis*-azobenzene (7.1). In the case of the *cis-trans* isomer, a similar situation would apply to the *trans* azo group, its elevation above the surface would reduce its ad-

sorption energy to zero, but in this case rotation about the delocalized azo group would permit almost complete return of the third phenyl group into the plane of the surface. This would result in a significant contribution to  $S^\circ$  of the solute, (1-1.5 units) and we would predict that the *cis-trans* isomer would definitely be more strongly adsorbed than the *cis-cis*. A straightforward calculation of  $S^\circ$  for the *trans-trans* isomer gives a value equal to 7.0, which is slightly less than that estimated for the *cis-cis* isomer. The present hypothesis is thus consistent with the experimental separation order found in the *p*-bis-(phenylazo)-benzene isomers, although the complexity of the configuration of adsorbed solute (and of the relevant  $S^\circ$  calculations) makes quantitative predictions of separation order for such solutes generally difficult, and probably impossible in many cases. As a general observation, however, the present hypothesis of tilted adsorption suggests that *reversal of the normal adsorption cis > trans, is always possible in the azobenzenes whenever a strongly adsorbing group is introduced into the para position of one or both phenyl rings (e.g. p-amino-azobenzene, 4,4'-diaminoazobenzene, 4,4'-azopyridine).*

Finally, in the case of the azopyridines adsorbed on silica<sup>20</sup>, we can not offer direct calculations for this adsorbent but it is interesting to note that the same separation orders are expected on alumina. Thus, for the 2,2'-azopyridines, the normal reason for preferential adsorption of the *cis*-isomer no longer applies, because in adsorbed *trans*-2,2'-azopyridine all nitrogens are in the highly favorable 1,10-phenanthroline configuration, rather than in the highly unfavorable 3:4-benzacridine configuration of *trans*-azobenzene. *cis*-2,2'-Azopyridine would thus certainly be more strongly adsorbed than *trans* on alumina, as in fact it is found to be on silica. In the case of 3,3'-azopyridine, the normal separation order could be expected to apply, since the pyridine nitrogens can rotate into the approximate plane of the adsorbent surface in the adsorbed *cis* isomer.

In summary, the various experimental data on the separation order in the azobenzene and azopyridine derivatives seem theoretically reasonable, and some basis for qualitative prediction in this area seems possible. In certain cases, however, as in the *p*-bis-(phenylazo)-benzenes, accurate prediction of relative separation order may not always be feasible because of the complexity of the adsorbed solute configuration.

#### THE QUINONES AND FLUORENONES AS SOLUTES

Because the carbonyl group is both strongly adsorbing and electron withdrawing, we should expect to find many of the electronic effects observed in the adsorption of the di-aza-aromatics duplicated in the quinones. Table IV summarizes retention volume data for the adsorption on 3.8% H<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub> of several quinones and of some monocarbonyl compounds of related interest. Starting with the first five solutes of Table IV, we can calculate  $Q^\circ_i$  values for the keto oxygen in each of these configurations: 4.7 in perinaphthenone, 3.8 in fluorenone (3.7 for the same keto configuration in 2:3-benzofluorenone), and 3.2 in 1:2-benzofluorenone. Using the fluorenone value of  $Q^\circ_i$  for the keto oxygen (3.8) we can calculate  $S^\circ$  for benzophenone, and find  $\Delta$  equal -0.55. The weaker adsorption of benzophenone can be attributed to intramolecular steric hindrance to planar adsorption. Using the procedure of ADRIAN<sup>10</sup>, we estimate that in solution each phenyl ring is twisted out of the plane of the carbonyl



TABLE IV

ADSORPTION OF THE QUINONES AND SOME RELATED MONO-CARBONYL COMPOUNDS ON 3.8% H<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>

Solute	log R <sub>0</sub> <sup>c</sup>	log R <sub>p</sub>	S°	Δ	σ	
					Exptl.	Calc. <sup>a</sup>
					Q° + f(Q°) Q°'	
Perinaphthenone	1.16 <sup>b</sup> , 0.33 <sup>c</sup>	3.16	7.75			
Fluorenone	1.31 <sup>d</sup> , 0.33 <sup>b</sup>	2.60	6.87			
1:2-Benzofluorenone	0.76 <sup>f</sup>	2.81	7.20			
2:3-Benzofluorenone	1.49 <sup>e</sup>	2.99	7.48			
Benzophenone	2.13 <sup>g</sup> , 0.96 <sup>e</sup>	2.18	6.22	-0.55		
1,4-Quinone	1.13 <sup>e</sup>	1.93	5.83		4.5	
1,4-Naphthoquinone	1.58 <sup>d</sup> , 1.11 <sup>f</sup> , 0.46 <sup>b</sup>	2.50	6.72	-3.10	3.5	7.3
9,10-Anthraquinone	1.24 <sup>e</sup> , 0.90 <sup>f</sup> , 0.32 <sup>b</sup>	2.61	6.89	-2.22	2.4	5.9
5,12-Naphthacenequinone	1.40 <sup>f</sup>	3.45	8.20	-1.41	2.4	5.9
7,12-Benzanthracenequinone	1.40 <sup>e</sup> , 1.09 <sup>f</sup>	3.02	7.53	-1.93	2.5	5.6
1:2; 3:4-Dibenzoanthracene quinone	1.65 <sup>e</sup> , 1.40 <sup>f</sup>	3.58	8.40	-1.72	2.8	5.2
Anthanthrone	1.61 <sup>b</sup> , 0.20 <sup>e</sup>	4.40	9.68	-0.80	1.0	5.9
1,2-Naphthoquinone	0.82 <sup>c</sup>	3.24	7.87			
Acenaphthenequinone	1.75 <sup>c</sup>	4.44	9.75			
9,10-Phenanthrenequinone	0.79 <sup>c</sup>	3.75	8.67			
5,6-Chrysenequinone	0.91 <sup>c</sup>	4.41	9.70			
2,4,7-Trinitrofluorenone	1.26 <sup>b</sup>	5.01	10.64	-0.77	3.1	3.8
Anthrone	1.05 <sup>f</sup>	2.71	7.04	0.17	-0.8	3.8
2-Aminoanthraquinone		4.91 <sup>h</sup>	10.48	1.33		

<sup>a</sup> Calculated for electronic effects only, as described in the text.

<sup>b</sup> 40% v methylene chloride-pentane eluent (αε° = 0.214).

<sup>c</sup> Methylene chloride eluent (αε° = 0.269).

<sup>d</sup> 10% v methylene chloride-pentane eluent (αε° = 0.110).

<sup>e</sup> Carbon tetrachloride eluent (αε° = 0.115).

<sup>f</sup> 20% v methylene chloride-pentane eluent (αε° = 0.158).

<sup>g</sup> Pentane eluent (αε° = 0.00).

<sup>h</sup> Data of ref. 11.

group by 35–40°. From this we estimate as previously<sup>5</sup> that  $\Delta$  in the system of Table IV equals  $-0.5$  to  $-0.6 S^\circ$  units, in excellent agreement with the observed value.

With the  $Q^\circ_i$  values for a keto group in the above configurations, we can calculate  $S^\circ$  values for the quinones which have similar keto configurations (all but 1,4-benzoquinone and the *ortho* quinones of Table IV). As in the case of the di-aza-aromatics, subtraction of our calculated  $S^\circ$  values from experimental values gives  $\Delta$  values, and it remains to be seen if these experimental  $\Delta$  values can be rationalized with the known electronic interactions in these molecules.

Unfortunately, no  $\sigma$  values (or experimental data from which they may be derived) have been reported for the ring-incorporated keto group (as in fluorenone), and we cannot therefore derive values of  $F$  and  $M$  as was possible in the aza-aromatics for the  $-N=$  group. An additional complication in applying the DEWAR-GRISDALE treatment is the presence of five-membered ring compounds (the fluorenones), inasmuch as these do not lend themselves to the same simple quantum mechanical formulation used previously for the aza-aromatics (because the hydrocarbon analogues are non-alternates). Consequently, only a crude application of theory to the solutes of Table IV is possible. As a first approximation, we might use the  $F$  and  $M$  values of the  $-CO-CH_3$  group to approximate those of the keto  $>C=O$  group. We must recognize in adopting these values, however, that the keto group of the fluorenones and the quinones differs from that of the acetyl substituent in being attached to the aromatic ring system at two points, and the same is true of the keto group as a reaction center. The DEWAR-GRISDALE treatment considers the transmission of electronic effects in solutes such as the disubstituted benzenes to be between the ring carbons attached to the substituent and the reaction center. Using the same convention in treating the ring-incorporated keto group, we see that four rather than one transmission routes must be considered in the activation of one keto group by the other in the quinones: each carbon attached to the activating (substituent) keto activates each carbon attached to the "reaction center" keto group. Thus, in calculating the  $\sigma$  value of one keto group in 1,4-quinone for activation of the other, we might consider the quinone molecule to be constituted as in XI, with resonance possible between the bonded carbons, but not across the functional group Z (keto group). The field effect from atom 2 could be transmitted to atoms 3 and 5, however.



XI

Thus,  $\sigma$  for either keto group is then given as  $F(1/r_{2,3} + 1/r_{2,5} + 1/r_{5,6} + 1/r_{3,6})$  plus  $M(q_{2,3} + q_{5,6})$ , where the  $q_{i,j}$  values apply to the "aromatic" system ethylene. Using DEWAR AND GRISDALE's values of  $F$  and  $M$  (0.7 and 1.2), we calculate  $\sigma$  for either keto group in 1,4-quinone equal 4.5. Similarly, we calculate the other  $\sigma$  values shown in Table IV in an exactly analogous fashion. Next, the adsorption energy of the oxygen(s) in the various fluorenone and quinone derivatives of Table IV can be calculated, analogous to either  $Q^\circ_n$  or  $Q^\circ_{n'}$  for the aza-aromatics. The sum of these oxygen adsorption energies,  $[Q^\circ_o + f(Q^\circ_o) Q^\circ_{o'}]$ , is shown for certain of the solutes in Table IV. Now, if our theoretical development is valid, by analogy with the aza-

aromatics, the experimental values of  $\Delta$  in Table IV should be equal to the quantity  $\sigma [Q^{\circ}_o + f(Q^{\circ}_o)Q^{\circ}_{o'}]A$ . In Fig. 4, this relationship is tested by plotting experimental values of  $\Delta$  versus  $\sigma [Q^{\circ}_o + f(Q^{\circ}_o)Q^{\circ}_{o'}]$ : a quite satisfactory correlation is noted, with the slope of the plot (value of  $A$ ) equal  $-0.12$ . The calculated values of  $\Delta$  in Table IV (considering only electronic effects) show an average deviation from experimental values of  $\pm 0.2$  units, which is reasonable agreement when it is realized that the

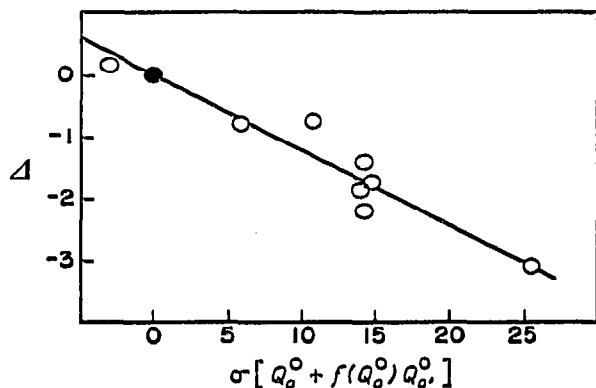


Fig. 4. Correlation of  $\Delta$  values in substituted keto-aromatics and quinones with solute intramolecular electronic effects.

experimental values of  $S^{\circ}$  (for different eluents) vary by  $\pm 0.2$  units average. To conclude, the extension of the DEWAR-GRISDALE treatment to the quinones gives a quantitative correlation of electronic effects on adsorption. The smaller value of  $A$  for the keto group adsorbing on alumina is partially due to the different basis used in calculating  $\sigma$  values. If we were to adopt the same convention in the aza-aromatics, this would lower  $A$  by a significant amount. The sensitivity of the keto group to electron withdrawal by substituent groups is less than that of the aza group  $-N=$ , however, as may be seen by comparing the  $\Delta$  values in 6-nitroquinoline ( $-0.66$ ) and 2,4,7-trinitrofluorenone ( $-0.77$ ). That is, three nitro substituents in the second ring produce roughly the same adsorption energy loss in fluorenone as one nitro group in the second ring does in quinoline.

Extending the previous calculation to 1,4-quinone, we can calculate  $Q^{\circ}_i$  for the keto group in the unstable cyclopentadienone, equal 6.1. This value may be somewhat high because our adaptation of the DEWAR-GRISDALE treatment as above probably overestimates the  $\sigma$  value in 1,4-quinone (and also in 1,4-naphthoquinone). Table I summarizes these  $Q^{\circ}_i$  values for the keto oxygen as a function of crowding, and there is seen to exist the same regular decrease in  $Q^{\circ}_i$  with increasing crowding as in the analogous pyridine derivatives. Similarly,  $Q^{\circ}_i$  values for the furan oxygen and thiophene sulfur groups are summarized in Table I, as derived from unreported  $R^{\circ}$  data on the benzo derivatives of these compounds. Again, we see the same trends in  $Q^{\circ}_i$  with increased crowding of the ring hetero atom, although the magnitude of the effect in these latter solutes is less because the adsorption energy of the thiophene sulfur and furan oxygen is relatively small. In the case of the pyrrole derivatives, also reviewed in Table I, we see an opposite trend of  $Q^{\circ}_i$  with crowding of the strong adsorbing group ( $-NH-$ ), and this has previously been related<sup>6</sup> to the fact that the pyrroles adsorb as acids on alumina, whereas the pyridines and keto-aromatics have

been shown to adsorb with at least some electron transfer to the adsorbent. When an acid group becomes sufficiently crowded, however, as in 2,6-di-*tert.*-butylphenol<sup>7</sup>, its group adsorption energy is also reduced. As a general rule, most organic solutes probably adsorb on alumina with electron transfer and show some reduction in group adsorption energy with increased crowding.

As in the case of the di-aza-aromatics, the *ortho* quinones are seen to be much more strongly adsorbed on alumina than the corresponding isomeric *para* quinones. Again, this may be attributed to the adsorption of both keto groups in the *ortho* quinones on a single adsorbent site. Values of  $Q^\circ_i$  for the combined two oxygens of the *ortho* quinones are shown in Table IV, as for the *ortho* di-aza-aromatics. These values are approximately constant (5.3–5.8) for the six-membered ring quinones, but acenaphthenequinone is considerably more strongly adsorbed ( $Q^\circ_i$  equal 6.9 for two oxygens). In the latter solute, where the keto groups are attached to a five-membered ring, it is theoretically expected that the mutual electronic deactivation of each keto group by the other will be reduced, relative to deactivation in the six-membered ring quinones, because of reduced resonance possibilities in a five-membered ring. The greater adsorption energy of acenaphthenequinone is hence at least qualitatively reasonable. The solute 2-aminoanthraquinone is a more complex example of electronic interaction between solute groups, and will be discussed in a following section.

Prior studies of the relative adsorption of the quinones on alumina and silica have been largely fragmentary, and no overall theory such as the present one has been previously attempted. HOYER (see ref. 8) has shown the importance of hydrogen bonding in determining the separation of certain anthraquinone derivatives on silica, and PETERSSON<sup>24</sup> has recently reported thin-layer chromatographic data for separation of a number of benzoquinone derivatives on silica. Unfortunately, steric effects predominate in both these series of solutes, and comparison with our data (even overlooking the difference in adsorbent) is impossible. FUNAKUBO AND NAGAI<sup>25</sup> have studied the relative adsorption of anthraquinone, 2-methylanthraquinone and anthrone on both alumina and silica, and find adsorption increasing in this order for both adsorbents. They suggest that the greater adsorption of anthrone is due to the keto-enol equilibrium of this compound on the adsorbent, where the enol form would be expected to adsorb much more strongly. Our data suggest the same adsorption order found by the latter workers, since anthrone ( $S^\circ$  equal 7.04) is more strongly held than anthraquinone, ( $S^\circ$  equal 6.89) and the effect of a 2-methyl substituent in anthraquinone should slightly increase  $S^\circ$  (since the methyl group is electron donating). It is not, however, necessary to postulate a keto-enol equilibrium in anthrone; rather, in anthraquinone each keto group strongly suppresses the adsorption of the other, and in anthrone the carbonyl group is slightly activated by the electron donating methylene group. NAGAI AND FUNAKUBO<sup>20</sup> have also studied the adsorption of 1,2- and 1,4-naphthoquinone on alumina from hexane, in the non-linear isotherm region, finding the 1,4-isomer more strongly adsorbed. This observation, which does not agree with the data of Table IV, may be the result of non-linear isotherm adsorption, or of some peculiarity in the alumina used by these workers.

To summarize, our correlations of adsorption energy in the keto-aromatics and quinones show precisely the same type of electronic and steric interaction found in the aza-aromatics. Quantitative calculation of electronic effects in the keto-aromatics and quinones seems equally feasible.

## ELECTRONIC AND STERIC EFFECTS IN OTHER SOLUTE TYPES

Having examined the effect of intramolecular steric and electronic interactions on the adsorption energy of the aza- and keto-aromatics, it is of interest to consider the existence of similar effects in the adsorption of other solute types. The substituted benzenes and naphthalenes have been examined previously<sup>2</sup>, and to a first approximation it was concluded that electronic interactions between substituent groups in these solutes are unimportant in determining adsorption energy. A detailed examination of the effect of electronic and steric interactions in the adsorption of these solutes on alumina is planned for the following paper in this series. We can, however, make a few preliminary comments in the light of the present investigation. First, electronic interaction between substituents on an aromatic ring will always be less than interactions between a substituent on a ring and a functional group forming part of that ring (*e.g.* substituted pyridines); this is a simple consequence of the DEWAR-GRISDALE model, or of any reasonable theory of electronic effects in organic molecules. Second, the response of solute adsorption energy to intramolecular electronic interactions will always be greatest in those solutes where adsorption results in maximum transfer of charge to or from the solute. This means that electronic effects should be greatest for the adsorption of solutes functioning as acids (*e.g.* phenols) or bases (*e.g.* anilines) toward the adsorbent. In confirmation of this, we have seen that the  $\Delta$  values for the substituted quinolines are about three times as great as for the substituted fluorenones. We can calculate  $\rho$  for the substituted acetophenones, a class of solutes which are probably typical of most substituted benzenes with respect to adsorption mechanism (the acetophenones do not adsorb as acids or bases), and which should give one of the largest  $\rho$  values for the non-acid non-base disubstituted benzenes, because  $Q^\circ$  for the aceto group is relatively large (3.7). Extending the DEWAR-GRISDALE treatment for the keto-aromatics we calculate  $\rho$  for the substituted acetophenones equal  $-0.5$ . By comparison with some typical acidic and basic solutes, the substituted pyridines have  $\rho$  equal  $-2.7$  and the phenols<sup>3</sup>  $+2.0$ . This implies that the effect of intramolecular interactions on solute adsorption energy will in general be small for the polysubstituted aromatic hydrocarbons.

In view of our comments on the large  $\rho$  values for the substituted acids and bases, the previously observed<sup>6</sup> value of  $\rho$  for the substituted anilines ( $-0.3$ ) is anomalously small. The anilines and pyridines appear to possess a similar adsorption mechanism and the adsorption energies of the  $-N=$  group in pyridine and of the  $-NH_2$  group in aniline are identical within experimental error. Extension of the DEWAR-GRISDALE calculations to the anilines would therefore have predicted a  $\rho$  value of about 1.0. As an explanation of the aniline adsorption data<sup>6</sup>, it has been proposed that the anilines function as basic solutes when there are no strongly electron withdrawing substituents, and as acidic solutes when there are strongly electron withdrawing substituents. If this were in fact true, a plot of  $\Delta$  versus  $\sigma$  for the anilines should go through a minimum,  $\Delta$  increasing with  $\sigma$  at large values of  $\sigma$ , and  $\Delta$  increasing as  $\sigma$  becomes more negative for negative values of  $\sigma$ . This postulate is tested in Fig. 5, where the  $\Delta$  values of the substituted anilines<sup>6</sup> are plotted versus  $\sigma$ . The  $\Delta$  value for 2-aminoanthraquinone is also included, since it gives a very large  $\sigma$  value (by the calculation of DEWAR AND GRISDALE, as previously). The resulting curve in Fig. 5 confirms our expectation, a definite minimum in the  $\Delta$  values occurring

at intermediate values of  $\sigma$ . We tentatively conclude that the previous explanation for the dependence of  $\Delta$  on  $\sigma$  in the anilines is correct.

It has also been proposed<sup>6</sup> that the acetanilide derivatives adsorb as acids, by analogy with the acidic adsorption of some of the anilines. The value of  $\rho$  for the substituted acetanilides ( $-0.4$ ) does not confirm this postulate, suggesting rather a dependence of solute adsorption energy on electronic effects which correspond to the adsorption of a weak base (with little actual charge developed on the solute). Possibly,

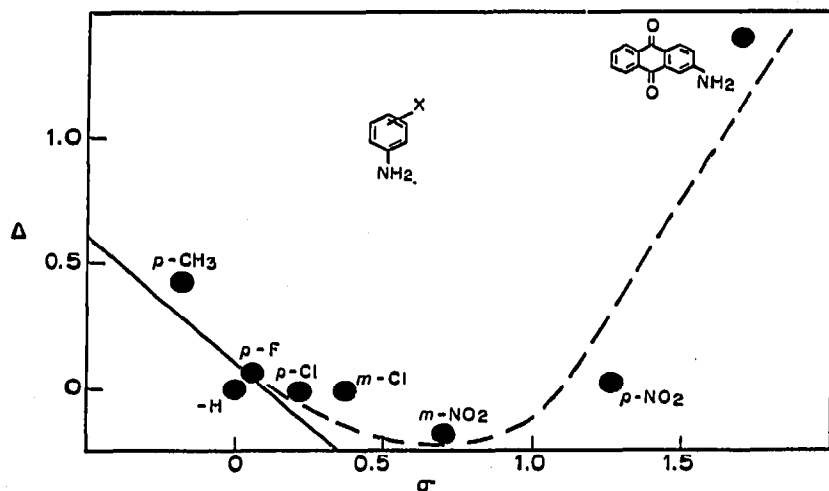


Fig. 5. Dependence of  $\Delta$  in substituted aniline derivatives on  $\sigma$ .

because of steric hindrance to adsorption in the acetanilide amide group, the carbonyl is the principal contributor to the adsorption energy of the amide group; the observed value of  $\rho$  is about what would have been expected for this adsorption mechanism.

The monosubstituted hydrocarbons offer another example of electronic effects contributing to solute adsorption energy. In these cases, however, the effects are again rather small, and can be lumped into the  $Q^{\circ}_i$  value of the substituent group<sup>2</sup>. From the  $q^{\circ}_j$  values associated with the methyl- and ethyl-substituted benzenes<sup>1</sup>, taking the  $Q^{\circ}_i$  value for a methyl group from aliphatic derivatives ( $-0.03$ ), we can calculate the magnitude of the purely electronic effect in the monosubstituted benzenes as  $\Delta = -0.6 \bar{\sigma}$ , where  $\bar{\sigma}$  is the average of *meta* and *para*  $\sigma$  values for the substituent group in question. The corresponding value of  $\Delta$  is  $-0.32$ ; this value is roughly comparable to that ( $-0.12$ ) for the keto-aromatics, when it is realized that the actual  $\sigma$  values for the 1-, 2- and 6-positions in a monosubstituted benzene are probably underestimated by the function  $\bar{\sigma}$ . The adsorption of both the benzene nucleus and keto group on alumina are believed to occur with weak transfer of electronic charge from the solute to the adsorbent.

Some final examples of the electronic and steric interaction of adsorbing solute groups are summarized in Table V. Whereas the usual adsorption order in the di-aza-aromatics is 1,2 > 1,3 > 1,4, we see a reversal of this adsorption sequence for the aminopyridines. This may be caused by adsorption of the amino group as an acid when activated by strongly electron withdrawing substituents (such as the ring  $-N=$  group), and the activation of the ring  $-N=$  group by electron withdrawing substituents. Thus, in 4-aminopyridine the resonance structure. XII is strongly

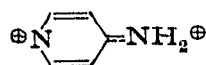
TABLE V

ADSORPTION ENERGIES ON ALUMINA OF SOME OTHER DIFUNCTIONAL SOLUTES; ELECTRONIC AND STERIC EFFECTS

Solute	$S^\circ$
2-Aminopyridine	8.0 <sup>a,b</sup>
3-Aminopyridine	8.2 <sup>a,c</sup>
4-Aminopyridine	> 9.3 <sup>a</sup>
7-Azaindole	8.6 <sup>d</sup>
1-Azacarbazole	9.5 <sup>a</sup>
1,2-Diaminobenzene	9.2 <sup>e</sup>
1,3-Diaminobenzene	8.8 <sup>e</sup>
1,4-Diaminobenzene	8.8 <sup>e</sup>
Dimethyl phthalate	8.2 <sup>e</sup>
Dimethyl isophthalate	7.7 <sup>e</sup>
Dimethyl terephthalate	7.6 <sup>e</sup>
1,2-Nitroanisole	6.4 <sup>e</sup>
1,3-Nitroanisole	5.6 <sup>e</sup>
1,4-Nitroanisole	6.1 <sup>e</sup>
1,2-Nitroaniline	7.4 <sup>e</sup>
1,3-Nitroaniline	7.7 <sup>e</sup>
1,4-Nitroaniline	7.9 <sup>e</sup>

<sup>a</sup> Value from present study, dioxan elution from 3.9% H<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>.<sup>b</sup> Previous values 8.3 (ref. 11) and 7.6 (ref. 3).<sup>c</sup> Previous value 7.7 (ref. 6).<sup>d</sup> Average of previous values 8.5 (ref. 11) and 8.7 (ref. 3).<sup>e</sup> Data of ref. 2.

stabilized by adsorption of the  $-N=$  group on an acidic adsorbent site and the  $-NH_2$



XII

group on a basic site, and as a consequence, the adsorption energy of this solute is considerably greater than calculated in the absence of electronic effects (calculated  $S^\circ$  equal 9.1). While similar resonance structures may be drawn for 2-aminopyridine, this precludes adsorption of both nitrogen groups on the same site as postulated for pyridazine. The advantage of an *ortho* grouping of the two nitrogen atoms as in pyridazine is thus completely lost in 2-aminopyridine. Furthermore, the 2-amino group now partially interferes with the adsorption of the  $-N=$  group, as is the case in 2-methylpyridine<sup>1,6</sup>. Finally, there is a statistically greater possibility of the simultaneous adsorption of the amino group on an acidic site and of the  $-N=$  group on a basic site in the case of 4-aminopyridine than of 2-aminopyridine. The preferential adsorption of the 4-isomer relative to 2-aminopyridine is thus not surprising. The intermediate adsorption energy of 3-aminopyridine can be attributed to the absence of both resonance activation of the adsorbing groups as in XII and steric hindrance to adsorption of the  $-N=$  group as in 2-aminopyridine.

The adsorption energies of 7-azaindole, 1-azacarbazole and 2-aminopyridine show almost identical adsorption energies for the  $-\text{N}=\text{C}-\text{NH}-$  group (6.7, 7.0 and 6.8, respectively). The above explanation of the adsorption of the aminopyridines would have led to the prediction that the adsorption energy of the  $-\text{N}=\text{C}-\text{NH}-$  group in the above two indole derivatives would be greater than in 2-aminopyridine, since the additional vinyl substituent on the  $-\text{NH}-$  group in the indole derivatives should make this group even more acidic. Possibly involved here is a transition between adsorption of the  $-\text{NH}-$  group as a base in 2-aminopyridine (because of the preferential location of a strong site for adsorption in this fashion) and adsorption of the  $-\text{NH}-$  group in the two indole groups as an acid, with a relative independence of adsorption energy on the acid strength of the  $-\text{NH}-$  group, as in the substituted anilines. On this basis we would predict a considerably stronger adsorption of the non-*ortho* azaindole derivatives, as in the case of the aminopyridines.

Table V also summarizes previous data on the adsorption of those disubstituted benzenes where all three isomers were available. In the case of the diaminobenzenes, dimethyl esters of the benzene dicarboxylic acids, and nitroanisoles, the expected preferential adsorption of the *ortho* isomer is seen in every case. The situation is reversed for the nitroanilines, with the *ortho* isomer being least strongly adsorbed. If anything, electronic interactions through the ring would be expected to slightly increase the adsorption of *o*-nitroaniline. This seems to be a clear case of the *hydrogen bonding* between the amino and nitro groups decreasing the adsorption energy of the amino group, and possibly of the nitro group as well. In general, we would predict that *ortho* disubstituted benzenes in which intramolecular hydrogen bonding cannot occur, and where the adsorbing groups are capable of adsorbing on the same type site, will be preferentially adsorbed on alumina, relative to *meta* and *para* isomers.

#### GLOSSARY OF TERMS

- $A$  = A parameter which measures the relative change in the adsorption energy of a solute group  $i$  as a result of electronic activation by a substituent; equal  $\rho/Q^\circ_i$ .
- $F$  = Parameter in the DEWAR-GRISDALE treatment which correlates the field effect of the substituent.
- $f(Q^\circ_k)$  = Localization function for strong adsorbing group  $k$ .
- $M$  = Parameter in the DEWAR-GRISDALE treatment which correlates the resonance effect of the substituent.
- $Q^\circ_i, Q^\circ_x$  = Adsorption energy of solute groups  $i$  and  $x$ .
- $Q^\circ_n$  = Adsorption energy of stronger adsorbing nitrogen atom in a di-aza-aromatic.
- $Q^\circ_{n'}$  = Adsorption energy of weaker adsorbing nitrogen atom in a di-aza-aromatic.
- $Q^\circ_o$  = Adsorption energy of stronger adsorbing oxygen group in a quinone.
- $Q^\circ_{o'}$  = Adsorption energy of weaker adsorbing oxygen group in a quinone.
- $q^{\circ}_j$  = Solute geometry factor.
- $Q^\circ_{x,y}$  =  $q^{\circ}_j$  value resulting from change in adsorption energy of group X by virtue of interaction with group Y.
- $q_{ij}$  = Electronic interaction factor for two atoms in a molecule (DEWAR-GRISDALE treatment).



$R^\circ$	= Solute linear equivalent retention volume (ml/g).
$R_p$	= Value of $R^\circ$ for pentane eluent.
$r_{ij}$	= Separation of two atoms in a molecule (DEWAR-GRISDALE treatment).
$S^\circ$	= Solute adsorption energy; calcined alumina and pentane eluent.
$V_a$	= Adsorbent surface volume (ml/g).
$\alpha$	= Adsorbent activity function.
$\Delta$	= Difference between calculated and experimental $S^\circ$ values, equal $S^\circ_{\text{exptl}} - S^\circ_{\text{calc}}$ .
$\epsilon^\circ$	= Eluent strength parameter.
$\sigma, \rho$	= HAMMETT equation parameters.
$\bar{\sigma}$	= Average of $\sigma$ values for <i>meta</i> and <i>para</i> substituents.
$\sigma_Y$	= $\sigma$ value for group Y.

## ACKNOWLEDGEMENTS

The author is grateful to his associate, Dr. J. K. FOGO, for editing the original manuscript, and to Mr. F. O. WOOD for assistance in the experimental work.

## SUMMARY

Hetero-aromatic solutes in which the hetero group is strongly adsorbing and forms part of the aromatic ring (*e.g.* pyridine, fluorenone) are markedly affected in their adsorption on alumina by intramolecular electronic and steric effects. Crowding of the hetero group by adjacent solute groups in these compounds results in strong reduction of the hetero group adsorption energy. The presence of electron withdrawing substituents in the derivatives of the fluorenones, quinones, di-aza-aromatics and pyridines also reduces the adsorption energy of the hetero group; because the nitrogen atom in the aza-aromatics and the carbonyl group in the quinones are strongly electron withdrawing, the di-aza-aromatics are generally no more strongly adsorbed than corresponding mono-aza-aromatics, while the quinones are about as strongly adsorbed as corresponding mono-carbonyl compounds. The presence of two strongly adsorbing solute groups in adjacent positions, however, as in the *ortho* quinones and pyridazine derivatives, strongly increases solute adsorption energy, because both solute groups can simultaneously bond with a single strong adsorbent site. Similar factors appear to determine the relative separability of the *cis* and *trans* azobenzene isomers. Using the theory of intramolecular electronic effects derived elsewhere from the study of organic reaction rates and equilibria, it is possible to quantitatively calculate the changes in solute adsorption energy which occur in the pyridines, di-aza-aromatics, fluorenones and quinones as a result of substituent electronic interactions. Electronic effects in other solute types are also examined theoretically, and concluded to be generally much smaller, with the exception of certain cases where the solute may function as either an acid or base. Less strongly adsorbing hetero-aromatic solutes (*e.g.* thiophenes, furans) show similar, but smaller responses to substituent steric and electronic interactions.

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*J. Chromatog.*, 17 (1965) 73-98