208. *The Electronic Structure of Some Aza-derivatives of Naphthalene, Anthracene, and Phenanthrene.*

By H. C. Longuet-Higgins and C. A. Coulson.

Theoretical calculations are made of the distribution of π-electrons in a number of mono- and di-aza-derivatives of naphthalene, anthracene, and phenanthrene. Relative values are given for the net charges at different positions in such molecules, and these are found to be closely correlated with the chemical behaviour of such molecules in substitution reactions, especially by anionoid reagents. The method of calculation employed leads naturally to the idea that the effects of successive substitutions should be approximately additive, in agreement with experiment. A discrepancy is pointed out between estimated and observed basic strengths, and it is suggested that the electric moment of a monoaza-hydrocarbon and changes in certain resonance integrals on quarternation may be important in determining its basic strength.

It was pointed out by Wheland and Pauling (*J. Amer. Chem. Soc.*, 1935, **57**, 2091) that the reactivity of heteroaromatic systems towards anionoid and cationoid reagents was closely correlated with the π-electron distributions in such molecules, as determined by the method of molecular orbitals, if certain reasonable values were assigned to the energy parameters. More recently, we have successfully extended such calculations to quite complex systems containing nitrogen atoms (*Trans. Faraday Soc.*, 1947, **43**, 87), and have given a simple theoretical interpretation to the undoubted correlation between the calculated electron distributions and the observed chemical behaviour (*Proc. Roy. Soc.*, 1947, *A*, **191**, 39; **192**, 16).

In calculating the π-electron distribution in an unsaturated molecule, it is usual to begin by assuming that each π-electron moves in a molecular orbital ψ_j which can be expressed in the form

$\sum\limits_r c_{rj}\,\phi_r$, where $\phi_1, \phi_2, \ldots$ are appropriate atomic orbitals associated with atoms 1, 2, . . . of the system. The coefficients c_{rj} and the possible molecular orbital energies are then determined by solution of a set of linear equations called the secular equations. If the molecular orbitals $\psi_1, \psi_2, \ldots$ are numbered in order of increasing energy, and there are $2n$ π-electrons in the system, then the mean number of π-electrons in the atomic orbital ϕ_r is given by

$$q_r = 2\sum_{j=1}^{n} c_{rj}{}^2$$

and it is this quantity, conveniently designated as the electron density at position r, which has been found to be principally important in determining the reactivity of the position towards heterolytic reagents.

The labour involved in the straightforward calculation of q_r is comparatively slight for small or highly symmetrical molecules, but becomes very considerable for unsymmetrical molecules with more than about ten atomic orbitals. However, it is not difficult to obtain approximate values for q_r in quite large molecules with the aid of first-order perturbation theory. This method of calculation was discussed by Wheland and Pauling (*loc. cit.*), but has not been very widely used hitherto. In this paper we shall present and discuss the results of such calculations on a number of aza-derivatives of naphthalene, anthracene, and phenanthrene.

Method.—The coefficients, c_{rj}, and therefore the electron densities q_r, in an unsaturated molecule, are determined completely by the values of certain energy integrals α_s and β_{tu} (Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39), so in calculating the π-electron distribution in an aza-hydrocarbon we may proceed as follows : We start with the parent hydrocarbon, and find its electron densities, q_r^0, say. Replacement of the group $\gg$CH by $\gg$N or $\gg$C— by $\gg\overset{+}{\text{N}}$— will alter some of the energy integrals α_s and β_{tu} upon which the electron densities depend. If this alteration is not very large, the electron densities in the aza-hydrocarbon will be given approximately by the equation

$$q_r = q_r^0 + \sum_s \left(\frac{\partial q_r}{\partial \alpha_s}\right)^0 (\alpha_s - \alpha_s^0) + \sum_{t,u} \left(\frac{\partial q_r}{\partial \beta_{tu}}\right)^0 (\beta_{tu} - \beta_{tu}^0) \; . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

where q_r, α_s, and β_{tu} refer to the aza-hydrocarbon, and the superscript denotes quantities referring to the parent hydrocarbon; that is to say, we may use first-order perturbation theory to calculate q_r, taking the parent hydrocarbon as basis.

The formal definitions of α_s and β_{tu} are as follows : α_s, which is conveniently described as the Coulomb term for atom s, is defined by the equation

$$\alpha_s = \int \phi_s \mathrm{H} \phi_s \mathrm{d}\tau = \int \phi_c \mathrm{H} \phi_c \mathrm{d}\tau$$

H being the effective Hamiltonian operator for a single electron, and ϕ_c being the $2pz$ orbital of a carbon atom in benzene. It is usual to assume that α_s is zero for every unsaturated carbon atom in a hydrocarbon, and that in general its value depends only on the chemical nature of atom s and its nearest neighbours; β_{tu}, on the other hand, is defined by the equation

$$\beta_{tu} = \int \phi_t \mathrm{H} \phi_u \mathrm{d}\tau$$

and is very small indeed when atoms t and u are not bonded. For this reason it is described as the resonance integral of the bond tu. Like α_s, its value is assumed to depend only on the chemical nature of atoms t and u; in particular, it is generally assigned a fixed value β for all aromatic carbon–carbon bonds.

Now, in certain circumstances equation (1) can be considerably simplified. If the given aza-compound is derived from an unsaturated hydrocarbon containing no odd-membered rings, then it can be shown that $q_r^0 = 1$ (Coulson and Rushbroke, *Proc. Camb. Phil. Soc.*, 1940, **36**, 193) and that $(\partial q_r/\partial\beta_{tu})^0 = 0$ (Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **192**, 16). Further, from the arguments of the preceding paragraph, $\alpha_s^0 = 0$ for every unsaturated carbon atom in a hydrocarbon. Equation (1) therefore takes the form

$$q_r = 1 + \sum_s \pi_{r,s}^0 \alpha_s \; . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

where $\pi_{r,s}^0$ stands for $(\partial q_r/\partial\alpha_s)^0$, and is the quantity known as the mutual polarisability of atoms r and s in the hydrocarbon. It is convenient to express $\pi_{r,s}^0$ in the form $x_{r,s}\,\beta$, and α_s in the form $y_s\beta$, where $x_{r,s}$ and y_s are dimensionless; the net positive charge $1 - q_r$ at atom r in the aza-compound is then given by the equation

$$1 - q_r = -\sum_s x_{r,s}y_s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

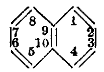
measured in units of the electronic charge.

Comparison of Methods of calculating q_r.—Equation (3) tells us that if we can find the values of $x_{r,s}$ for the hydrocarbon, and have some means of estimating the numbers y_s for the aza-derivative, we can calculate very simply the approximate net charges at the various atoms of the aza-compound.

At first sight it might be thought that finding the terms $x_{r,s}$ for a hydrocarbon would be almost, if not quite, as laborious as direct solution of the secular equations for one of its aza-derivatives. However, it often happens that the hydrocarbon is more symmetrical than the derivative—for instance, naphthalene is more symmetrical than quinoline—and this makes the former process considerably easier. Further, if we are interested in the electron densities in a number of derivatives of the same hydrocarbon, the perturbation method outlined in the last section enables us to calculate all these distributions very quickly once the quantities $x_{r,s}$ are known. For example, direct solution of the secular equations for an unsymmetrical aza-anthracene requires about a fortnight; whereas by first-order perturbation theory approximate values can be obtained for the electron densities in 20 or 30 such molecules within a week, starting *ab initio*.

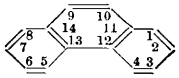
Although in principle the perturbation method is less accurate than direct solution of the secular equations for giving the net charges $1 - q_r$, both methods are open to the severe objection that values must be guessed for the Coulomb terms α_s in the aza-compounds, so there is less to choose between the two methods than might at first appear. Further, it is the relative values of the electron densities or net charges that are of primary interest to the chemist, and it has been found that the two methods of calculation give consistent results in this respect, provided the same values are assigned to the Coulomb integrals. In any case, there is reason to suppose that the uncertainty in the Coulomb integral for heteroaromatic nitrogen gives rise to a probable error in the absolute magnitudes of the net charges which far exceeds that due to the use of first-order perturbation theory.

Values of $x_{r,s}$ *for Naphthalene, Anthracene, and Phenanthrene.*—In Tables I, II, and III are given values of $x_{r,s}$ for naphthalene, anthracene, and phenanthrene, as all these molecules have hetero-derivatives for which the calculation of electron densities would be of interest from the chemical point of view. (The numbering used is shown in the attached formulæ.) The figures given for $x_{r,s}$ have been calculated on the assumption that all the carbon–carbon resonance integrals are equal to β, and using the equations given for the calculation of $\pi_{r,s}^0$ by Coulson and Longuet-Higgins (*Proc. Roy. Soc.*, 1947, *A*, **191**, 39). It should be remembered that $x_{r,s} = x_{s,r}$.



Naphthalene.

Anthracene.



Phenanthrene.

TABLE I.

Mutual atom polarisabilities in naphthalene (the figure given is $x_{r,s} = \beta \times \pi_{r,s}$).

$s =$	1.	2.	9.	$s =$	1.	2.	9.
$r = 1$	0·443	−0·213	−0·089	$r = 6$	0·007	−0·033	−0·089
2	−0·213	0·405	0·007	7	−0·033	0·000	0·007
3	0·018	−0·110	−0·049	8	0·027	−0·033	−0·089
4	−0·139	0·018	0·004	9	−0·089	0·007	0·330
5	−0·023	0·007	0·004	10	0·004	−0·049	−0·077

TABLE II.

Mutual atom polarisabilities in anthracene (the figure given is $x_{r,s}$).

$s =$	1.	2.	9.	13.	$s =$	1.	2.	9.	13.
$r = 1$	0·4540	−0·2306	0·0428	−0·0777	$r = 8$	0·0080	−0·0106	0·0428	−0·0179
2	−0·2306	0·4108	−0·0544	0·0088	9	0·0428	−0·0544	0·5257	−0·1249
3	0·0220	−0·0990	0·0142	−0·0364	10	−0·0402	0·0142	−0·2175	0·0085
4	−0·1512	0·0220	−0·0402	0·0027	11	0·0033	−0·0176	0·0085	−0·0261
5	−0·0084	0·0040	−0·0402	0·0033	12	−0·0179	0·0000	−0·1249	0·0053
6	0·0040	−0·0124	0·0142	−0·0176	13	−0·0777	0·0088	−0·1249	0·3313
7	−0·0106	0·0010	−0·0544	0·0000	14	0·0027	−0·0364	0·0085	−0·0593

TABLE III.

Mutual atom polarisabilities in phenanthrene (the figure given is $x_{r,s}$).

$s =$	1.	2.	3.	4.	10.	11.	12.
$r =$ 1	0·4391	−0·1935	0·0177	−0·1209	0·0242	−0·1025	0·0033
2	−0·1935	0·4028	−0·1235	0·0152	−0·0146	0·0076	−0·0633
3	0·0177	−0·1235	0·4068	−0·1892	0·0079	−0·0609	0·0098
4	−0·1209	0·0152	−0·1892	0·4292	−0·0080	0·0041	−0·1105
5	0·0001	−0·0118	0·0021	−0·0170	0·0042	−0·0121	0·0147
6	−0·0083	0·0002	−0·0091	0·0021	−0·0423	0·0002	−0·0131
7	0·0006	−0·0107	0·0002	−0·0118	0·0002	−0·0128	0·0036
8	−0·0098	0·0006	−0·0083	0·0001	−0·0450	0·0036	−0·0086
9	−0·0449	0·0002	−0·0422	0·0042	−0·2699	0·0126	−0·0553
10	0·0242	−0·0146	0·0079	−0·0080	0·4424	−0·0637	0·0070
11	−0·1026	0·0076	−0·0609	0·0041	−0·0637	0·3335	−0·0911
12	0·0033	−0·0633	0·0098	−0·1106	0·0070	−0·0911	0·3494
13	−0·0086	0·0036	−0·0131	0·0147	−0·0553	0·0003	−0·0488
14	0·0036	−0·0128	0·0002	−0·0120	0·0126	−0·0213	0·0003

These figures illustrate well the law of alternating polarity, which requires $\pi_{r,s}$ to be positive or negative according as atoms r and s are separated by odd or even numbers of bonds, and also the general tendency for interactions between distant atoms to be smaller than interactions between atoms in the same ring. In fact, there is a close resemblance between the interactions in the terminal rings of phenanthrene and anthracene and the interactions in naphthalene.

Values of the Coulomb Terms.—The evaluation of the terms y_s ($= \alpha_s/\beta$) is a much more uncertain business than the calculation of $x_{r,s}$. If the Coulomb term for nitrogen is denoted by α_N, and that of an adjacent carbon atom by α', then the ratio of α_N to α' can be estimated roughly from the relative reactivities of the different positions in pyridine, say. In this way Wheland and Pauling showed that this ratio must be of the order of 8 : 1, and this is the figure we shall adopt. On the other hand, the value of α_N/β ($= y_N$, say) is extremely uncertain. For example, if we take the values $y_N = 2$, $y' = \frac{1}{4}$ for pyridine, as suggested by Wheland and Pauling, we find that the calculated dipole moment in pyridine due to the π-electrons is about 4·8 D., depending slightly on the angle assumed at the nitrogen atom. If we add to this the moment of the single C–N σ bonds (estimated at about 0·8 D.) and the moment of the lone-pair electrons on the nitrogen atom (estimated at about 0·5 D.), we obtain a theoretical value for the total moment of about 6·1 D., whereas the observed moment is actually 2·2 D. This enormous discrepancy must mean either that the above values of y_N and y' are much too large, or that some further effect has been neglected in the calculation. For example, there might be an induced moment in the σ-bonds due to the uneven distribution of the π-electrons; such an induced moment would act in the opposite direction to the π-electron moment, and might reduce the total moment of the molecule considerably below what it would otherwise be. That such " back-polarisation " does in fact occur is strongly suggested by the fact that even in a saturated zwitterion such as betaine the observed dipole moment is less than half what would be expected from the formal charge displacement (Sutton, private communication). Fortunately, however, the absolute values of the terms y_s are not important for the present investigation : it will be seen from equation (3) that multiplication of all of them by a constant factor k merely multiplies the net charges by the same factor k, without altering their ratios.

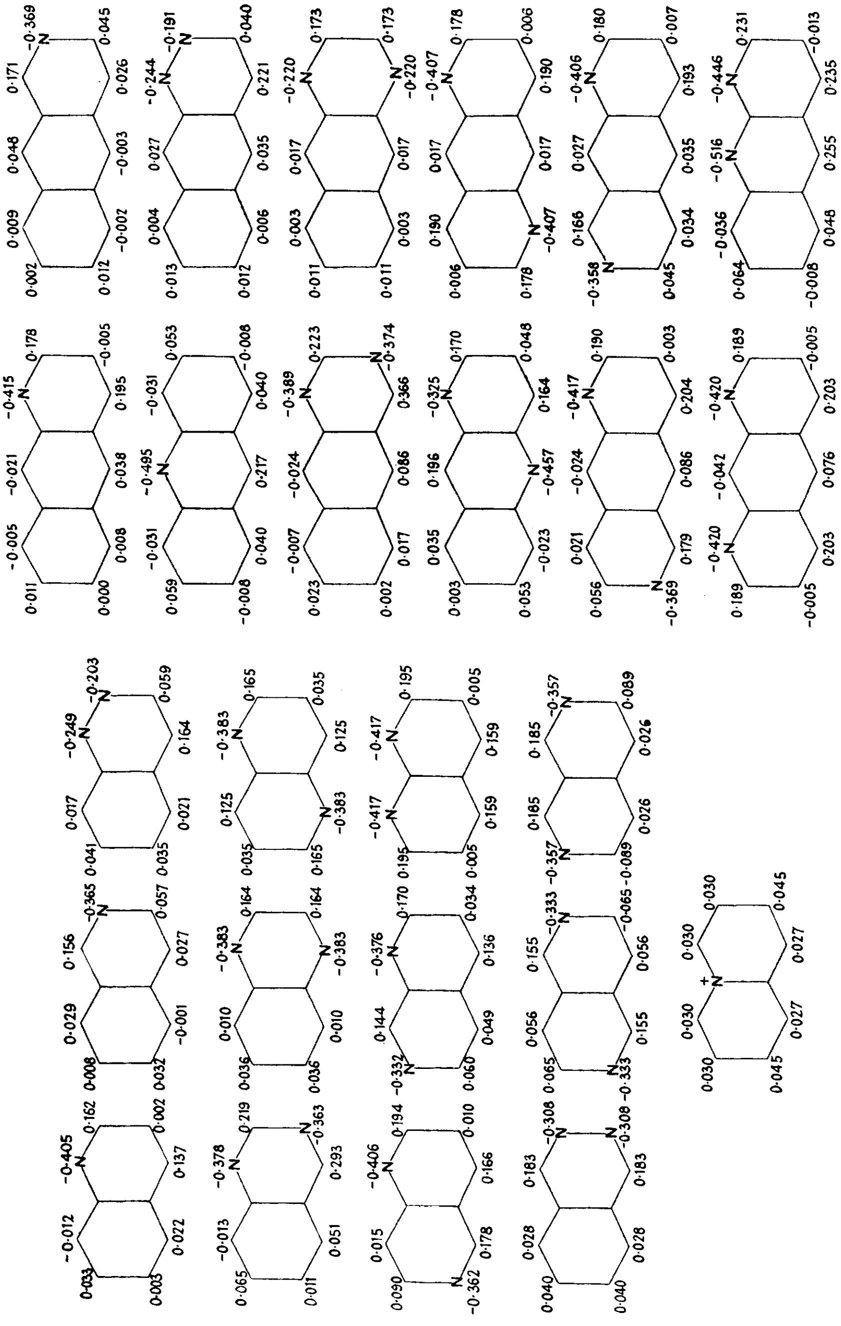
Results.—In calculating the net charges in the monoaza-hydrocarbons it has been assumed that α_N/α' ($= y_N/y'$) is equal to 8; and the net charges are expressed as multiples of y_N; that is to say, the figures given in the following lists would be equal to the net charges if α_N were equal to β, and α' equal to $\beta/8$.

In the diaza-hydrocarbons it has been assumed that the perturbations due to the two nitrogen atoms are additive; this is equivalent to assuming that the terms y_s are in the following ratios :

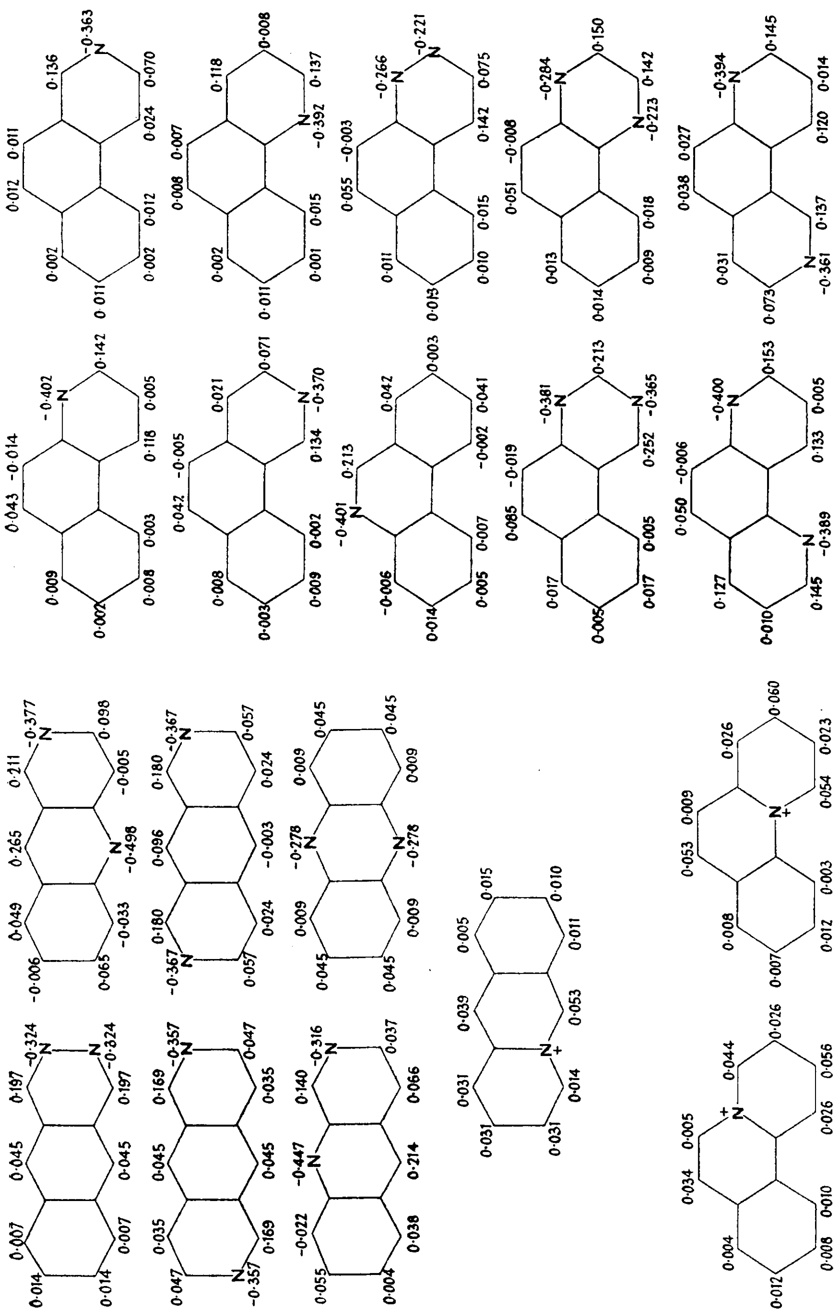
$$y_N : y_N' : y' : y'' = 8 : 9 : 1 : 2$$

where y_N' refers to a nitrogen atom bonded to another nitrogen atom, y' refers to a carbon bonded to one nitrogen, and y'' to a carbon bonded to two nitrogens. This assumption implies that the net charges in a diaza-hydrocarbon should be the sum of the net charges for the corresponding two monoaza-hydrocarbons, which is likely to be true on almost any reasonable hypothesis.

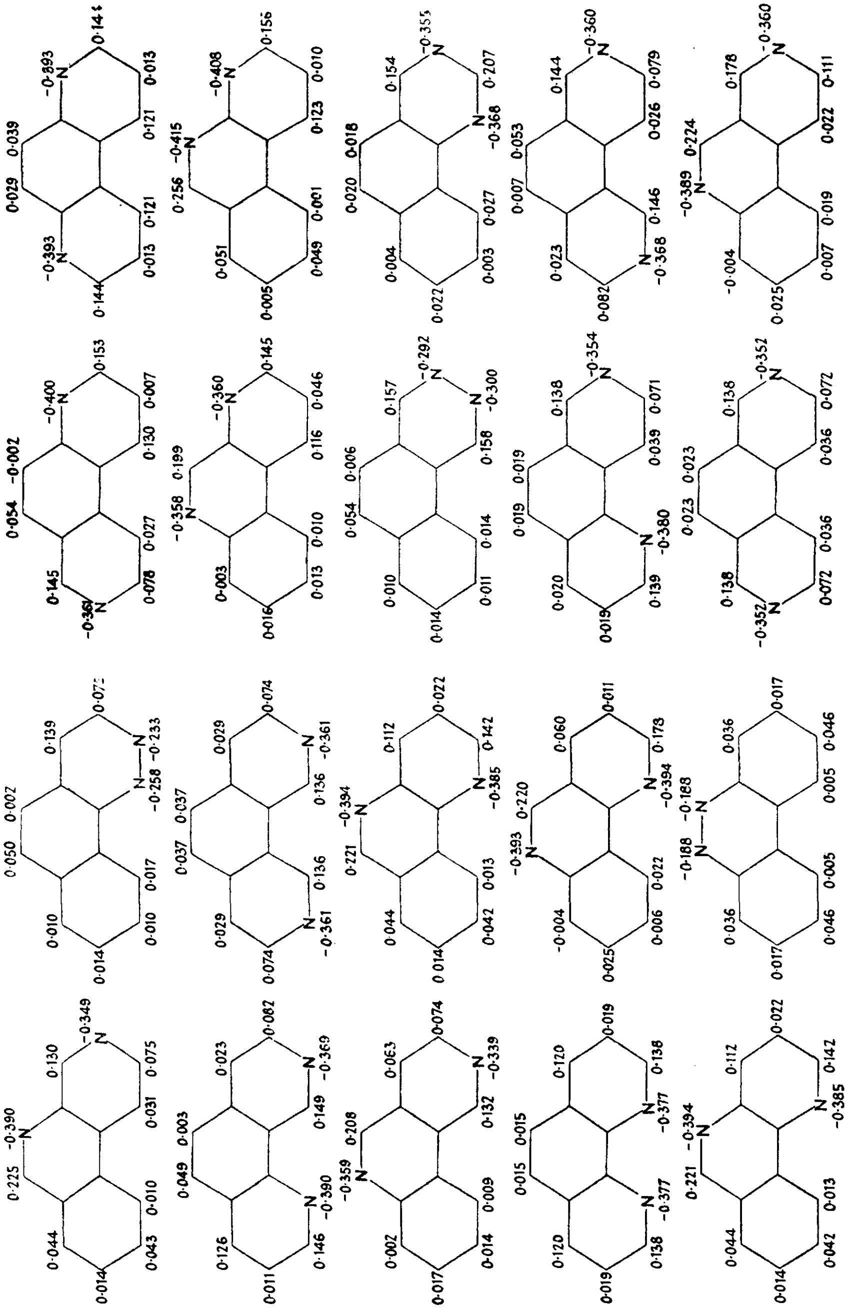
The figures given in the accompanying diagrams are the relative net charges at the external positions of all the mono- and di-aza-naphthalenes, -anthracenes, and -phenanthrenes. For completeness we have included the four cations which arise from replacing the interior carbon



Aza-derivatives of naphthalene and anthracene.



Aza-derivatives of anthracene (contd.) and phenanthrene.



Aza-derivatives of phenanthrene (contd.).

atoms in these molecules by N^+. The relation of these figures to the known chemistry of these molecules is discussed in the next section.

Discussion of Results.—On the assumption that the net charges are of primary importance in determing the substitutive behaviour of a heteroaromatic molecule one would draw the following general conclusions from the accompanying figures : First, that the effects of aza-substitution on an aromatic hydrocarbon die away with distance from the seat of substitution; one would therefore expect considerable chemical resemblances between, say, 1-aza-anthracene on the one hand and quinoline on the other, especially in the reactions of their heterocyclic rings. Secondly, as mentioned earlier, one would expect that the effects of two or more replacements of CH by N should be additive; this is a quite general conclusion following from the assumption that one such replacement has sufficiently small effects to be regarded as a perturbation applied to the hydrocarbon.

Both the above general expectations are verified in practice. An example of the first is the three diazaphenanthrenes obtained by the Skraup reaction on *o*-, *m*-, or *p*-phenylenediamine, which all closely resemble quinoline in their electron distributions and in their chemical properties. An example of the second is the series : naphthalene, 1-aza-, 3-aza-, 1 : 3-diazanaphthalene; along this series the reactivity of the 4-position towards anionoid reagents increases steadily; and other examples of the approximate additivity of substitutive effects could be multiplied indefinitely.

Coming to a more detailed analysis, one finds on the whole that the greater the net charge at a given carbon atom the more reactive is that position to anionoid (nucleophilic) reagents. For example, the 9-position in phenanthridine is particularly sensitive towards anionoid reagents : 9-aminophenanthridine can be prepared by the sodamide reaction in excellent yield. Associated with this is the activity of 9-chlorophenanthridine, which will condense with amines, etc., under only moderately drastic conditions, and the high reactivity of the methyl group at this position, which condenses with aldehydes and is readily oxidised; for instance, oxidation of 1 : 3 : 9-trimethyl-2-azaphenanthridine leads to attack of the 9-methyl group in preference to the others, with separation of an insoluble azaphenanthridone, which thereby escapes further oxidation. All these phenomena are characteristic of positions of low electron density (high net charge), as is the prototropic rearrangement of the corresponding hydroxy-derivative to give a stable molecule of the pyridone type. This prototropic change is characteristic of the 2-hydroxypyridine residue, and occurs in such compounds as *iso*quinoline, etc. Examples of this last are *iso*quinolone, acridone, and cyanuric acid. On the assumption that a position becomes markedly active to electrophilic reagents when the relative net charge there exceeds about 0·2, one may formulate the following rules for the aza-hydrocarbons investigated :

(1) In the derivatives of naphthalene, anthracene, and phenanthrene containing a 1-nitrogen atom, the 2- and 4-positions will show anionoid activity; and in those containing a 2-nitrogen atom the 1-position will be active.

(2) 9-Aza-anthracenes and 9-azaphenanthrenes will show strong anionoid reactivity at their 10-positions.

(3) If the Coulomb integral of the nitrogen atom in an aza-compound is increased by quaternary alkylation, the reactivity of a position of high net charge will be enhanced still further, owing to the proportional increase in this charge.

These rules are, of course, in general agreement with experience.

In substitution by cationoid or by nucleophilic reagents it would be expected that the positions of lowest or of highest net charge, respectively, would be attacked. Unfortunately, not much experimental evidence is available beyond what has already been quoted, but, in general, experiment follows the line indicated by theory. The situation with regard to cationoid substitution is less clear-cut than with anionoid substitution, because in most of the molecules listed the positions of lowest net charge differ only slightly in the values of these charges. This means that any errors in the approximations used will assume greater importance, and also that second-order effects will probably come into play. For example, in 1 : 7-diazanaphthalene, where the lowest net charges are 0·034 and 0·049 at the 3- and the 5-position, respectively, it might easily happen that the 5-position would be more easily nitrated than the 3-position owing to greater ease of polarisation there; for it is known that in naphthalene itself the α-positions have greater self-polarisability than the β-positions. It has been shown that effects of this type become important when differences in electron density are very small, so it would be surprising if there were no discrepancies between theory and experiment as far as cationoid activity is concerned.

There is one discrepancy, which must be pointed out, between the basicities of some of these molecules and the calculated net charges at their nitrogen atoms. According to figures for the relative net charges, one would expect the basic strengths of pyridine, quinoline, and acridine to increase in that order; in fact their $\mathrm{p}K_a$ values in water at 20° are 5·2 (Britton and Williams, *J.*, 1935, 796), 4·8 (Albert, *Nature*, 1944, **153**, 467), and 4·3 (Albert, Rubbo, and Goldacre, *ibid.*, 1941, **147**, 332), respectively. Strictly, of course, one should compare the electron densities with the heats rather than the free energies of ionisation, but it seems unlikely that the entropies of ionisation differ very much between these bases, so the anomaly must be regarded as real. It is possible that the anomaly is connected with the fact that the dipole moments of these bases are in the opposite order to what would be expected from their π-electron distributions; the observed moments are 2·21, 2·14, and 1·95 D., respectively. It seems quite likely therefore that the basic strength of a monoaza-hydrocarbon depends largely on its dipole moment; and if this is so then any error in the calculation of the dipole moment (see earlier) would appear as a corresponding error in the estimated value of the basic strength. There is clearly scope for further investigation of such a relationship.

Added, December 17*th*, 1948.—Since this paper was submitted for publication, a suggestion has come to our notice (Dyatkina, *Doklady Akad. Nauk. U.S.S.R.*, 1948, **59**, 517) that the basic strength of an aza-hydrocarbon depends on the change of resonance integral in the C–N bonds when a proton is attached to the nitrogen atom. In this paper we have assumed that the change in $\mathcal{E}$, the energy of the mobile electrons, upon addition of a proton to the nitrogen atom, depends solely upon the change in α_N, the Coulomb term for the nitrogen atom, according to the equation

$$\delta\mathcal{E} = (\partial\mathcal{E}/\partial\alpha_N)\delta\alpha_N = q_N\delta\alpha_N$$

If this were so, the basic strength of a heterocycle should be greater the greater the value of q_N; and, as already mentioned, this prediction is at variance with the experimental facts. The discrepancy may, however, be resolved by following Dyatkina, and writing

$$\begin{aligned}\delta\mathcal{E} &= \frac{\partial\mathcal{E}}{\partial\alpha_N}\delta\alpha_N + \sum_t \frac{\partial\mathcal{E}}{\partial\beta_{tN}}\delta\beta_{tN} \\ &= q_N\delta\alpha_N + 2\sum_t p_{tN}\delta\beta_{tN}\end{aligned}$$

where t denotes an atom bonded to the nitrogen atom, and p_{tN} is the mobile order of the bond t–N. In this equation q_N equals $1 - Q_N y_N$, where Q_N is the relative net charge on the nitrogen atom, and $y_N = \alpha_N/\beta$. Hence

$$\delta\mathcal{E}/\beta = (1 - Q_N y_N)\delta y_N + 2\sum_t p_{tN}\delta z_{tN}$$

where $\delta y_N = \delta\alpha_N/\beta$ and $\delta z_{tN} = \delta z_{tN} = \delta\beta_{tN}/\beta$.

In this equation δy_N, y_N, δz_{tN}, and p_{tN} are positive quantities, and $\delta\mathcal{E}$, β, Q_N are negative; hence the magnitude of $\delta\mathcal{E}$ (and hence the basic strength of the heterocycle) varies in the same direction as that of the expression

$$-Q_N y_N + 2\sum_t p_{tN}\frac{\delta z_{tN}}{\delta y_{tN}} = D, \text{ say}$$

Values of Q_N are given in the diagrams above, and the mobile bond orders p_{tN} are nearly the same as in the parent hydrocarbons (see Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **192**, 16). One may therefore tabulate values of D for different values of y_N and $\delta z_{tN}/\delta y_{tN}$ as follows:

Data on basic strengths of some heterocycles (see text).

	$-Q_N$.	$2\Sigma p_{tN}$.	D_1.	D_2.	D_3.	D_4.
Pyridine	0·359	2·667	0·359	0·447	0·642	1·405
Quinoline	0·405	2·560	0·405	0·459	0·633	1·361
Acridine	0·495	2·424	0·495	0·490	0·633	1·311

D_1 is the value of D when $y_N = 1{\cdot}0$, $\delta z_{tN}/\delta y_{tN} = 0{\cdot}0$
D_2 ,, ,, ,, $= 0{\cdot}5$, ,, $= 0{\cdot}1$
D_3 ,, ,, ,, $= 0{\cdot}3$, ,, $= 0{\cdot}2$
D_4 ,, ,, ,, $= 0{\cdot}2$,, $= 0{\cdot}5$

Clearly, if $\delta z_{tN} = 0$, the basicity is governed entirely by Q_N, as we originally supposed, and acridine should be more basic than pyridine; but if $\delta z_{tN}/\delta y_{tN}$ is comparable to y_N, the theoretical order of basicity in the above series is reversed, and pyridine should be the most basic, as observed. Unfortunately, as pointed out earlier, there is no independent means of estimating y_N or $\delta z_{tN}/\delta y_{tN}$ at present, so this theory can hardly be claimed to explain the observed basic strengths. However, considerations of this type may account for the breakdown of the very simple approach, since it is not unreasonable to suppose that the change in β_{tN} on addition of a proton is comparable with y_N times the change in α_N.

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BALLIOL COLLEGE, OXFORD.
WHEATSTONE PHYSICS LABORATORY,
KING'S COLLEGE, LONDON.

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