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MOLECULAR ORBITAL TREATMENT OF SOME PYRAZINES

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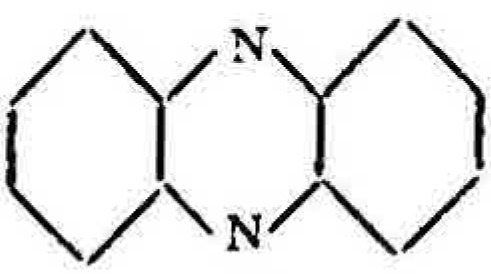
SUMMARY

A molecular orbital treatment of phenazine, dicyclopenta pyrazine and dicyclohepta pyrazine is given. The resonance energies of these molecules, their π-electron density distribution and bond orders have been calculated. The resonance energy value calculated for phenazine by the m.o. method agrees with that experimentally determined. Although dicyclopenta pyrazine and dicyclohepta pyrazine have not yet been chemically prepared the calculated resonance energies are comparable with that of phenazine. In this connection the similarity between these two pyrazines and pentalene and heptalene has been pointed out. The rule postulated by Longuet-Higgins and Coulson (1949) that the net charge in a diaza hydrocarbon should be the sum of the net charges for the corresponding two monoaza hydrocarbons has been confirmed by results obtained by direct solution of the secular determinants in the respective cases.

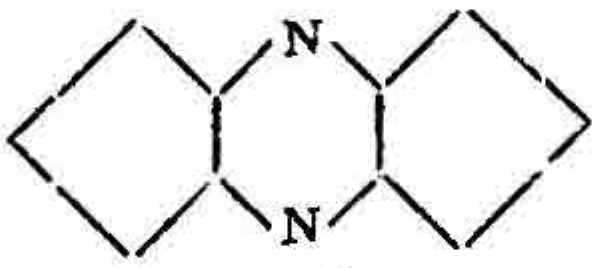
1. INTRODUCTION

For the quantum mechanical study of molecules two methods, namely, the valence bond (V.B.) method and the molecular orbital (m.o.) method are available. In recent years the m.o. method has been widely used for the study of chemical reactivity, resonance energy, spectra and other related topics (Coulson, 1952) (Eyring, Walter and Kimball, 1948). In the present paper the results obtained by the application of the well-known LCAO m.o.

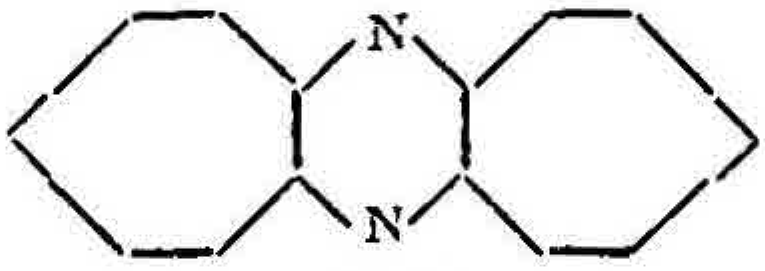
method (Wheland and Pauling, 1935) (Longuet-Higgins and Coulson, 1947) to some pyrazines are presented. The pyrazines dealt with are phenazine (I), dicyclopenta pyrazine (II) and dicyclohepta pyrazine (III). Of these only (I) is known, while (II) and (III) have not yet been prepared chemically and attempts to prepare them have met with failure (Godchot and Mousseron, 1932) (Treibs, 1936). However, the present calculations indicate that these molecules have resonance energies comparable to that of anthracene. The π-electron density distribution and bond orders in these three molecules have also been calculated. The resonance energy calculated for phenazine with reference to one of its kekule structures is almost the same as that previously calculated for anthracene. The experimentally determined resonance energies of phenazine and anthracene substantiate this result (Albert and Willis, 1946). A discussion of the resonance energies, charge distribution and bond orders of these molecules is also given. It is of interest to note here that a treatment similar to the present has been given recently by Crawford (1952) for 2, 3-dinaphthylene which has not yet been chemically prepared.



(I)



(II)



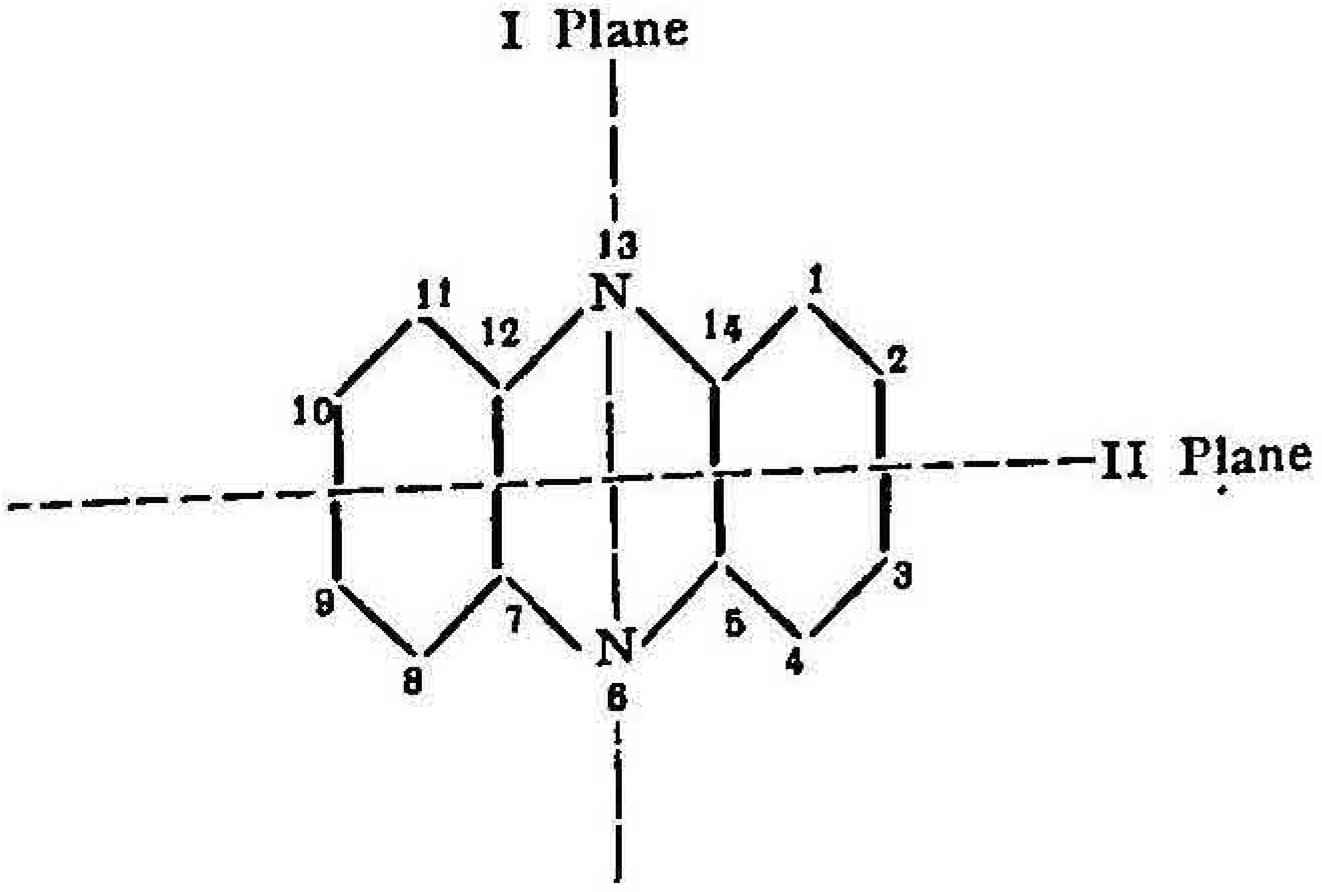
(III)

2. METHOD OF CALCULATION AND CHOICE OF PARAMETERS

The method of calculation has been already outlined by numerous authors that we need not outline it here (refer for example, Wheland and Pauling, 1935; also Coulson, 1952). In the application of the m.o. method we have to make a suitable choice for the values of the parameters α and β, namely, the coulomb integral and the resonance integral respectively. In the present calculations we have taken the value of the resonance integral between any two bonded atoms as equal to β, the resonance integral in benzene. Setting α equal to the coulomb integral of a carbon atom in benzene, Longuet-Higgins and Coulson (1947) have taken the value of α_k as $\alpha + 2\beta$ or $\alpha + 0\cdot25\,\beta$ according as k is a nitrogen atom or a carbon atom bonded to nitrogen. In a later paper (Longuet-Higgins and Coulson, 1949) these authors have arrived at the charge distribution in a number of aza-derivatives of naphthalene, anthracene and phenanthrene using the above parameters. They have, however, remarked that, from dipole moment considerations of pyridine, the value of $\alpha + 2\beta$ for the coulomb integral of nitrogen may be high. Since we are interested in the relative values of the charges in most cases this fact may not be very important. On the other hand, the calculation of resonance energies and especially π-bond moments may be affected seriously by errors in the choice of these parameters. In fact, from a study of the dipole moment of some heterocyclics containing nitrogen Orgel, Cotrell, Dick and Sutton (1951) find that the value of $\alpha_N = \alpha + \beta$ itself is too high. Löwdin (1951) finds that a value of $\alpha_N = \alpha + 0{\cdot}6\,\beta$ gives moment values consistent with experimental data. It may be remarked here that the value of α_N obtained from purely dipole moment considerations may not represent the true value. In the calculation of the total moment of a molecule, the π-bond moment is added vectorially to the σ-bond moment neglecting induced moment effects arising from the π-σ moment interactions. This point has been already brought forth by Longuet-Higgins and Coulson (1949). In view of these facts we have taken here the value of $\alpha_N = \alpha + 2\,\beta$ and the resonance energy value obtained for phenazine using this parameter is almost equal to that of anthracene, this being the experimentally observed fact (Albert and Willis, 1946). The charge distributions obtained may be, however, too large on an absolute scale but this will not affect the arguments regarding chemical reactivity since the relative values alone are to be considered (Coulson, 1952).

3. ILLUSTRATION OF THE METHOD—PHENAZINE

The method of calculation may be illustrated with the case of phenazine. The molecule has been shown to have zero moment (Le Fevre, 1938) and from an analogy with the corresponding hydrocarbon anthracene we may assume the molecule to be planar. In fact, all the three structures, I, II and III of Fig. 1 are assumed to be planar in these calculations. We treat the molecule of phenazine as a system of fourteen π-electrons. The secular determinant will therefore have fourteen rows and fourteen columns but we can make use of symmetry properties to reduce it to determinants of lower order. As shown in Fig. 2 we have two planes of symmetry and the molecular orbitals may be classified into four symmetry groups, *aa*, *as*, *sa* and *ss* according as they are antisymmetric or symmetric with regard to reflection in the I or II symmetry plane.



Thus we have the m.o.'s

$$\psi\,(aa):\ C_1\,[(\phi_2-\phi_{10})-(\phi_3-\phi_9)]+C_2\,[(\phi_1-\phi_{11})-(\phi_4-\phi_8)] \\ +C_3\,[(\phi_{14}-\phi_{12})-(\phi_5-\phi_7)]$$

$$\psi\,(as):\ C_1'\,[(\phi_2-\phi_{10})+(\phi_3-\phi_9)]+C_2'\,[(\phi_1-\phi_{11})+(\phi_4-\phi_8)] \\ +C_3'\,[(\phi_{14}-\phi_{12})+(\phi_5-\phi_7)]$$

$$\psi\,(sa):\ C_1''\,[(\phi_2+\phi_{10})-(\phi_3+\phi_9)]+C_2''\,[(\phi_1+\phi_{11})-(\phi_4+\phi_8)] \\ +C_3''\,[(\phi_{14}+\phi_{12})-(\phi_5+\phi_7)]+C_4''\,[(\phi_{13}-\phi_6)]$$

$$\psi\,(ss):\ C_1'''\,[(\phi_2+\phi_{10})+(\phi_3+\phi_9)]+C_2'''\,[(\phi_1+\phi_{11})+(\phi_4+\phi_8)] \\ +C_3'''\,[(\phi_{14}+\phi_{12})+(\phi_5+\phi_7)]+C_4'''\,[(\phi_{13}+\phi_6)].$$

The secular determinant therefore factorizes into two three row and two four row determianants from which the values of C_k's are obtained after finding out the lowest roots by the usual methods (Eyring, Walter and Kimball, 1948). In the present calculations the roots of the determinants have been obtained by the use of Graeffe's method with subsequent application of the Newton-Raphson method (Morgenau and Murphy, 1948). The seven lowest roots thus obtained in the case of phenazine are given below. The values are for $y\left(=\frac{\alpha-E}{\beta}\right)$.

$-\ 3\cdot23223\ (ss)$

$-\ 2\cdot62511\ (sa)$

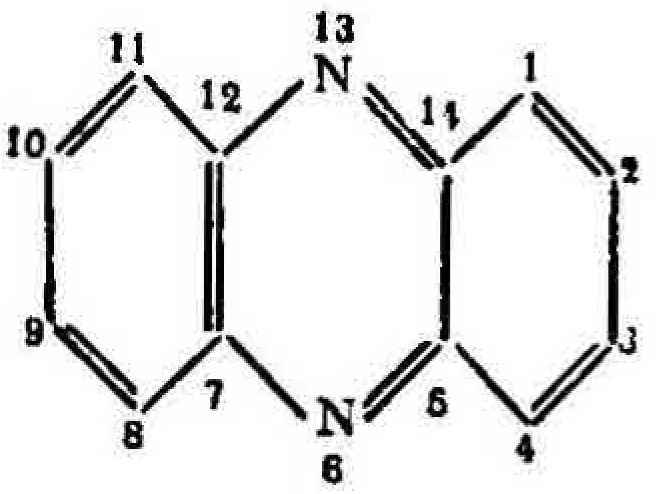
$-\ 1\cdot66376\ (ss)$

$-\ 1\cdot11632\ (as)$

$-\ 1\cdot04571\ (aa)$

$-\ 0\cdot82932\ (sa)$

These values of y correspond to the seven occupied m.o.'s of lowest energy in phenazine. From these roots of the secular equation the charge distribution and bond orders can be calculated by evaluation of the coefficients C_k's and normalization of each m.o. For the calculation of the resonance energy we find the total π-electron energy of the system and compare it with that for the kekule structure. For this purpose another secular determinant is set up for the kekule structure postulated and the energy of this structure calculated from the lowest roots obtained. In the case of phenazine we have calculated the π-electron energy for the structure (IV) given below and the value thus obtained is $14\alpha+19\cdot90754\,\beta$ as compared to the total π-electron energy of $14\,\alpha+25\cdot21594\,\beta$.



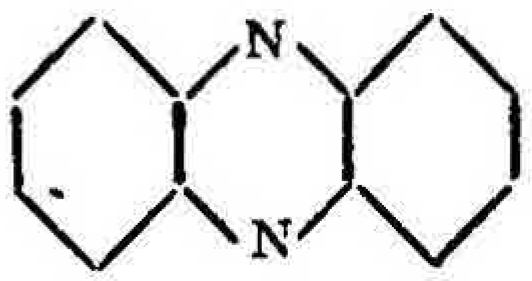
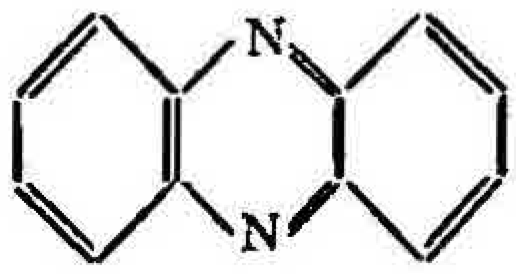
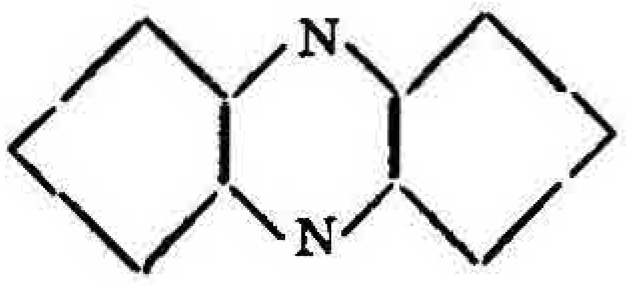
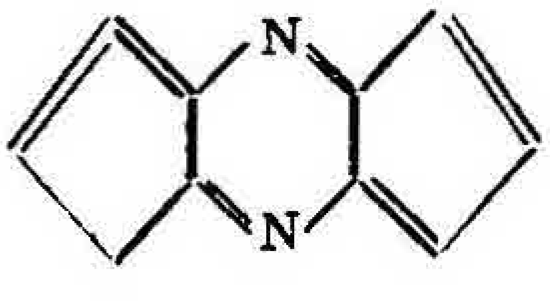
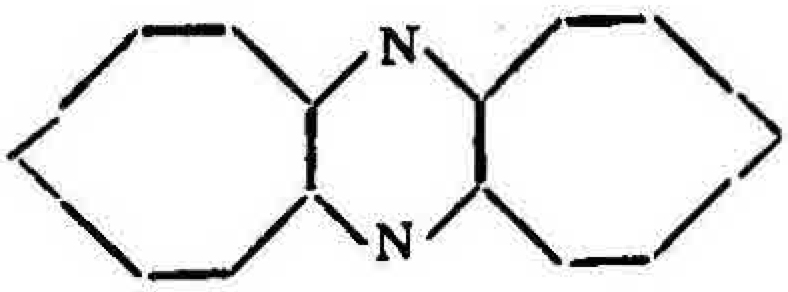
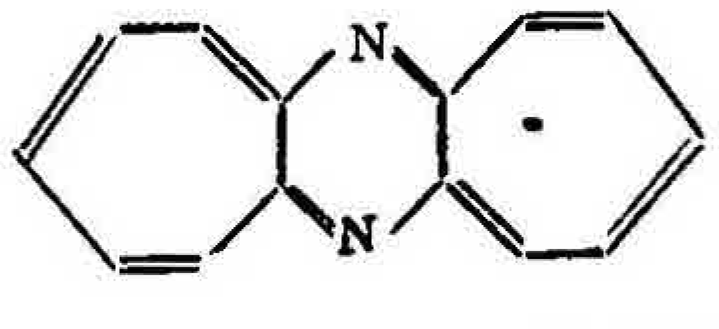
(IV)

The difference, which is the resonance energy of phenazine, is therefore $5 \cdot 3084\,\beta$.

4. RESULTS

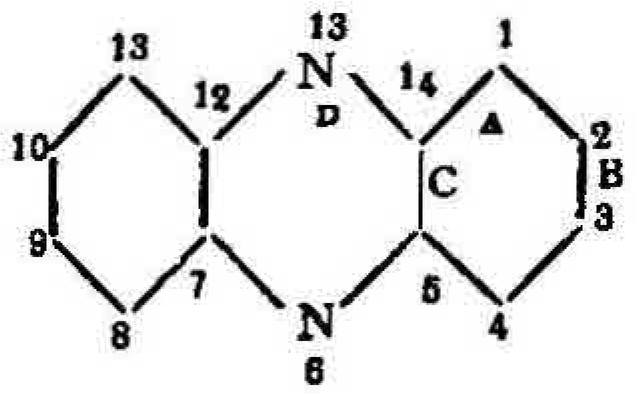
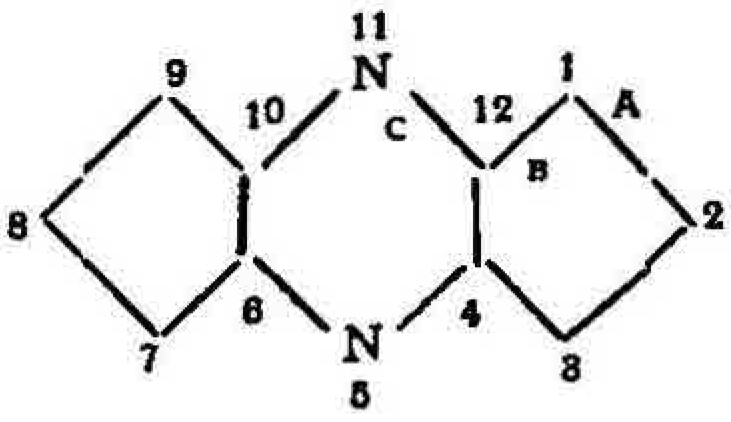
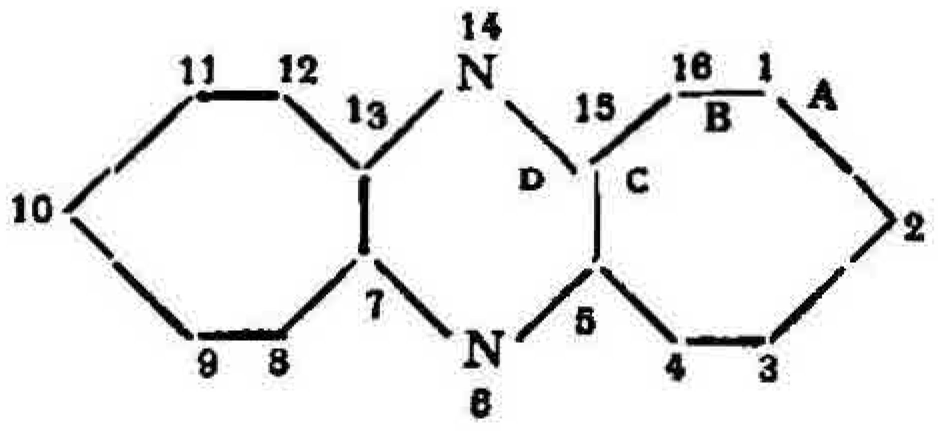
The results obtained by the application of the m.o. method.are given here for the three molecules dealt with.

TABLE I

Substance	Total π-electron energy	Energy of kekule structure	Resonance energy (in terms of β, the resonance integral)
1. Phenazine	 $14\alpha + 25 \cdot 21594\,\beta$	 $14\alpha + 19 \cdot 90754\,\beta$	$5 \cdot 3084\,\beta$
2. Dicyclopenta Pyrazine	 $12\alpha + 20 \cdot 09666\,\beta$	 $12\alpha + 15 \cdot 26556\,\beta$	$4 \cdot 8311\,\beta$
3. Dicyclohepta Pyrazine	 $16\alpha + 25 \cdot 53014\,\beta$	 $16\alpha + 19 \cdot 93866\,\beta$	$5 \cdot 59148\,\beta$

In the following table we give the π-electron distribution and mobile bond orders for the three molecules under consideration. The charge distribution is given as the net charge on each atom. In other words, the values given are $1-q_k$, where q_k is the total π-electron charge on atom k ($q_k = 2\Sigma C_k{}^2$). The mobile bond order p_{mn} between atoms m and n is then given by (Coulson, 1939) $p_{mn} = 2\Sigma\, C_m C_n$. Here, the C's are the coefficients in the secular equation.

TABLE II

Phenazine	Dicyclopenta Pyrazine	Dicyclohepta Pyrazine
		

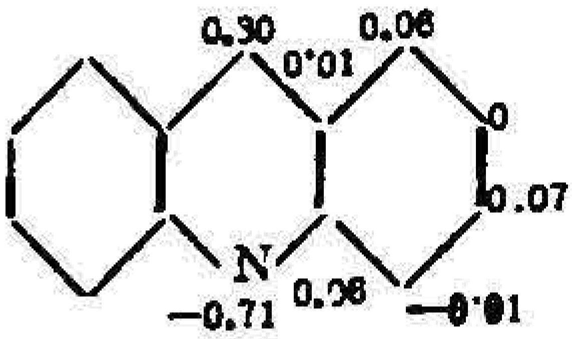
Atom	Net Charge	Atom	Net Charge	Atom	Net Charge
1, 4, 8 & 11	0·03	1, 3, 7 & 9	0	1, 3, 9 & 11	0·13
2, 3, 9 & 10	0·07	4, 6, 10 & 12	0·06	4, 8, 12 & 16	0·07
5, 7, 12 & 14	0·13	2 & 8	0·33	5, 7, 13 & 15	0·02
6 & 13	−0·48	5 & 11	−0·46	2 & 10	0·17
				6 & 14	−0·60

Bond	Bond Order	Bond	Bond Order	Bond	Bond Order
A	1·692	A	1·666	A	1·516
B	1·465	B	1·417	B	1·627
C	1·547	C	1·303	C	1·660
D	1·398			D	1·360

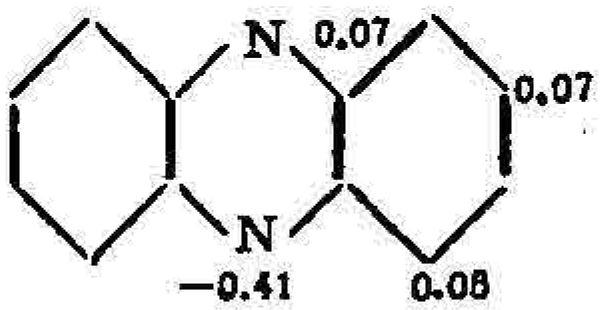
5. DISCUSSION OF RESULTS

The resonance energy of a molecule is in a sense a measure of its stability (Pauling, 1939). Various methods have been outlined by Pauling (*loc. cit.*) for the determination of the resonance energy and thermo-chemical studies have been of the greatest use in this direction. The m.o. method has been already shown to give consistent values of the resonance energy in terms of the resonance integral β (Wheland, 1934). A value of $\beta = 20\,k$. cal./mole brings quantitative agreement between thermo-chemical data and the m.o. results. Using this value we find the resonance energy of phenazine ($5\cdot3084\,\beta$) as $106\cdot2\,k$.cal./mole. The resonance energy of anthracene will also be of the same magnitude since the m.o. resonance energies do not differ much. It is of great interest to note here that a value of $105\,k$.cal./mole was obtained experimentally by Albert and Willis (1946) for the resonance energy of phenazine (refer also Willis, 1947). These authors have also established a value of $105\,k$. cal./mole for the resonance energy of anthracene. Thus the resonance energy values obtained by the m.o. treatment are seen to be in excellent agreement with experimental data in the case of phenazine. Having convinced ourselves of the validity of the m.o. results we shall now compare the resonance energies of dicyclopenta pyrazine and dicyclohepta pyrazine with that of phenazine. Using the value of $\beta = 20\,k$.cal./mole the values are:— dicyclopenta pyrazine $= 96\cdot6\,k$.cal./mole; dicyclohepta pyrazine $= 111\cdot8\,k$.cal./mole. Expressed per π-electron the resonance energies in the case of dicyclopenta pyrazine and dicyclohepta pyrazine are respectively, $0\cdot4026\,\beta$ and $0\cdot3495\,\beta$ as compared to $0\cdot3792\,\beta$ for phenazine. These values indicate that from the resonance energy point of view these molecules should be stable. However, in view of recent work on the non-benzenoid aromatic hydrocarbons pentalene and heptalene some remarks regarding these pyrazines may not be out of place. Coulson and Rushbrook (1940) have found that the m.o. treatment of pentalene is inconsistent in that the π-electrons are not uniformly distributed over the carbon atoms but tend to accumulate at certain points at the expense of others. Craig and Maccoll (1949) who have made a study of pentalene by both valence bond (V.B.) and m.o. methods find that while on both views a considerable resonance energy is associated with the molecule, the V.B. method shows that this will be the case only in a state which lacks full symmetry of the carbon framework. The same remark applies also to heptalene. It is therefore probable that these findings regarding pentalene and heptalene are applicable not only to the pyrazines mentioned here but also to their corresponding hydrocarbons.

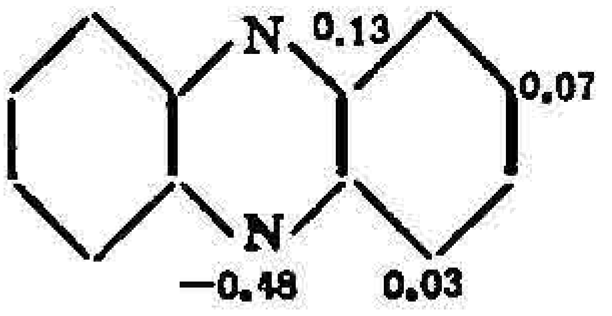
The charge distribution for phenazine has been previously obtained by Longuet-Higgins and Coulson (1949) by the use of the perturbation method originally outlined and applied by Wheland and Pauling (1935) in a quantum mechanical discussion of the orientation of substituents in aromatic compounds. It is generally accepted that the perturbation method is in principle less accurate than the direct solution of the secular determinant. However, our interest being centred around the relative distribution of charges, we may note that the results of charge distribution obtained here in the case of phenazine are in substantial agreement with those given by Longuet-Higgins and Coulson. These authors have also stated that the net charges in the diaza hydrocarbon should be the sum of the net charges for the corresponding two mono aza hydrocarbons. This means that the net charge, for example, in phenazine should be that obtained by the proper superposing of two molecules of acridine. The molecular diagrams given below illustrate this point clearly, the net charge values being those obtained by the direct solution of the secular determinants (for acridine refer Longuet-Higgins and Coulson, 1947).



Acridine (M.O.)



Phenazine (L.H. and C.)



Phenazine (M.O.)

The validity of the above mentioned rule is thus seen to be good. The bond orders obtained for dicyclopenta pyrazine resemble very closely those of pentalene. Regarding chemical reactivity in these molecules the following general observations may be made. The greater the net charge at a given carbon atom the greater will be its reactivity to anionoid reagents and the converse will be the case with regard to cationoid reagents. In phenazine, positions of anionoid reactivity will be atoms 2, 3, 9 and 10 (see Table II for numbering) and experimental observations confirm this. From the charge distributions in the case of dicyclopenta pyrazine and dicyclohepta pyrazine similar deductions may be made but the experimental evidence is as yet scanty.

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