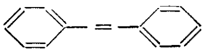
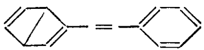
421. *Charge Distribution and Bond Orders in Aminostilbene and Related Molecules.*

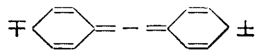
By C. A. Coulson and (Miss) J. Jacobs.

Calculations are reported, using the method of molecular orbitals, of the charge distribution and the bond orders in aminostilbene and some related molecules. These calculations relate both to the ground state of the molecule and to its first-excited state. They show the expected alternating character of the equilibrium charge distribution, and the results are interpreted in terms of the particular valence-bond structures (Kekulé, first-excited, ionic) which appear to be most important. The effect of one amino-group in one ring does not extend appreciably into the other ring.

When using the standard representation of a molecule in terms of resonance structures (*e.g.*, Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, 1940) it is usual to introduce unexcited (*i.e.*, Kekulé) structures, first-excited structures, and ionic structures. More excited structures are generally assumed to be negligible. For example, stilbene would conventionally be represented as a resonance hybrid of structures such as (I)—(III). In the lowest molecular energy level which is reached by absorption of light from the ground level, it has usually been supposed that the ionic structures (III) are fairly important; in classical language this corresponds to an electron oscillating from one end of the molecule to the other and hence being responsible for the intense absorption. In principle, such a description of the molecule is quite

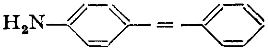

(I; Kekulé.)

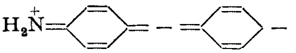

(II; first-excited.)


(III; ionic.)

proper; but in practice it suffers from the considerable drawback that there seems at present no satisfactory way of calculating the relative weights of the various types of structure. The situation is even less satisfactory in substituted and heterocyclic molecules. Thus in 4-aminostilbene, in addition to the Kekulé structures (IV), we expect ionic structures such as (V), which are similar to (III) except that the charge on the amino-nitrogen can only be positive. But there is no available estimate of the relative weights of (IV) and (V), though that of (V) in the substituted compound is usually supposed to exceed that of (III) in the unsubstituted. A summary of some evidence is given by Branch and Calvin (" Theory of Organic Chemistry," Prentice-Hall, 1941). In the excited level nothing whatever is known of the weights. Now this molecule and its derivatives have very important biological functions in carcinogenesis (Haddow, Harris, Kon, and Roe, *Phil. Trans.*, 1948, *A*, **241**, 147) which may depend on the charge distribution. For this reason, and because of our ignorance about the relative weights of structures such as those referred to earlier, we have thought it worth while to calculate the charge distribution and bond orders in this and some related molecules, using the method of molecular orbitals. In this method no specific reference is made to any constituent structures such as (IV) or (V), but the results of our calculations allow us to infer which structures are important and which are not, and to estimate approximately their weights. Our calculations are concerned both with the ground level of the molecule and with the first-excited level, as they are described by the method of molecular orbitals. There is no reason to suppose that these molecules are essentially different from other substituted systems of chain type, so that we may expect that the type of answer found for the systems studied in this paper will be found equally in others.

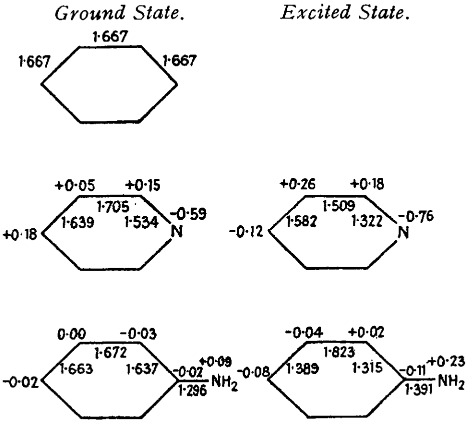
(IV.)





(V.)

FIG. 1.



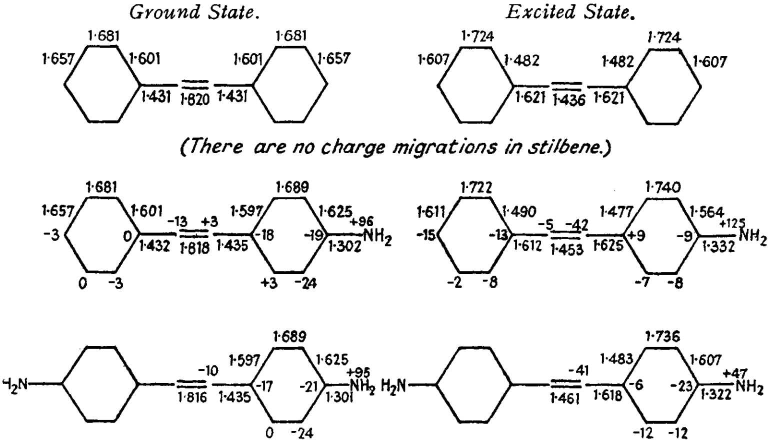
Bond orders and charge migrations in benzene, pyridine, and aniline. The bond orders are shown along the various bonds. The figures at the atoms denote the charge distribution, measured in fractions of an electron, relative to a neutral atom; e.g., *in the ground state of aniline, the nitrogen atom is deficient in electrons to the extent of* 0·09e *and therefore carries a net charge* + 0·09e.

The significance of bond orders in this connection may be seen from the particular example of 4-aminostilbene. If structures such as (V) are important, then not only should there be a negative charge on the 4′-carbon atom, but the two benzene rings should have considerable quinonoid character. This will be revealed by the bond orders : for if the six bonds in these rings have substantially equal orders, we can treat the rings as aromatic, but if the orders of bonds 2–3 and 2′–3′ are higher than the others, the rings are essentially quinonoid.

In making our calculations we have used quite standard technique, which need not therefore be described. It is precisely the same as that used by Longuet-Higgins and Coulson (*Trans. Faraday Soc.*, 1947, **43**, 87) and originally introduced by Wheland and Pauling (*J. Amer. Chem. Soc.*, 1935, **57**, 2086) : that is to say, we calculate solely the motion of the π electrons, and we assume (i) that all resonance integrals β, whether between carbon and carbon, or carbon and nitrogen, are equal, (ii) that all overlap integrals S may be neglected, (iii) that the Coulomb integral α_N for a nitrogen is related to α_C for a carbon by the equation $\alpha_N = \alpha_C + 2\beta$, and (iv) that for a carbon atom C′ adjacent to a nitrogen $\alpha_{C'} = \alpha_C + \frac{1}{4}\beta$. It is very probable (Longuet-Higgins and Coulson, this vol., p. 971) that the values 2β and $\frac{1}{4}\beta$ used above are too great, perhaps by as much as a factor of 2 or 3, though, as Wheland has shown (*J. Amer. Chem. Soc.*, 1941, **63**, 2025), their ratio cannot differ greatly from that quoted. Fortunately (Longuet-Higgins and Coulson, *loc. cit.*), the precise values of these differences between α_N, $\alpha_{C'}$, and α_C are not very important, since the charge shifts are practically proportional to the differences of Coulomb integral and will therefore be correctly described in relative order. A similar correct relative sequence may be expected for the bond orders. Thus, when interpreting the charge migration in Figs. 1 and 2, it is safest to treat them as determining relative, rather than absolute, values. Similarly, the differences between the bond orders shown and the aromatic value 1·667 found for benzene, are likely to be more reliable relatively than absolutely.

Our calculations fall into two groups: (i) the simple series, benzene, pyridine, and aniline; (ii) the larger molecules stilbene, and 4-amino- and 4 : 4′-diamino-stilbene. The results are all shown in Figs. 1 and 2. We have omitted the excited level of benzene from Fig. 1 because, on account of the extremely high symmetry of this molecule, degeneracies appear in the electronic energy levels of a type quite distinct from those found in any of the other molecules. Also, in the case of aniline, the method of molecular orbitals predicts two allowed transitions with approximately equal energies. These transitions are of quite different types; we have therefore chosen that one which appears to us the more plausible and corresponds the more nearly with the transition in the stilbene group, where this ambiguity does not appear. The values in the ground levels of group (i) molecules have already been published (Wheland and Pauling, *loc. cit.*; Longuet-Higgins and Coulson, *loc. cit.*) but are repeated for comparison. All other values in Figs. 1 and 2 are new.

FIG. 2.

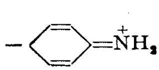


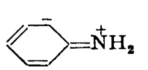
(There are no charge migrations in stilbene.)

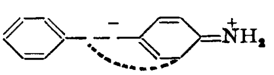
Bond orders and charge migrations in stilbene, 4-aminostilbene, and 4 : 4′-diaminostilbene. Positions not labelled may be found by symmetry. The net charges on the atoms are shown in units of **e**/1000.

These figures are almost self-explanatory. But in Fig. 1 we notice the essential difference between molecules with the nitrogen atom as part of the ring or as substituent in it. The ground level of aniline is more nearly aromatic (all bond orders = 1·667) than that of pyridine; but on excitation aniline assumes a distinctly quinonoid character, showing the importance of structures such as (VI). Since the charge on the *p*-carbon atom is now twice as great as that on the *o*- or *m*-carbons, we see that (VI) is more important than (VII). The greater importance of both (VI) and (VII) in the excited than in the ground level is revealed by the fact that the $>C{=}\overset{+}{N}H_2$ bond order increases appreciably on excitation. In pyridine, however, all the bond orders decrease on excitation, and the small amount of quinonoid character present in the ground state is completely removed. In aniline, excitation results in a migration of charge from the nitrogen : in pyridine the migration is on to the nitrogen. It is almost certain that our calculations have exaggerated these effects, so that, for example, excited pyridine is not so polar a molecule as Fig. 1 would suggest. Indeed, comparison of our predicted resonance dipole moments with those inferred from the observed total molecular moment suggests that, in both groups of molecule dealt with here, our calculated charge displacements are about twice too large. But there can be no doubt about the essential difference between these two molecules.

One or two points in Fig. 2 are noteworthy. In all these molecules the excitation appears to reside almost entirely in the central ethylene link, converting — = — into = — =. This appears to be almost unaffected by the presence either of one or of two *p*-amino-substituents.


(VI.)

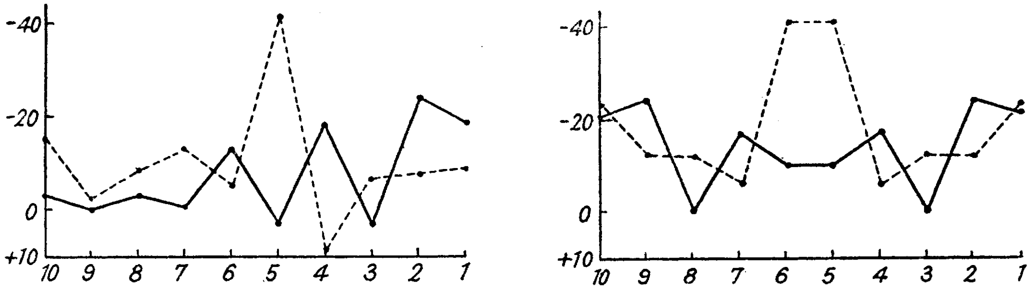

(VII.)


(VIII.)

In the ground state of stilbene there is a little—but only a little—quinonoid character of the kind represented in (III), so we are led to believe that these particular structures are not very important. Conclusions similar to this have already been obtained by B. Pullman (*Bull. Soc. chim.*, 1948, **15**, 533) on other grounds, and may therefore be said now to be quite definite. On excitation there is rather more quinonoid character, and in the amino-compounds the quinonoid character of the substituted ring is greater still. This indicates the importance of structures such as (V) and also (VIII). The apparently great importance of (VIII) in the excited state is quite unexpected, but it seems inevitable if we are to interpret our molecular orbital calculations in terms of structures of the conventional kind.

It will also be noticed that the two amino-groups are practically independent of each other. Thus the charge migrations in the 4 : 4′-compound are very little different from a superposition of the migrations in the 4- and the 4′-compound separately.

FIG. 3.



(a) 4-*Aminostilbene.* (b) 4 : 4′-*Diaminostilbene.*

Charge distribution in the ground and excited states. The atoms are here numbered for convenience along the chain consecutively from the NH_2; *thus* 5 *and* 6 *are the atoms of the central ethylene link. The unit of charge is* e/1000.

In the ground state the perturbation introduced by a single amino-group is hardly noticeable in the unsubstituted ring. Similar conclusions have been reached by Mme. A. Pullman (*Compt. rend.*, 1948, **226**, 486), who has published a charge and bond-order diagram for the ground state of aminostilbene, using the method of resonance among valence-bond structures. Her diagram agrees with our own as closely as the differences between the two methods would be expected to allow. The chief distinction between the two diagrams is in the scale of the charge migrations; Mme. Pullman's are about 2—3 times as large as ours. As we believe that our migrations are probably too large, hers should *a fortiori* be larger; but the relative values correspond well.

The last point which we wish to make refers to the alternating character of the charge migrations in the two aminostilbenes. It has been shown quite generally by Coulson and Longuet-Higgins (*Proc. Roy. Soc.*, 1947, *A*, **192**, 16) that the effect of a substituent in the ground state of an aromatic or conjugated system is to increase or decrease the net charge on consecutive atoms in an alternating manner. This is particularly well illustrated in these aminostilbenes. Fig. 3 shows this alternating effect, and it also exhibits the decreasing influence of the substituent as we move away from the point of substitution. It appears that electronic excitation of the molecule to some extent destroys these alternations, though it increases the average charge migration. Quite apart from any other considerations, this would imply a greater reactivity than in the ground state. Thus the general picture of electronic excitation presented by Figs. 2 and 3 is that of an increased asymmetry of charge, resulting in reduced bonding and a greater proportion of the π electrons free to initiate reactions, particularly with electrophilic reagents.

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