110. *Note on the Theory of Aromatic Substituents and Rearrangements with Special Reference to the Benzidine Change.*

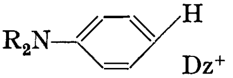
By E. D. Hughes and C. K. Ingold.

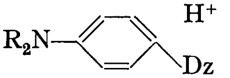
The views previously expressed by Ingold and Ingold with regard to the distinction between the electron displacements involved in the orientation of aromatic substitution and their sequel in the substitution itself are explicitly modified. The nature of the modification, which depends on the recognition of the quantal nature of mesomerism, is illustrated by reference especially to the benzidine change.

In their paper of 1926 (J., 1310) on the theory of aromatic substitution, Ingold and Ingold distinguished between what they called the " directive process," in which small electron displacements involving the unsaturation electrons of the aromatic ring confer special reactivity on certain positions, and the " subsequent change," in which the covalency rearrangement of the substitution is accomplished locally, without requiring a more extensive disturbance to the benzenoid character of the ring. This was their way of providing theoretically that the disturbance to aromatic character should be small in comparison with a covalency displacement : to the assumption of disturbances equivalent to the production in general of definite quinonoid intermediate products there were evident strong objections.

Robinson has recently emphasised a similar point in relation to his theory of oscillatory electron displacements (this vol., p. 220). In doing so he referred to the suggestion of Ingold and Ingold, who accordingly feel that they ought before now to have explained that they changed their point of view some time ago. The modification was, however, implicit in a theory published in 1929—1933 (Burton and Ingold, *Proc. Leeds Phil. Soc.*, 1929, **1**, 421; Ingold, J., 1933, 1120; cf. also *Chem. Rev.*, 1934, **15**, 225, and *Trans. Faraday Soc.*, 1934, **30**, 52), and was believed to be sufficiently emphasised by the altered basis of the numerous discussions of reaction mechanism published subsequently to that period. It would seem, however, that a clearer statement is desirable.[*]

Essentially the alteration of view consists in this, that, with the recognition of the quantal nature of mesomerism, theories which involve what we may call the ***chronology*** of electron displacements (those which specify a succession of electron displacements in an identical nuclear framework) become superseded. As example, consider a *p*-substitution by a diazonium ion orientated by a dialkylamino-group. The rate of reaction, and therefore the orientation which is a function of this and other rates, will depend on the probability and energy of the transition state. For fixed nuclear positions in this state, the electron distribution can be described in terms of the wave functions of certain structures.[†] In the absence of an orienting effect the structures necessary for an approximate description would be (I) and (II). What the orienting effect does (in the same approximation) is to add structure (III), thereby decreasing the energy of the transition state and facilitating the substitution,[‡] both absolutely and relatively to other possible reactions. Since (III) does not represent a formed compound, but only a structure required for the description of a state according to a recognised quantal method, there is no chemical objection to its inclusion.


(I.)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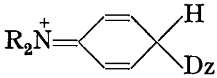
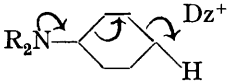

(III.)

From this point of view then it is not useful to try to specify from where immediately the electrons come which bind the diazonium ion at successive moments during the determinative period of the substitution; for indeed, it is the added uncertainty, created by the orienting effect, about where they might come from, which, according to the uncertainty principle, results in the loss of energy (electronic zero-point energy) on which the kinetic and chemical manifestations depend. As Burton and Ingold pointed out (*loc. cit.*), two or more converging (or diverging) electron displacements, in our example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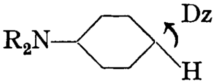
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may for given nuclear positions be effectively simultaneous without violating the octet principle, and must be so regarded in order to secure that spreading of the electron distribution which is the source of the energy changes. Thus from our point of view " chronological " theories disappear, and it is noteworthy that, although at an earlier period many authors used them, often with elaborately adorned formulæ in illustration, these have to a large extent dropped out from recent literature with advantage (as we think) in simplicity and consistency.[§]

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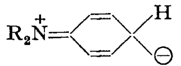
[*] For a short time Ingold and Ingold envisaged activation in meta-substitution; however, this idea was quite explicitly modified in 1927 when the general relationship between orientation and activation was elucidated (Ingold and Shaw, J., 1927, 2918. Cf. also Ingold, Lapworth, Rothstein, and Ward, J., 1931, 1959; Ingold and Smith, J., 1938, 905; Bird and Ingold, *ibid.*, p. 918; Benford and Ingold, *ibid.*, p. 929; Ri and Eyring, *J. Chem. Physics*, 1940, **8**, 433).

[†] Sets of Kekulé and Dewar benzene structures will for brevity be represented by single structures.

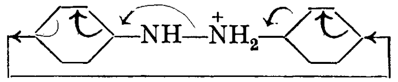
[‡] It is true that the initial state also has a contributing structure of the quinonoid type (III*a*); but because of the absence of a second bond-forming atomic nucleus near the para-carbon atom, this comparatively unstable structure will modify the initial state much less than structure (III) modifies the transition state. We have here the quantal equivalent of what has long been recognised, *viz.*, that orientation by the tautomeric electron displacement is essentially a polarisability effect (Ingold and Shaw, *loc. cit.*). In the text we make the simplification of neglecting the minor effect on the initial state in comparison with the major and determinative one on the transition state.

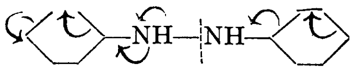

(III*a*.)

[§] We ought perhaps to point out the distinction between chronology in the time-scale of electronic motions (to which the text refers) and chronology in the much coarser time-scale of nuclear motions. In the usual theory of adiabatic reactions the nuclei are considered to move classically on a potential surface, and if we say that the electrons keep pace with them (chronology in the time-scale of nuclear

A particularly good example of this simplification is the benzidine rearrangement. This has been discussed by Ingold (*Rec. Trav. chim.*, 1929, **48**, 797; cf. Ingold and Kidd, J., 1933, 984) who assumed an ionic fission of the NN-bond, activated for heterolysis * by fluctuations in the local protonic environment. It has most recently been discussed by Robinson (*loc. cit.*), who arrived at the expression (IV), which he mistakenly attributed to Ingold and Kidd, perhaps through lack of clarity on their part. Their actual representation was (V), which differs from (IV) by a combined proton—a not unimportant difference having regard to the difficulty of the idea of electron recession from an ammonium pole. Formula (V) means that the heterolysis takes place in the formally neutral molecule, and not in its fully formed cation, although the acid catalysis shows that one or more adding protons are present in the transition state of the rearrangement. On this view then, covalently bound protons first enter into the representations of the change in certain split structures which form important components in the quantal description of the transition state, *e.g.*, (VI)

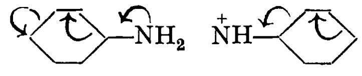
(IV.)





(V.)

(VI.)



(read without the arrows). In such a system the covalency displacements (arrows) needed to produce those other split structures which represent the development of the appropriate form of para-reactivity can be assumed without coming into conflict with any of the usual conceptions.

We may collect these points as follows: (*a*) A nearby proton (at least one) disturbs the electronic system of the benzidine molecule; (*b*) therefore this proton (at least) is present in the transition state; that is to say, its co-ordinates enter into the specification of the state; (*c*) but its covalent bonding with nitrogen does not precede the NN-heterolysis; (*d*) and, accordingly, when the transition state is described in terms of canonical structures, the proton will enter into each, but will appear covalently bound only in those structures in which the NN-bond is split. (*e*) Therefore if the test question is put " Does the para-reactivity arise in the neutral hydrazobenzene molecule or in the positive ion of its salts? ", our answer would be: " Neither; it arises in *a partly formed* ion (see VI); which moreover, even if fully formed, would not be the cation of a salt of hydrazobenzene, because it would contain one bond too few."

A powerful argument against homolysis of the NN-bond (fission into neutral parts) is that the benzidine change does not occur under conditions in which this form of dissociation is known to be considerable (Taylor and Baker, " Sidgwick's Organic Chemistry of Nitrogen," p. 386). Apart from such special reasons, it is always a safe assumption that an acid-catalysed reaction, since it involves proton transfers, must in general involve heterolysis rather than homolysis. Heterolysis being assumed, the question to which Ingold and Kidd addressed themselves was whether the fragments remain in contact or become separated during the rearrangement. As mentioned by Robinson (*loc. cit.*), a substantial indication that they remain in association was obtained by Jacobson (*Annalen*, 1922, **428**, 76), who from numerous unsymmetrical hydrazobenzenes AB failed to isolate any symmetrical

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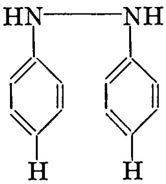
motions), we mean that the electronic wave-functions do so. But, for periods of time which are long for electronic motion the nuclei can be considered fixed (*e.g.*, in the transition state), and it is for such periods, in which the electronic wave-functions remain constant, that we refuse to discuss the chronology of electron motions. We would not, for example, admit the possibility of specifying the path of an oscillation of electrons, or of a circulation—except, of course, as a time-dependent wave-function shown to result from some (relatively slowly occurring) oscillation or circulation of nuclei, or from a disturbance by an external field.

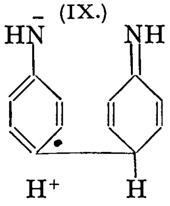
* The terms " homolysis " and " heterolysis " have been suggested for bond fission according to the schemes $X\cdot|\cdot Y$ and $X|\cdot\cdot Y$ respectively (the dots represent shared electrons), independently of the states of electrification of X and Y and of any concomitant covalency changes (*Trans. Faraday Soc.*, 1938, **34**, 227).

benzidines AA or BB. Had the matter been left there, however, the objections would have been possible (*a*) that minor products are often difficult to isolate, and (*b*) that, if AB ionises, it will do so in a preferred direction, and that the parts A^+ and B^- (unlike neutral parts) will lead necessarily to an unsymmetrical product of the type AB. Ingold and Kidd's method was simultaneously and homogeneously to rearrange a suitably chosen pair of symmetrical hydrazobenzenes AA and BB, whose separated parts, A^+, A^-, B^+, B^-, certainly should produce AB, which was shown by thermal analysis to be absent. A collateral argument may be mentioned : if the fragments separate, they do so because their attraction for the solvent is greater than for each other; in the case of a reactive solvent this must lead to solvolysis (*e.g.*, hydrolysis to an arylhydroxylamine and an arylamine), no certain evidence of which exists.*

For these reasons we suppose the transition state, though largely ionic, to be also partly covalent; *i.e.*, we assume its condition to be intermediate between the ionic and covalent extremes. It may be assumed that the positive and negative charges, distributed between the nitrogen and ortho- and para-carbon atoms of the fragments, and assisted by a partial and correspondingly distributed covalency, and by graphitic forces, hold the rings in nearly parallel planes in the transition state of the benzidine rearrangement. Because of the effect (see below) of orienting forces on the electronic energy, it is to be expected that, leading out from the hydrazobenzene in different directions of configuration space, there will be several transition states, separated by energy hills, and corresponding to different relative orientations of the fragments in real space, and, of course, to different end-products (benzidine, diphenylines, *o*-benzidines, *o*- and *p*-semidines). We proceed to consider the *p*-benzidine transition state. As we do not yet know whether one or two adding protons are included in this state we shall omit them, and, quite formally, write negative charges on any atoms which ultimately receive protons.

In describing the electronic system of the benzidine transition state, we may refer first to the covalent (unsplit) component structures. According to the simplifying system of representation adopted (footnote, p. 609), if it were not for the orienting effect we should have to enumerate only the two component structure, (VII) and (XI), in an initial approximation. The orienting effect, however, adds three more structures, (VIII), (IX), and (X). Disregarding stereochemical perspective, these may be depicted as follows :


(VII.)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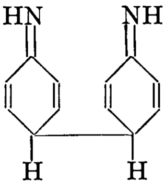
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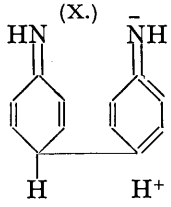
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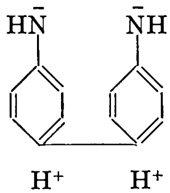
(XI.)

There are octet-preserving routes by which *any* of these structures can be converted into *any* other. Of the many possible conversions some involve a " clockwise " and others a " counterclockwise " displacement of the electrons, whilst yet others result from either clockwise or counterclockwise electron circulation. In conformity with the general point of view explained above, we do not enquire in what sequence clockwise and counterclockwise displacements follow one another, although various hypotheses of the " chronological " type could be made by combining the possibilities; we do not, for example, assume an " oscillation." The important point is that the existence of all this free inter-communication between the different conventional electron distributions (and, of course, between the

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* It has been suggested for tetraphenylhydrazine, where certainly the likelihood of separation into ions is greater than for diarylhydrazines, owing to the larger resonance energy rendered available by the four phenyl groups.

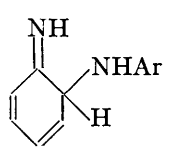
infinitude of intermediate unconventional ones) determines, on account of the uncertainty principle, an orienting effect energetically powerful enough to overcome what might have been thought to be an insurmountable inhibitory factor, namely, the considerable deformation of the nuclear system in the transition state of the rearrangement (see below).

Turning to the ionic (split) structures, we should have to enumerate only four in the absence of the orienting effect, according to the simplifying conventions and standards of approximation here adopted.[*] The orienting effect, however, introduces many new structures. All are mutually interconvertible, and are interconvertible with the covalent structures, the whole assembly defining an extensive mesomeric system. Thus a consideration of the ionic structures adds further strong emphasis to the conclusions already reached.

The stereochemical features of the benzidine change seem to us to be sufficiently striking to deserve discussion. There are two apparent difficulties. One is that, although in many substitutions and rearrangements much of the energy which must be added to the breaking bond in order to determine the fission can be assumed to be supplied by the forming bond, yet in the benzidine change most of the NN-bond energy must, for stereochemical reasons, be assumed to have been added before any large proportion of the CC-bond energy has been released. Much of the energy needed for the fission might be available as increased energy of electrostriction and solvation. A considerable amount is certain to be supplied from the resonance energy developed during the formation of the transition state, just as in the dissociation of hexaphenylethane. Moreover, even a small proportion of the CC-bond energy might constitute a significant contribution, for the NN-bond strength is quite small (about 24 kg.-cals./g.-mol.). Thus, although count also has to be taken of the polarisation energy associated with the covalency changes, it becomes most improbable that any plausible assumption concerning the energy flow could lead to thermally inaccessible values of the activation energy of the rearrangement.

This granted, there remains the difficulty that, however easily benzidine may in theory be formed, one might on stereochemical grounds have expected *oo*′-diaminodiphenyl to be formed still more easily. We know that it is not, and that even *op*′-diaminodiphenyls (diphenylines) are produced more freely than their *oo*′-isomerides (*o*-benzidines). The experimental facility series,[†] benzidines $>$ diphenylines $>$ *o*-benzidines, and *p*-semidines $>$ *o*-semidines, point consistently to a greater tendency in hydrazobenzenes to para- than to ortho-reactivity; and in explanation we suggest that *p*-quinonoid structures, such as (VIII), (IX), and (X), introduce a greater resonance energy into the transition state in which they participate than do the corresponding *o*-quinonoid structures. Resonance energy is determined partly by the energies of the structures and partly by the relation between their electronic distributions, both these factors influencing the extent to which the electron mobility of the system is increased by its mesomerism. We have no reliable information as to how the first of these factors should operate in the case considered, but the second at least should work in favour of the suggested difference.

A similar discussion could be given for the semidine rearrangement, in which (XII), (XIII), and (XIV) are typical structures for the description of a transition state, (XIII) being regarded as much more important than (XIV) in conformity with the accepted electrophilic character of reagents for aromatic hydrogen substitution. A corresponding theory can be applied to certain other rearrangements, *e.g.*, that of phenylhydroxylamine.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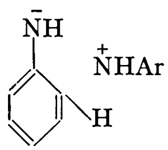
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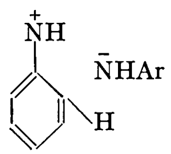
(XIV.)

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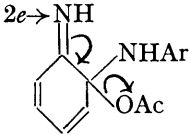
[*] One of these is (VI), read with Kekulè rings and without arrows, and bearing in mind also the convention subsequently introduced (p. 611) concerning the representation of adding protons.

[†] A corresponding order may not apply to the rearrangement products of α-hydrazonaphthalene, but the published evidence on the subject needs revision.

The above view as to the positive polar character of the migratory group in the semidine change is maintained in spite of the recorded displacements of various groups other than hydrogen from the position of substitution. The displacement of groups which can be assumed to be ejected in a positive form presents no difficulty, but some groups, such as OAcyl, are almost certainly ejected as anions. Such displacements, however, have never been observed in the absence of a strong reducing agent; they obviously involve a reduction (empirically OR is replaced by H), and therefore the addition of extraneous electrons to the system; accordingly, the internally migrating group is still allowed to be positive. Employing one structure of the transition state as a " reaction formula " (just as we often employ a Kekulé structure for the benzene ring)* a plausible reduction mechanism may be illustrated thus:



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