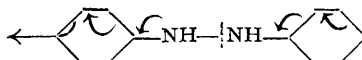


134. Stereochemistry of the Benzidine Transformation.

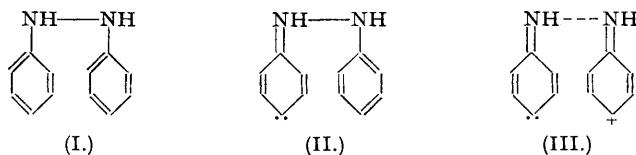
By D. LL. HAMMICK and S. F. MASON.

The benzidine transformation consists essentially in the rupture of the hydrazo, NH-NH, linkage, and the setting up of *p-p'* (or *p-o'*, etc.) bonds. The transformation is known to be intramolecular (Ingold and Kidd, *J.*, 1933, 984), and the two fragments must therefore be restrained from separating during the transition. Mechanisms hitherto proposed for the transformation have not dealt adequately with these forces. It has been postulated (Robinson, *J.*, 1941, 220) that partial *p-p'* bonding takes place before the complete fission of the hydrazo link. The object of this paper is to examine the stereochemical limitation placed on existing theories by this postulate and to suggest structures that may contribute to an activated intermediate free from stereochemical objections.

RECENTLY (*J.*, 1941, 608), Hughes and Ingold have examined the possible structures resonating in the transition complex formed during the benzidine transformation, postulating the electromeric shifts indicated below :



They assume heterolysis of the NH-NH link under the influence of nearby hydrogen ions, concurrent with polarisation of the *para* positions, leading to bond formation between them and the bonding of one or more protons to the nitrogen atoms. Stereochemically this cannot be a continuous process since structures arising from the above electronic displacements do not permit the approach of the *para* carbon atoms to within bond distances.



Thus in structures (I), (II), and (III) the distances between the *para* carbon atoms, calculated from the known bond lengths and angles, are 4.26, 5.51, and 6.76 Å. respectively.* Structure (III) is of course hypothetical, but taken as the relative position of the two fragments in space immediately after the heterolysis of the NH-NH link, it is seen that the *para* positions are separated by a distance some four times the length of a single C-C link. Heterolysis of the NH-NH link in any of the structures or hybrid of them would therefore give two fragments with the *para* positions separated by 4 Å. at least, a fact difficult to reconcile with the undoubted intramolecular nature of the process, assuming continuous transition essential for such reactions.

Robinson (*J.*, 1941, 220) takes into account the hydrogen ion catalysis of the reaction by proposing the

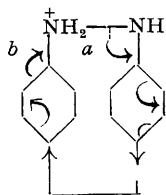
* The data in this, and following calculations, have been taken from Wells, "Structural Inorganic Chemistry" (1945). All bond angles have been assumed to be tetrahedral except in the carbonium ions which have been taken as planar (Bartlett, *J. Amer. Chem. Soc.*, 1939, **61**, 3184). In the bonds to nitrogen this is justified as the bond angles in ammonia are 108° (Wells, *loc. cit.*); moreover the nitrogen atoms in many of these structures are quadricovalent. The bond lengths used in the calculations are as follows :

Single C-C bond, 1.54 Å.
Double C=C bond, 1.33 Å.
Benzene C-C bond, 1.39 Å.

Single N-C bond, 1.46 Å.
Double N=C bond, 1.27 Å.
Single N-N bond, 1.48 Å.

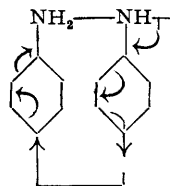
From these data the various *p-p'*, *o-p'*, and *p-o'* separations were calculated trigonometrically. It should be noted that no attempt has been made to represent actual angles in the structures given.

formation of the hydrazobenzene mono-cation as the first step in the transformation. The charged centre then initiates the following electron shifts :

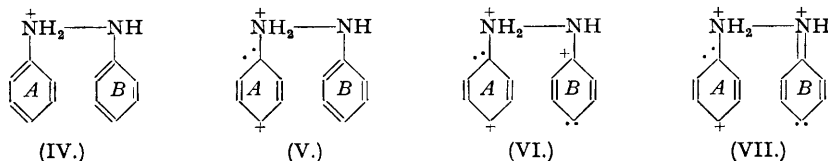


One difficulty in this mechanism, as was pointed out by Hughes and Ingold (*loc. cit.*) lies in the proposed electron recession from a positively charged centre (shift *a*). Process (*b*) moreover could not proceed to any appreciable extent as this would make the nitrogen atom quinquivalent. Robinson avoids these difficulties by postulating a partial reversal of the electron shifts leaving the $\text{NH}_2\text{-NH}$ bond weakened and the *para* positions partially bonded. The problem of the stereochemical feasibility of this *para* linking is recognised but left unsolved, however.

The above criticisms of the electron shifts do not arise if the electromeric effects are postulated as below :



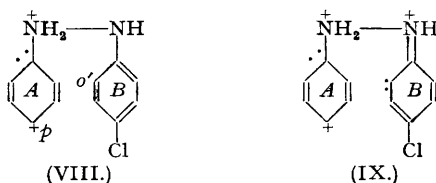
The various structures that might be formed from these shifts are as follows :



The distance between the *para* carbon atoms in structure (IV) is found to be 4.26 Å. In structure (V) the minimum distance between these two atoms would be 1.50 Å. as the charged nitrogen atom is no longer in the plane of the attached benzene ring; *para* bonding would therefore be stereochemically possible in this structure, the single C-C bond distance being 1.54 Å. This structure, by itself, cannot represent the activated transition state because it indicates none of the polarisation effects in ring B that would be set up by the highly polar ring A, leading to *para* bonding. In structures (VI) and (VII), where the minimum *para* separations would be 1.68 Å. and 2.71 Å. respectively, the ring B *para* positions possess this polarity. Structure (VI) however possesses a positively charged carbon atom linked to a nitrogen atom with an unshared pair of electrons. We should therefore expect structure (VII), with an extra bond between these two atoms, to play a more significant rôle in the transition hybrid, were it not for the fact that it contravenes the Pauling adjacent charge rule. This rule, however, only applies to normal molecules (but is clearly contravened by hydrazine dihydrofluoride), whereas structure (VII) would represent a highly activated state with a weakened NH-NH bond.

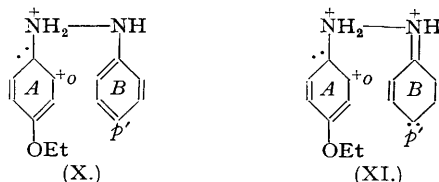
The process of the transformation may then be pictured as the bonding of a proton to a nitrogen atom, followed by the above electromeric shifts consequent upon the setting up of the resultant charged centre. The contribution of structure (VII), and perhaps (VI), would determine the extent of *para* bonding if this were rendered stereochemically possible by structure (V) playing a major rôle in the resonance hybrid. This means that the resonance energy of ring A would be largely destroyed, some 39 kg.-cals./mol. being required for this purpose. This, and the 23.6 kg.-cals./mol. required for the rupture of the NH-NH link, might be provided in part by the simultaneous formation of the *p-p'* C-C bond (giving 58.6 kg.-cals./mol.), so that the energy of activation need not be high by this mechanism.

The transformation is completed by the covalent bonding of a proton to the nitrogen atom of the ring B, and the elimination of the *p*-hydrogen atoms as hydrogen ions. In mono-*p*-substituted hydrazobenzenes the benzidine transformation only occurs when the *p*-substituent can be eliminated as a positive ion (CO_2H , SO_3H). Where the *p*-substituent cannot be eliminated as a positive ion, two possible changes can occur. If the substituent lowers the basicity of the ring B, a proton will be initially bonded to the other ring, A. The relevant structures that might arise from the consequent electron shifts are :



The distances between the *p*-*o'* positions in the structures (VIII) and (IX) are 1.51 Å., so that partial bonding is stereochemically possible between these positions, and would lead to the formation of a diphenylene. These compounds are in fact formed by the rearrangement of *p*-Cl, *p*-Br, *p*-I, *p*-OAc, and *p*-NMe₂ hydrazobenzenes, all these substituents lowering the basicity of a *p*-amino group under the conditions of the benzidine transformation (acid medium).

If the substituent enhances the basicity of the ring to which it is attached, *i.e.*, EtO and MeO, a proton will be bonded to the *p*-nitrogen atom. The following structures may then take part in the transition state :



Here the distances between the *o*-*p'* positions are 3.74 Å. in structure (X), and 3.70 Å. in structure (XI). These distances are much larger than the corresponding separations in the preceding case (both 1.51 Å.) and in the benzidine transformation proper (1.50 Å. and 2.71 Å. respectively); in fact semidines only are produced.

The absence of an *o*-benzidine transformation in the benzene series, and the small yields of diphenylenes obtained from hydrazobenzenes with free *p*-positions, are not likely to be due to steric effects, as the *o*-*o'*, and the *p*-*o'* positions are near enough for partial bonding prior to the NH-NH link fission (but not the *o*-*p'* positions as has already been noted). The reason is probably to be sought more in the energy content of structures formed during reaction.

It is well known that non-resonating forms of *p*-quinonoid structures are more stable than the corresponding *o*-quinonoid forms. A rough measure of this difference in stability is given by the free energy changes in the hydrogenation of *p*-benzoquinone and *o*-benzoquinone, calculated from their respective reduction potentials.

$$-\Delta G = nFE^\circ.$$

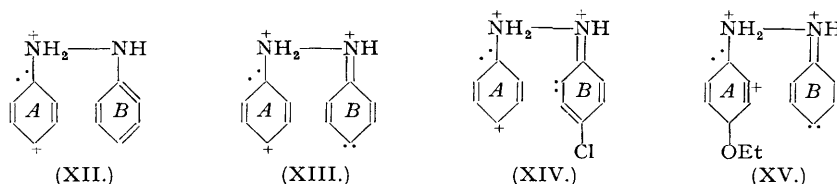
	Reduction potential, v.	$-\Delta G_{\text{aq}}^{25^\circ}$, kg.-cals.
<i>p</i> -Benzoquinone (a)	0.699	32.2
<i>o</i> -Benzoquinone (a)	0.794	36.6
α -Naphthaquinone (b)	0.470	21.65
β -Naphthaquinone (c)	0.555	25.5

(a) Fieser and Peter, *J. Amer. Chem. Soc.*, 1931, **53**, 793.
 (c) Fieser and Fieser, *ibid.*, 1934, **56**, 1565.

(b) La Mer and Baker, *ibid.*, 1922, **44**, 1954.

If these values of $-\Delta G_{\text{aq}}^{25^\circ}$ are taken as rough estimates of the relative stability of the *o*-quinonoid and *p*-quinonoid configurations of the benzene ring, it is seen that some 4.6 kg.-cals. would be necessary to convert a benzenoid to an *o*-quinonoid structure, above that energy necessary to convert a benzenoid to a *p*-quinonoid structure. This only applies to "fixed" *ortho* and *para* quinonoid structures; where they are canonical structures in a resonance hybrid, their contributions are presumably slightly different, but not sufficiently to affect the stability of the hybrid to a great extent unless they play the major rôle in such a hybrid.

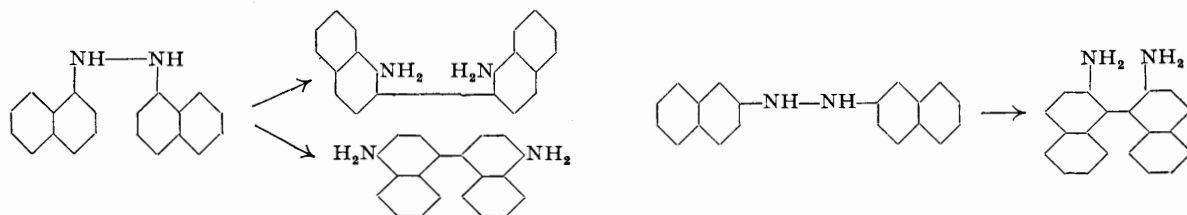
In the activated hybrid postulated, ring A (structure XII) has largely lost its resonance, whilst ring B retains it, there being a polar modification symbolised in structure (XIII).



Where there is a *p*-substituent that reduces the basicity of the attached ring (ring B, structure XIV), the reaction-initiating proton is covalently linked to the nitrogen atom of the other ring (A) which becomes structurally *p*-quinonoid. It is postulated that resonance is largely retained in ring B, so the assumption of an *o*-quinonoid polarity in this ring would entail no significantly greater amount of energy than the assumption of a *p*-quinonoid polarity. Hence diphenylene formation is energetically, as well as stereochemically, feasible.

Where there is a *p*-substituent that raises the basicity of the attached ring, proton bonding takes place on the *p*-nitrogen atom of the same ring (ring A, structure XV). If diphenylene formation were to occur, this ring would have to assume an *o*-quinonoid structure. Since the virtual absence of resonance is postulated in this ring, the energy required for its formation would be higher; this, coupled with the greater separation of the *o*-*p'* reactive centres, would seem to prohibit diphenylene formation, in accordance with the fact that only semidines result from hydrazobenzenes with this type of *p*-substituent.

Hydrazonaphthalenes on undergoing the benzidine transformation may yield 4 : 4'-diaminodinaphthyls, 2 : 2'-diaminodinaphthyls, or the dibenzcarbazoles produced by the elimination of ammonia from the latter; 2 : 4'-derivatives, analogues of the diphenylines, are not produced, *e.g.* :



The prevalence of an *o*-benzidine type of transformation in the naphthalene series would indicate that β -naphthaquinonoid structures are more stable than *o*-benzoquinonoid, relative to the α -naphthaquinonoid and the *p*-quinonoid structures respectively.

This is demonstrated, in part, by the differences in the free energies of hydrogenation (see Table); between α - and β -naphthaquinones it is 3.85 kg.-cals./mol., as opposed to 4.4 kg.-cals./mol. between the *o*- and *p*-benzoquinones. This would be due to the conjugation of the 3 : 4 double bond in β -naphthaquinone with the remaining benzene ring, whilst the corresponding 3 : 4 double bond in *o*-benzoquinone is only conjugated with the 5 : 6 double bond.

Another factor of importance is the degree of double bond character in the α - β link of naphthalene. Resonance amongst the three canonical structures of naphthalene gives this link 2/3 double bond character, so that α -substituents influence the β -position to a greater extent than they influence the corresponding *ortho* position in benzene. Likewise β -substituents influence position 1 to a greater extent than position 3.

The occurrence of an *o*-benzidine type of transformation in hydrazonaphthalenes may thus be ascribed to two factors, the relative stability of "fixed" β -naphthaquinonoid structures and the ease of α - β polarisation in naphthalene.

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