

are comparable may reflect, in part, the inductive effect of the nitrogen atoms as well as a decreased resonance effect due to the fact that those structures which place negative charge at positions *ortho* to the substituent are now no longer equivalent. In the 5-methyl compound, the effect is again essentially uniform, but here there is no *meta* value for comparison.

TABLE III
METHYL SUBSTITUENT EFFECTS IN PYRIMIDINE^a

Substituent	Position				Sum
	2	4	5	6	
2-Methyl	..	5	9.6	5	19.6
4-Methyl	6.9	..	6.1	7.3	20.3
5-Methyl	8.6	8.1	..	8.1	24.8

^a All values are the displacements of the proton shifts in c.p.s. at 40 Mc./sec. relative to the same position in the unsubstituted ring.

B. Imidazole.—The spectrum of imidazole which consists of a triplet and a doublet of twice the triplet intensity is clearly that of an A₂B system, that is, H₄ and H₅ are a magnetically equivalent set despite the apparent difference of the N₁ and N₃ atoms. This equivalence has its origin in the fact that the N₁ proton is very mobile and undergoes rapid exchange either with water present or with other imidazole molecules, the various structures present being stabilized by resonance. A similar line of reasoning accounts for the fact that the 4-methyl and 5-methyl derivatives are indistinguishable.

The chemical shifts shown in Table II are in accord with expectations based on the structure of imidazole, and the coupling constants are all relatively small (*meta* values). The values of the methyl shifts are reasonable in view of the inductive situation at the various positions.

The methyl substituent effects in imidazole have been summarized in Table IV. The situation

is qualitatively similar to that in pyrimidine, in that the 4-methyl group produces a greater total effect than the 2-methyl substituent, and both totals are well below the previously observed value of 30–33 c.p.s. It thus appears that here again charge has been transferred to the nitrogen atoms in the order 2-methyl > 4-methyl. Incidentally, these observations parallel the order in which the basicities increase: imidazole < 4-methylimidazole < 2-methylimidazole.¹² The N-methyl derivative presents a somewhat different situation, since there is no mobile proton present and the original symmetry is now destroyed. It is not too surprising, therefore, that its basicity is not as great as that of the other two methyl derivatives

TABLE IV
METHYL SUBSTITUENT EFFECTS IN IMIDAZOLE^a

Substituent	Position			Total
	2	4	5	
2-Methyl	..	7.4	7.4	14.8
4-Methyl	5.8	..	15.1	20.9
N-Methyl	11.6	3.1	10.8	25.5

^a All values are the displacements of the proton shifts in c.p.s. at 40 Mc./sec. relative to the same position in the unsubstituted ring.

The relatively large total methyl effect in N-methylimidazole is interesting in that it may in part reflect the general extent to which conjugated heteroatoms in the ring absorb the charge transferred by a long-range mechanism from the substituent.

Acknowledgments.—The authors are indebted to the National Institutes of Health and to the Army Chemical Center for their support of various phases of this work; and to the Southern Research Institute, Birmingham, Ala., for supplying all the compounds used in this study.

(12) Reference 1, p. 344–345.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY, PITTSBURGH, PENNSYLVANIA AND THE BELL TELEPHONE LABORATORIES, INCORPORATED, MURRAY HILL, NEW JERSEY¹⁰]

Hückel Molecular Orbital Computations to Describe the Benzidine Rearrangement^{1a}

BY LAWRENCE C. SNYDER^{1b}

RECEIVED JULY 31, 1961

Major qualitative features of the product distribution in the acid catalyzed benzidine rearrangement have been explained by Dewar in terms of a postulated monoprotonated pi complex. In this study, a molecular orbital model is employed to describe a pi complex and its subsequent unfolding to sigma complexes corresponding to possible products. Computations have been made in the Hückel approximation to describe the rearrangement of hydrazobenzene, 2,2'-hydrazonaphthalene, 1,1'-hydrazonaphthalene, 9',9'-hydrazoanthracene, hydrazotoluenes and hydrazoanilines. It is found that under assumption of either of two extreme pi complex wave functions, a covalent or a charge transfer structure, the product distributions predicted by the model are in qualitative agreement with experiment. The results support the model of a monoprotonated pi complex as an intermediate but fail to elucidate its wave function. Observed ionization potentials for benzyl radical and aniline suggest that the states corresponding to the extreme structures would be almost degenerate for an isolated monoprotonated pi complex. If one adds to the model a hypothetical description of the effect of solvation on the product distribution, then the usual minor role of *ortho*-benzidine as a product and the solvent effect on the diphenylene to *para*-benzidine ratio can be explained, and Dewar's generalization on the selective formation of diphenylenes can be interpreted to favor the covalent structure as predominant in the pi complex.

Introduction

The growing body of experimental knowledge of the product distribution and kinetics of the benzi-

dine rearrangement makes the explanation of its mechanism more difficult and interesting. Many

(1) (a) Presented in part at the 138th meeting of the American Chemical Society, New York, September, 1960. Taken in part from a

thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Carnegie Institute of Technology, 1959. (b) National Science Foundation predoctoral fellow 1953–1954, 1956–1958.

current discussions of the mechanism include a pi complex.^{2a,8} Dewar² has postulated a mono-protonated pi complex and has explained major features of the product distribution in terms of it. This study adopts a molecular orbital model of a mono-protonated pi complex and of its unfolding to form sigma complexes corresponding to possible products. Computations are made in the Hückel approximation⁴ to test product distribution predictions based on the model.

Hydrazobenzene and its substituted derivatives rearrange in the presence of acids to varying relative proportions of a characteristic set of products shown in Fig. 1. Hydrazobenzene I reacts with hydrochloric acid in 95% ethanol to form⁶ *para*-benzidine II (~70%), diphenylene III (~30%) and smaller amounts⁸ of *ortho*-benzidine IV (~0.3%), *ortho*-semidine V (~0.3%) and *para*-semidine VI (~1.0%). Small proportions of the corresponding aniline and azobenzene disproportionation products are also usually formed. Hydrazoaromatics with aromatic nuclei other than benzene undergo rearrangement to analogous products. Under catalysis by acid 2,2'-hydrazonaphthalene rearranges to 2,2'-diamino-1,1'-binaphthyl; and 1,1'-hydrazonaphthalene rearranges to approximately equal quantities of 1,1'-diamino-2,2' - binaphthyl and 4,4' - diamino - 1,1' - binaphthyl.⁷⁻⁹ Dibenzcarbazoles may appear as a minor product.

Dewar^{2,7} has emphasized two generalizations on the product distribution from hydrazobenzenes with ring substituents. One is that biphenylene is formed only if the *para* position of the more basic ring is free. The other is that the more basic ring carries the free amino group in a semidine product. The basicity of the rings is to be compared on the basis of the corresponding anilines. The above rules fail occasionally, for example, when applied to hydrazobenzenes substituted with a halogen at one *para* position.¹⁰ It should also be noted that 3,3'-5,5' substituted hydrazobenzenes rearrange in 2:1 sulfuric acid to products which include the corresponding *ortho*-benzidine as a major component.¹¹ The product distribution from hydrazobenzenes has been found to depend fairly strongly on the solvent employed. Less polar solvents favor a higher biphenylene to *para*-benzidine ratio^{8,12} and the formation of *ortho*-benzidine.¹³

(2) "Theoretical Organic Chemistry," Butterworths, 1959, contribution "Aromatic Rearrangements" by M. J. S. Dewar. (b) M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Oxford Press, London, 1949, pp. 235-240.

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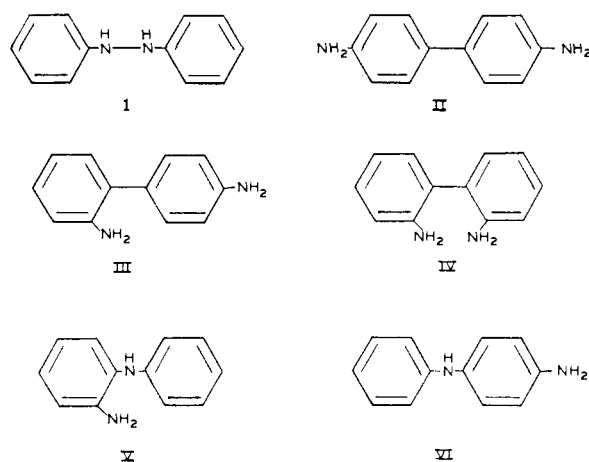


Fig. 1.—Hydrazobenzene I and its rearrangement products, *para*-benzidine II, diphenylene III, *ortho*-benzidine IV, *ortho*-semidine V and *para*-semidine VI.

The benzidine rearrangement is almost certainly intramolecular, as has been shown by Smith, Schwartz and Wheland¹⁴ using a radioactive tracer technique and by Ingold and Kidd¹⁵ with the rearrangement of binary mixtures of hydrazocompounds. Kinetic studies show the rate of rearrangement to be first order in the concentration of hydrazo compound and usually second order in acid concentration, with a positive salt effect.^{5,16,17} The several products appear to be formed by closely related mechanisms because their relative amounts have been found to be independent of acid concentration in several studies: the rearrangement of hydrazobenzene to benzidine and biphenylene⁵; of *para*-hydrazo toluene to *ortho*-semidine and disproportionation products¹⁷; and of 4-chloro-hydrazobenzene to biphenylene, *ortho*-semidine and disproportionation products.¹⁸ The relative amounts also appear to be independent of temperature in some cases studied.^{5,17}

The compulsive reason for adopting the idea of a pi complex intermediate is the observed intramolecularity of the benzidine rearrangement. Under the assumption that the rearranging fragments remain planar, the pi complex provides a qualitatively satisfactory explanation of their bonding; but a bonding picture making use of conventional directed valence bonds either requires bonds of extraordinary length or suggests that *ortho*-benzidines should be a major product. The assumption that the pi complex is mono-protonated clearly distinguishes the rearranging fragments and permits explanations of the selective formation of biphenylenes and semidines based on the idea that the nitrogen atom of the more basic fragment is protonated.² The alternative assumption that both nitrogen atoms of the pi com-

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(13) R. B. Carlin and W. O. Forshey, Jr., *ibid.*, **72**, 793 (1950).

(14) D. H. Smith, J. R. Schwartz and G. W. Wheland, *ibid.*, **74**, 2282 (1952).

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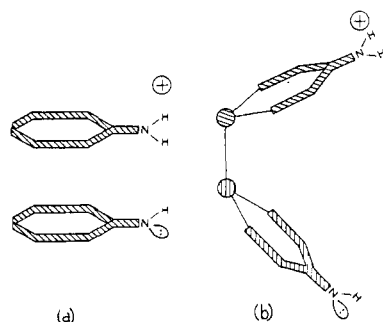


Fig. 2.—The pi complex (a) and a sigma complex (b).

plex are protonated makes an explanation of the bonding of the complex very difficult. Probably, however, the only directly observed properties which may be attributed to the postulated pi complex are the transient deep blue and violet colors reported by Wittig, Joos and Rathfelder¹⁹ to have occurred upon the addition of acid to certain cyclic hydrazo compounds. It must also be noted that the position in the rearrangement mechanism of the pi complex relative to the rate controlling interaction of the hydrazo-compound with the second proton is not known from present experimental information.

The Pi Complex.—One may regard the pi complex to be formed from the pair of radical fragments produced by the homolytic fission of the N-N bond of the hydrazo compound. It is assumed that the nitrogen atoms contribute one pi atomic orbital and electron to the pi electronic system of the resulting fragments. The corresponding radical fragments from hydrazobenzene have seven pi electrons with the unpaired electron in the non-bonding molecular orbital Φ_u of the upper fragment and Φ_l of the lower. The radical fragment is isoelectronic with benzyl radical. If two such fragments are brought together with one above the other and in parallel planes, as depicted in Fig. 2, their unpaired pi electrons would be expected to form low energy singlet electronic states describable in terms of a covalent structure ${}^1\Psi_{cov}$ and the symmetrical and antisymmetrical structures ${}^1\Psi_s$ and ${}^1\Psi_a$, where

$${}^1\Psi_{cov} = N\{\Phi_u(1)\Phi_u(2) + \Phi_u(2)\Phi_l(1)\}$$

$${}^1\Psi_s = N'\{\Phi_u(1)\Phi_u(2) + \Phi_l(1)\Phi_l(2)\}$$

$${}^1\Psi_a = N''\{\Phi_u(1)\Phi_l(2) - \Phi_l(1)\Phi_u(2)\}$$

A low energy triplet state would be expected to correspond to the structure ${}^3\Psi_{cov}$, where

$${}^3\Psi_{cov} = N'''\{\Phi_u(1)\Phi_l(2) - \Phi_u(2)\Phi_l(1)\}$$

The two-electron spin functions have been omitted above. The constants N are normalization factors. If one assumes that the two fragments approach to an interplanar distance of 3.2 Å., which is approximately the distance between aromatic rings in [3.3]paracyclophane²⁰ and solid quinhydrone,²¹ then the overlap between atomic

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orbitals of the upper and lower fragments should be of the order of magnitude 0.1.²² The ground state wave function should be predominantly ${}^1\Psi_{cov}$ with a small contribution of ${}^1\Psi_s$. Because of the small overlap and interaction, the pi molecular orbitals of the individual fragments are expected to remain a good basis for the description of this system, and it is appropriately called a pi complex.^{22,23} This pi complex should show a new electronic absorption corresponding to a transition from the ground state to ${}^1\Psi_a$.^{23,24} A similar analysis has been related by Hausser and Murrell²⁴ to observations of the magnetic susceptibility and absorption spectrum of solutions of N-ethyl-phenazyl radical. They postulate that a diamagnetic pi complex is formed at low temperatures. They attribute a new absorption band at 8000 Å. to the pi complex. From the temperature dependence of the 8000 Å. absorption, Hausser computed its dissociation energy to be 2000 cal./mole.²⁵

Dewar^{2a} has postulated that the products of the benzidine rearrangement are formed upon the unfolding of a monoprotinated pi complex. The assumption that the pi complex is monoprotinated greatly facilitates the interpretation of Dewar's well known generalizations on the role of the more basic ring in the selective formation of biphenylenes and semidines. In this theoretical study, it is assumed that an unshared electron pair on the nitrogen atom of the more basic fragment is protonated. The ground state wave function for the monoprotinated pi complex should contain a larger proportion of the structures ${}^1\Psi_a$ and ${}^1\Psi_s$. The prediction of simple Hückel theory, which does not properly account for electronic repulsion, is that the ground state wave function corresponds closely to the transfer of an electron from the unprotonated to the protonated fragment of the pi complex.²⁶ This situation is embodied in the charge transfer structures ${}^1\Psi_{ct\pm}$ which are linear combinations of ${}^1\Psi_a$ and ${}^1\Psi_s$

$${}^1\Psi_{ct\pm} = \frac{1}{\sqrt{2}}({}^1\Psi_s \pm {}^1\Psi_a)$$

The plus function corresponds to transfer of an electron to the upper fragment, and the minus function to the lower. In subsequent discussion, the upper fragment is assumed to be protonated.

Because of the limitations of the Hückel approximation, its conclusion that an electron is transferred to the protonated fragment is suspect. In the limit that large distances separate the fragments, the relative energy of the covalent structure and the charge transfer structure can be approximated with the ionization potentials of aniline (I_a) and of the unprotonated radical fragment (I_l), thus

$$E_{cov} - E_{ct+} = I_a - I_l$$

(22) M. J. S. Dewar, *Nature*, **156**, 784 (1945).

(23) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

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(26) This conclusion is the result of a Hückel approximation computation in which a resonance integral of 0.2 β is taken between neighbor pi atomic orbitals on the upper and lower fragments

The ionization potential of aniline is $+7.70 \pm 0.02$ ev. from photoionization measurements.²⁷ The electron impact ionization potential of benzyl radical is $+7.76 \pm 0.08$ ev.²⁸ and the photoionization value should be about 0.5 ev. less. This difference may well be offset by the increase of similar magnitude expected if NH replaces CH₂ as it does in the radical fragment of interest. There is, therefore, little basis in this ionization potential data for taking the monoprotonated pi complex ground state to be predominantly either the covalent or charge transfer structure. In solution, solvent molecules and acid anions present may interact with the differing charge distributions of these structures to alter their relative energies and the frequency of light absorbed in transitions between them. The colors observed by Wittig, *et al.*,¹⁹ upon adding acid to solutions of cyclic derivatives of hydrazobenzene may be reasonably attributed to an electronic transition between ground and excited state linear combinations of the covalent and charge transfer structures of the pi complex.

Although one must expect the true monoprotonated pi complex wave function to be some linear combination of ${}^1\Psi_{\text{cov}}$ and ${}^1\Psi_{\text{ct}+}$, it is convenient to apply models for the rearrangement under the assumption of one of the extreme structures. Therefore numerical computations have been performed so that the model adopted may be tested with either the covalent or charge transfer structure.

A Molecular Orbital Model of Product Formation from the Pi Complex.—A molecular orbital model based on the following physical picture is adopted. The parallel fragments in the pi complex may rotate and unfold to form sigma complexes (Fig. 2) in which a carbon or nitrogen atom from each fragment is bonded. Where the aromatic nuclei are not phenyl, it is assumed that the fragments cannot rotate relative to each other because the diminished overlap of their pi electronic systems would reduce their bonding interaction. In further reactions the sigma complex formed upon unfolding becomes the product with similar bonding. The formation of products from sigma complexes of lower energy relative to the pi complex is assumed to be favored. The monoprotonated pi complex may be regarded as an intermediate which is followed by transition states near the several sigma complexes. While these transition states may not control the over-all rate of the reaction, they are considered to affect the product distribution. On the basis of their experiments, Vecera, Synek and Sterba⁶ concluded that different transition states control the over-all rate and product distribution in the acid catalyzed rearrangement of hydrazobenzene.

To describe the pi electronic systems of the individual fragments and their complexes, we employ molecular orbitals computed in the Hückel approximation.⁴ The following assumptions have been made in the computation of these orbitals and their energies. All nearest neighbor resonance

integrals of pi atomic orbitals are set equal to β (~ -20 kcal./mole). The coulomb integral of a carbon pi atomic orbital is taken to be α and equal to the coulomb integral of a nitrogen pi atomic orbital on an unprotonated fragment. To represent the effect of protonation of the nitrogen atom lone pair electrons,²⁹ we increase the nitrogen coulomb integral to $\alpha + 1.4\beta$.³⁰ Longuet-Higgins³¹ found an increase of 1.2β to be consistent with data on the ionization constants of hetero-aromatic amines. An amine substituent is assumed to contribute two pi electrons and one pi atomic orbital with a coulomb integral of $\alpha + 1.4\beta$. A methyl substituent group has been represented as a single heteroatom which contributes two electrons and one orbital to the pi system. The heteroatom coulomb integral is taken to be $\alpha + 3.3\beta$ and a resonance integral of 0.8β connects it with the fragment carbon atom to which it is bonded.³²

In the Hückel approximation, the energy E of a pi electron system is given by

$$E = \sum_{n=1}^m \nu_n E_n, \nu_n = 0, 1, 2$$

where the sum is over the m molecular orbitals Φ_n with energies E_n and occupation numbers ν_n . The charge q_i on the i^{th} atom is taken to be the charge Z_i on the atom stripped of all pi electrons, plus the charge density computed for electrons in pi molecular orbitals

$$q_i = Z_i - \sum_{n=1}^m \nu_n (C_{ni})^2$$

where C_{ni} is the coefficient of the i^{th} atomic orbital in the n^{th} molecular orbital. An index of the basicity of the fragment nitrogen atom unshared pair electrons may be conveniently defined and computed in this approximation.^{31,33} This index (ΔE_b) is the change in fragment pi system energy upon changing the nitrogen coulomb integral to its protonated value of $\alpha + 1.4\beta$: that is $\Delta E_b = E(\text{protonated}) - E(\text{unprotonated})$. This may provide a better index of relative ring basicity than the experimental values for corresponding anilines, since the anilines have filled molecular orbitals while the radical fragments of interest do not. Hyperconjugation is currently regarded to be greatly enhanced in pi systems here describable as having partly filled molecular orbitals relative to those with filled orbitals.³⁴

Since the interaction of the fragments in the pi complex probably is small, we take the energy of the pi complex to be the sum of the pi system energies computed for the isolated fragments.

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(32) "Conference on Hyperconjugation," Pergamon Press, 1959, contribution by A. Streitwieser, Jr., and P. M. Nair "A Simple Molecular Orbital Treatment of Hyperconjugation."

(33) The unshared pair of electrons on the nitrogen atom bearing one methyl group in trimethylthionine is probably about as basic as the unshared pair on the fragment nitrogen atom. The equivalence point of trimethylthionine is pH 12.2 [K. Bergmann and C. T. O'konski, *J. Phys. Chem.*, in press].

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TABLE I
 ATOM LOCALIZATION ENERGIES^a (A_n) FOR AROMATIC AMINE RADICAL FRAGMENTS

Fragment ^b	Atom												ΔE_n	ΔE_b					
	N	1	2	3	4	5	6	7	8	9	10	11			12				
Aniline	1.14 ^c	2.28	1.60	1.91	1.65	1.91	1.60										-0.63 ^a	-1.82 ^a	
	0.72 ^c	3.26	1.73	2.56	1.82	2.56	1.73												
1-Naphthylamine	1.36	2.26	1.66	2.06	1.61	1.79	2.05	1.94	1.88	2.40	2.62							-.44	-1.95
	0.81	3.11	1.63	2.55	1.64	1.97	2.51	2.08	2.40	2.44	3.07								
2-Naphthylamine	1.27	1.47	2.35	1.80	1.81	1.80	1.87	1.97	1.71	2.56	2.38							-.51	-1.93
	0.74	1.50	3.22	1.90	2.36	2.33	2.05	2.48	1.92	3.08	2.49								
9-Anthrylamine	1.56	1.99	2.00	2.17	1.85					2.17	1.49	2.44	2.77					-.27	-2.00
	0.95	2.39	2.01	2.50	1.90					2.96	1.45	2.36	3.07						
2-Methylaniline	1.17	2.22	1.76	1.87	1.68	1.87	1.63											-.62	-1.84
	0.73	3.18	1.88	2.43	1.83	2.48	1.74												
3-Methylaniline	1.15	2.29	1.55	2.06	1.60	1.92	1.56											-.63	-1.83
	0.72	3.26	1.71	2.71	1.81	2.57	1.73												
4-Methylaniline	1.19	2.25	1.64	1.87	1.84	1.87	1.64											-.61	-1.86
	0.73	3.19	1.74	2.47	1.97	2.47	1.74												
2-Aminoaniline	1.32	2.15	2.15	1.79	1.84	1.84	1.79											-.52	-1.96
	0.76	2.99	2.15	2.16	1.86	2.31	1.74												
3-Aminoaniline	1.21	2.36	1.45	2.36	1.50	1.99	1.50											-.57	-1.89
	0.72	3.26	1.63	2.94	1.74	2.58	1.70												
4-Aminoaniline	1.34	2.22	1.80	1.80	2.22	1.80	1.80											-.50	-1.99
	0.75	3.03	1.76	2.25	2.23	2.25	1.76												

^a In units of $-\beta$, where $-\beta \cong +20$ kcal. ^b Name of amine corresponding to the protonated radical fragment is listed. ^c Upper number corresponds to the protonated radical, the lower to the unprotonated radical.

Thus the covalent structure ${}^1\Psi_{cov}$ for the mono-protonated pi complex of hydrazobenzene is represented by placing six electrons pairwise into the three lowest molecular orbitals and one electron in the fourth molecular orbital of each fragment. To describe the charge transfer structure ${}^1\Psi_{ct+}$, the last pair of electrons is placed in the fourth molecular orbital of the protonated fragment. On the basis of these assignments of electrons to molecular orbitals, theoretical properties of the monoprotinated pi complex may be computed for either extreme wave function.

In a sigma complex, the two fragments are thought to be bonded through a single atom on each (Fig. 2). The atoms bonded in the sigma complex may be qualitatively regarded as removed from conjugation with the residual pi systems of their fragments. The relative energy required to form different sigma complexes can be estimated in terms of a molecular orbital quantity first defined and used by Wheland^{4,35} and often called an atom localization energy. Atom localization energies are defined to correspond to the increase in energy of a pi electronic system upon removing one pi atomic orbital from conjugation with the remainder of the system and the assignment of zero, one, or two of the electrons to that atomic orbital. The atom localization energies (A_n) used in this study were computed for the localization of one of the radical fragment electrons on the n^{th} atomic orbital. The other pi electrons are assigned to molecular orbitals computed for the remainder of the pi system. In the present approximation, the energy of the sigma complex relative to the pi complex covalent structure is the sum (L_{mn}) of atom localization energies A_m and A_n at the bonded atoms m and n, plus an energy of interaction E_σ characteristic of the elements joined. Thus the energy of several sigma complexes relative to their common pi complex may be compared through the sums L_{mn} . For a particu-

lar pair of fragments, sigma complexes with lower values of L_{mn} presumably are formed more easily from the pi complex.

In the Hückel approximation, the charge transfer structure is stabilized relative to the covalent structure by the difference ΔE_n of the nonbonded molecular orbital energy in the protonated and unprotonated fragments: that is, $\Delta E_n = E_n(\text{protonated}) - E_n(\text{unprotonated})$. Thus the relative ordering of sigma complex energies and the related predictions of product distribution are the same for the covalent and charge transfer structures of the pi complex.

Computational Applications.—Numerical computations have been completed to describe the unprotonated and protonated radical fragments for several symmetrical hydrazo compounds: hydrazobenzene, 1,1'-hydrazonaphthalene, 2,2'-hydrazonaphthalene, 9,9'-hydrazoanthracene; *ortho*, *meta* and *para*-hydrazotoluenes; and *ortho*, *meta* and *para* hydrazoanilines. In Table I are summarized quantities computed for individual radical fragments. Atoms are numbered as indicated in Fig. 3.

Several qualitative features of the rearrangement can be reasonably interpreted in terms of the localization energy at the nitrogen atom of a fragment. If one considers the hydrazo compound to be a sigma complex in which is bonded a nitrogen atom from each fragment, then according to the adopted model, an increase in A_n decreases the stability of the sigma complex with respect to the separated radical fragments. As shown in Table I, protonation of a radical fragment increases A_n . For the aniline radical fragment the increase in A_n upon protonation is from 0.72 to 1.14 ($-\beta$). Thus protonation of the nitrogen unshared electron pairs of the hydrazo compound may be interpreted to weaken the N-N bond and thus facilitate the formation of the pi complex and subsequent products. The increased values of A_n in the protonated 1-naphthylamine, 2-naphthylamine and

9-anthrylamine radical fragments and the corresponding expected weakening of the N-N bond of the hydrazo compound may facilitate the observed "thermal" rearrangements of hydrazonaphthalenes in ethanol^{18,36} and explain the fact that 9,9'-hydrazoanthracene apparently has not yet been synthesized. In the Hückel approximation, amino and alkoxy substituents are similar and, if at an *ortho* or *para* position, increase the localization energy A_n at a protonated fragment nitrogen atom. Croce and Gettler³⁷ found 2,2'-dimethoxyhydrazobenzene and 2,2'-diethoxyhydrazobenzene to rearrange with an immeasurably fast rate, in contrast to the conveniently studied rearrangement of hydrazobenzene. They were also able to study the kinetics of the rearrangements of 2-methoxyhydrazobenzene and 2-ethoxyhydrazobenzene and observed unusually low Arrhenius activation energies. This acceleration of the rearrangement may also be attributable to an analogous weakening of the N-N bond.

The observed classes of products are correctly related by the model to computed sums of atom localization energies (L_{mn}). In Table II are listed the L_{mn} for sigma complexes in which pairs of carbon atoms are bonded. For hydrazobenzene and the hydrazonaphthalenes, the observed products correspond to sigma complexes of minimum L_{mn} . Although the sums L_{mn} range from 2.94 to 5.84, all products observed correspond to sigma complexes with $L_{mn} < 3.50$. Two major features of the observed product distribution are not satisfactorily related to the sums L_{mn} . The first is that *ortho*-benzidine is usually a very minor product relative to *para* benzidine and diphenylene, and yet the L_{mn} for the sigma complex corresponding to *ortho*-benzidine is lowest for sigma complexes derived from hydrazobenzene. In the second place, the tabulated L_{mn} contain no real explanation of Dewar's generalization that biphenylenes are found in which the *para* atom of the more basic ring is joined to the *ortho* atom of the less basic ring. The relative energy of the respective sigma complexes favors such a rule by only 0.04β .

The atom localization energies at ring positions of the 2-aminoaniline and 4-aminoaniline fragments are substantially higher than at similar positions in the aniline and 3-aminoaniline fragments. The model predicts a resultant deactivation of usually reactive ring positions with respect to sigma complex formation. This is in general accord with experiment. While *m*-hydrazoaniline rearranges to the substituted *para* benzidine, hydrazobenzenes substituted at the 2 and 4 positions with amino or hydroxyl groups yield only disproportionation products.⁷

In Table III are listed L_{mn} for sigma complexes corresponding to semidine products. In semidines a carbon atom of one fragment is bonded to the nitrogen atom of the other. The sum is distinctly lower for those sigma complexes which join the nitrogen atom of the unprotonated fragment to the ring of the protonated fragment. This is in

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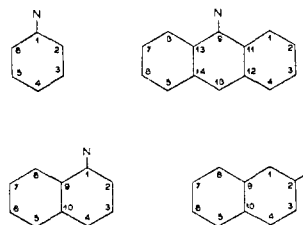


Fig. 3.—Numbering of atoms in radicals.

accord with Dewar's generalization of the selective formation of semidines, if one assumes the more basic nitrogen to be protonated. The minimum L_{mn} correspond to the observed products *ortho*-semidine and *para*-semidine.

TABLE II

SUMS (L_{mn}) OF ATOM LOCALIZATION ENERGIES CORRESPONDING TO C-C SIGMA COMPLEXES FROM SYMMETRICAL HYDRAZOCOMPOUNDS

Aniline L (m,n) ^a	1-Naphthylamine L (m,n)	2-Naphthylamine L (m,n)	9-Anthrylamine L (m,n)
3.33 (2,2) ^b	3.25 (4,4) ^b	2.97 (1,1) ^b	2.94 (10,10) ^c
3.38 (4,2) ^b	3.29 (2,2) ^b	3.63 (8,8)	3.75 (4,4)
3.42 (2,4) ^b	3.76 (5,5)	3.70 (3,3)	4.01 (2,2)
3.47 (4,4) ^b	4.02 (7,7)	3.92 (6,6)	4.38 (1,1)
3.64 (3,2)	4.28 (8,8)	4.13 (5,5)	4.67 (3,3)
3.73 (3,4)	4.56 (6,6)	4.17 (4,4)	4.80 (11,11)
4.01 (1,2)	4.61 (3,3)	4.45 (7,7)	5.13 (9,9)
4.10 (1,4)	4.86 (9,9)	4.87 (10,10)	5.84 (12,12)
4.16 (2,3)	5.37 (1,1)	5.57 (2,2)	
4.21 (4,3)	5.69 (10,10)	5.64 (9,9)	
4.47 (3,3)			
4.84 (1,3)			
4.86 (2,1)			
4.91 (4,1)			
5.17 (3,1)			
5.54 (1,1)			

^a In integer pairs, first number specifies atom on the protonated radical and second specifies atom on the unprotonated radical. ^b Complex corresponds to observed product. ^c Predicted rearrangement product on basis of localization energies.

TABLE III

SUMS OF ATOM LOCALIZATION ENERGIES (L_{mn}) CORRESPONDING TO C-N SIGMA COMPLEXES FOR HYDRAZOBENZENE

L	(m,n) ^a
2.32	(2,N) ^b
2.37	(4,N) ^b
2.63	(3,N)
2.87	(N,2)
2.96	(N,4)
3.00	(1,N)
3.70	(N,3)
4.40	(N,1)

^a In integer pairs, the first number specifies atom on protonated fragment and the second denotes the atom on the unprotonated fragment. ^b Observed product by application of Dewar's generalization.

Longuet-Higgins³¹ has found the basicity of the nitrogen unshared electron pair in heteroaromatics to increase with an increased lowering of the pi electronic energy upon protonation. This change in energy is ΔE_b in our approximation and is listed in Table I. The computed values of ΔE_b suggest that the aniline radical fragment is least basic and

that the 9-anthrylamine radical fragment most basic of those treated. An amino group is computed to increase the basicity much more than a methyl group; and *ortho* and *para* substituents increase the basicity more than *meta* substituents. If one assumes an alkoxy substituent to produce a basicity intermediate between that computed for methyl and amino substituents, then the obtained relative ring basicities allow a generally correct application of Dewar's generalizations on the selective formation of biphenylenes and semidines.⁷

In general, the computed sums of atom localization energies permit a satisfactory explanation of the observed products, including the selective formation of semidines. The selective formation of biphenylenes is less satisfactorily explained and the minor role of *ortho* benzidines in the product distribution contradicts the prediction of the model. These conclusions are valid for either extreme pi complex structure.

Postulated Effect of Solvent.—There is ample evidence of solvent effects on the product distribution in the benzidine rearrangement. The molecular orbital model employed here must be inadequate because it does not include the solvent as a factor influencing the product distribution. The postulation of an interaction of the solvent with the charge distribution in the pi complex allows one to relate the effect of solvent on product distribution to the model for the pi complex and provides a way to assess the relative importance of the covalent and charge transfer functions in the pi complex.

Vecera, Synek and Sterba⁸ have reported a study of the HCl catalyzed rearrangement of hydrazobenzene in water-dioxane and water-ethanol solutions. They find that in pure water, the biphenylene to *para* benzidine ratio is less than a third of its value in dioxane and less than half its value in ethanol. Ethanol-water mixtures gave intermediate values of the ratio. The over-all rate of rearrangement was found to pass through a minimum for both ethanol-water and dioxane-water mixtures. Carlin and Forshey¹³ have pointed out the extreme effect of solvent on the rearrangement product distribution of 3,3'-5,5' tetramethylhydrazobenzene. In 10% aqueous HCl, the biphenylene to *para* benzidine ratio is 0.66 and no *ortho*-benzidine is formed. In 95% ethanol saturated with HCl gas, the biphenylene to *para* benzidine ratio is 1.60.¹² In 2:1 sulfuric acid, the biphenylene to *para* benzidine ratio is 1.17 and about a third as much *ortho*-benzidine as biphenylene is formed. In general, the rearrangement of 3,3'-5,5' tetrasubstituted hydrazobenzenes in 2:1 sulfuric acid is unusual in that *ortho*-benzidines are commonly a major component of the product distribution.¹¹ Wittig, Joos and Rathfelder¹⁹ found a major solvent effect on product distribution in the acid catalyzed rearrangement of N,N'-tetramethylene-hydrazobenzene. In aqueous HCl the major product is the reduced molecule 1,4 dianilino-butane (26%), which is accompanied by N,N'-tetramethylene-*o*-semidine (20%) and N,N'-tetramethylene-biphenylene (16%). When the rearrangement is conducted in HCl saturated benzene,

the same products appear in the amounts (2%), (10%) and (60%), and in addition N,N'-tetramethylene-biphenylene (2%) is found.

It is possible to interpret these observations, and the selective formation of biphenylenes noted by Dewar, if one assumes that solvent molecules "solvate" the regions of high positive charge in the pi complex and that the solvating molecules sterically hinder the unfolding of the pi complex. In Table IV is listed the charge distribution in the protonated and unprotonated fragments as computed for the two extreme structures. For the covalent structure, the positive charge is located mainly (63%) on the protonated nitrogen and the adjacent carbon. No net charge resides on the unprotonated fragment. Steric hindrance of the *ortho* positions of the protonated fragment by solvating molecules would explain the observation that the biphenylene is formed in which the *para* position of the more basic (protonated) ring is bonded to the *ortho* position of the other. The minor role of *ortho*-benzidine is attributable to the same steric hindrance. If the charge transfer wave function is adopted, then the positive charge is computed to reside mainly (57%) on the nitrogen of the unprotonated fragment. The selective formation of biphenylenes is now incorrectly explained by steric hindrance of the adjacent *ortho* positions. If the wave function is predominantly the covalent function with a smaller proportion of charge transfer function, then some net positive charge will reside on both nitrogen atoms. The repulsive forces between these charges would be expected to be greatest in nonpolar solvents. Thus, as Vecera has noted,⁶ nonpolar solvents would favor the rotation of the initial pi complex, in which the fragment nitrogen atoms are adjacent, to a configuration which can unfold to biphenylene.

TABLE IV
COMPUTED CHARGE DENSITY (q_i) ON ATOMS OF THE MONO-
PROTONATED HYDRAZOBENZENE PI COMPLEX

Structure fragment	Atom				
	N	1	2	3	4
Covalent:					
Protonated	+0.403	+0.224	+0.073	+0.027	+0.174
Unprotonated	0.000	0.000	0.000	0.000	0.000
Charge transfer:					
Protonated	+0.135	+0.067	-0.075	+0.004	-0.058
Unprotonated	+0.571	+0.000	+0.143	+0.000	+0.143

It is concluded that under the assumption that the covalent structure is predominant in the mono-protonated pi complex, the major effects of solvent on product distribution can be qualitatively explained in terms of the interaction of the solvent with regions of high positive charge in the mono-protonated pi complex.

Conclusions.—The general agreement with experiment found here in computational applications of the adopted model supports the picture that a monoprotated pi complex unfolds by way a sigma complex to the observed products. In most respects the applications fail to distinguish the possible extreme structures for the pi complex wave function. Qualitative features of the effect of solvent on product distribution can be explained in terms of solvation of highly positive regions of

the pi complex. Such an explanation works best with the pi complex charge distribution corresponding predominantly to the covalent structure.

Suggested Experiments.—The possibility that the blue violet colors observed by Wittig, Joos and Rathfelder¹³ in the acid catalyzed rearrangement of cyclic hydrazobenzenes may be a property of the pi complex, provides a possibly important means of studying the nature of the pi complex and its role in the rearrangement mechanism. They observed these colors during the acid catalyzed rearrangements of N,N'-trimethylene-hydrazobenzene and N,N'-tetramethylene-hydrazobenzene. The color was not reported for the rearrangement of N,N'-pentamethylene-hydrazobenzene. It is reasonable to suppose that in the former two cases the shorter methylene chains greatly slowed the unfolding of the pi complex to products. The observed color may be attributed to the pi complex thus stabilized. The observation of such colors during the acid catalyzed rearrangement in solution has never previously been reported for hydrazo compounds not having a chain joining the nitrogen atoms. These cyclic hydrazo compounds may show during rearrangement additional physical properties which can be correlated with the transient colors and postulated structures for the pi complex.

It is clear that both nuclear magnetic and electron spin resonance spectra should be searched for time dependent features which may be associated with

the transient colors and postulated pi complex. The covalent and charge transfer structures should have qualitatively different chemical shifts of the proton resonances, relative to benzene protons. The electron spin resonance spectra may show the transient colors to be associated with the pi complex triplet state, with independent radical fragments, or with an oxidation product of the hydrazo compound.³⁸ A singlet ground state should give no resonance.

Finally, it is probable that hydrazo derivatives of paracyclophanes³⁹ can be synthesized. They may react thermally or with acid to provide additional interesting stable pi complexes.

Acknowledgments.—I wish to thank Professor R. B. Carlin and Dr. H. G. Ebner for pointing out relevant knowledge from experiments. Comments on theoretical sections by Professor R. G. Parr have been helpful. Discussions with Dr. A. M. Trozzolo, Dr. R. W. Murray and with Dr. D. E. Wasserman, and Dr. E. A. Chandross also have been of value.

(38) Experiments performed at Bell Telephone Laboratories since the submission of this manuscript support the latter possibility. Studies of the electron spin resonance spectra of the blue solutions which occur during the rearrangement of N,N'-tetramethylene-hydrazobenzene by trifluoroacetic acid in benzene suggest very strongly that the blue color is due to the positive ion produced by oxidation of the hydrazo compound. It is still possible that relatively stable pi complexes may be produced during the rearrangement of the cyclic hydrazo compounds.

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Rates of Proton Abstraction from Monosubstituted Acetylenes

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RECEIVED JULY 24, 1961

Rates of hydroxide ion catalyzed proton exchange between six alkynes, R—C≡CH, and aqueous *t*-butyl alcohol have been measured by n.m.r. line broadening techniques. Second-order rate constants have been shown to be independent of the base concentration and assumed to be independent of the alkyne concentration. Four of these define a line of slope (ρ^*) 2.3 when plotted against the Taft σ^* parameters for the groups R. Phenylacetylene gives a rate which misses this line by only 0.3 log unit, in accord with theoretical expectations. The point given by 3,3-diethoxy-1-propyl deviates widely from the correlation line and this is attributed to the relatively slow but complete abstraction of the 3-proton by hydroxide. The rate determining step for exchange is pictured as the removal of the terminal, acetylenic proton by hydroxide ion. The relative ionization constants of alkynes are thought to be governed by the rates of proton abstraction since the reverse reaction must have a very low activation energy. Several new equations have been developed relating peak shapes to exchange rates.

A number of papers have appeared describing the application of nuclear magnetic resonance (n.m.r.) spectroscopy to the measurement of proton exchange rates.¹⁻⁶ These methods, in their simplest form, are based on one of two ideas. (1) Two distinguishable protons will give rise to two lines in n.m.r. spectra provided that the frequency with which they exchange is small by comparison with the difference between the two absorption frequencies. These lines merge if the exchange fre-

quency is large with respect to the difference between the absorption frequencies and with intermediate exchange frequencies intermediate line shapes are predicted. (2) If a multiplet is caused by spin-spin coupling with a proton which is also exchanging the multiplet will merge to a single line if the exchange frequency is large with respect to J , the spin-spin coupling constant. Again, intermediate line shapes are predicted for intermediate exchange rates.

If an alkyne, R—C≡CH, is dissolved in a dilute, partially aqueous solution of hydroxide ion the exchange reaction shown in eq. 1 takes place.⁷⁻⁹

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