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THE DUPLEX BASICITY OF ARYLAMINES AND THE BENZIDINE REARRANGEMENT

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Amines are the best studied organic bases. Their basicity and their contributions to the π basicity of aromatic compounds are well known.[1] Yet because of their well-known basicity amino substituents have been avoided in studying the interactions of π bases with protonic acids. For example, complexes between hydrogen halides and a large number of aromatic compounds are reported[1,2] but none have amino substituents. The same is true for hydrogen bonding to π bases.[3,4]

In this work, N,N-dimethylaniline (DMA) was used as an example of a system containing both π and N as basic sites and hydrogen bonding of n-amyl alcohol to these sites was used to measure their basic strengths. In Fig. 1 are several infrared spectra which reveal at least three types of OH in DMA. Curve III shows all three types in a single spectrum, removing any question of shifts caused by solvent. In III, the band at 3634 cm.$^{-1}$ is free OH (compare I); the band at 3575 cm.$^{-1}$ is π bonded OH;[5] and the broadest band at ca. 3447 cm.$^{-1}$ (compare II) corresponds to N bonded OH by its characteristic shift and shape. Spectrum I shows the typical free OH and alcohol-alcohol bonded OH. Spectrum II shows only the π and N bonded OH. In this case, because of the high concentration of DMA (solvent), none of the alcohol is free and none is alcohol-

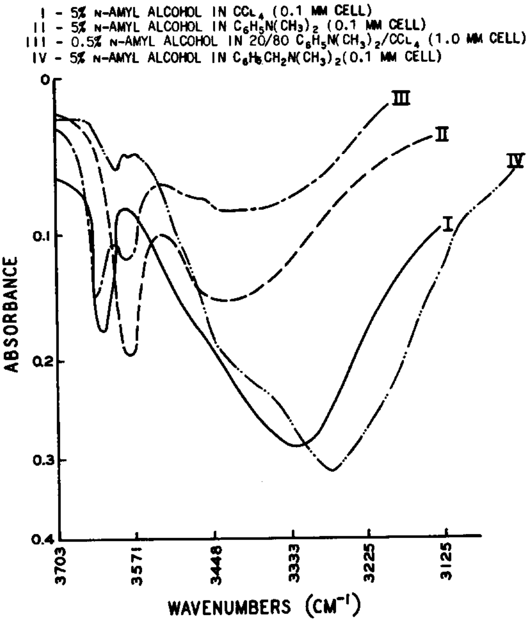

FIG. 1. Spectra of solutions as noted with similar solutions less alcohol in reference beam.

alcohol bonded. At other concentrations intensities of both π and N bands vary in direct proportion to alcohol and to DMA concentrations, i.e., both π and N complexes are 1:1 in alcohol to DMA.

Spectra II and IV show the relative importance of π and N bonding for DMA, an aromatic amine, and N,N-dimethylbenzylamine (DMBA), an "aliphatic" amine with an appended aromatic group. In DMA, the π band is strong and sharp, and the N band is weak though broad. The DMBA spectrum, IV, is more difficult to interpret. The band at 3597 cm.$^{-1}$ could be free OH shifted from a more typical value by the "solvent", DMBA. This interpretation is supported by what appears to be an alcohol-alcohol band at 3279 cm.$^{-1}$. This also indicates that only weak bases are competing with the normal alcohol monomer-polymer equilibrium. This leaves the blip at 3575 cm.$^{-1}$ for π bonding and the shoulder at 3436 cm.$^{-1}$ for N bonding. No matter which is the π band for DMBA, it is weak relative to the DMA π band. Thus, these spectra support the much-described delocalization of the N electrons to an adjacent ring π system. The intensity of the π band in DMA is surprising. Preliminary equilibrium measurements for π versus N hydrogen bonding show N to be only two or three times more basic than π.

Strong hydrogen bonding to π electrons in arylamines may play a role in reaction mechanisms such as the "thermal" benzidine rearrangement in alcohol.[6] Both π and N bonding are possible in the starting hydrazoaromatic compounds. Shine suggests[6] that N hydrogen bonding facilitates the "thermal" reaction. A similar and perhaps stronger case can be made for hydrogen bonding to π electrons in an intermediate. Since protons will bond to any base capable of accepting a hydrogen bond (e.g., π electrons), the π bonding phenomenon may be the key to both the thermal and acid catalyzed benzidine rearrangements. A proton bonded to the π electrons of one aryl group in hydrazobenzene would make that aryl group a good π acid. As such it could form a π complex with the remaining aryl group. This aryl-bonded-to-aryl-bonded-to-proton complex has all of the advantages of the aryl-bonded-to-aryl complex previously proposed.[7,8]

While this protonated π complex seems reasonable, a more attractive intermediate is a π bonded proton sandwich, aryl-bonded-to-proton-bonded-to-aryl. The sandwich could proceed to a transition state (or intermediate) pictured in Fig. 2a with an electron (from former N-N bond) between the proton and each ring. The sandwich combines the features of the π complex[7] and the π bonded proton first proposed as an intermediate in electrophilic substitutions.[9] While the latter has been rejected from a rate determining role in electrophilic substitution,[2,10] its existence is not denied. In fact, the formation of such a π complex has a much lower energy of activation than a σ complex and therefore, it could not contribute to the major energy barrier.[11]

The proposed sandwich should be more stable than the simple proton π complex. The bonding in the sandwich is similar to typical hydrogen bonding. If only the odd electron from each ring[12] is used to bond with the proton, then it is identical to the bonding in boranes[13] where the hydrogen bond brings two boron nuclei close enough to get a B-B bond with a resonance energy of 10.9 kcal./mole.[14] A similar advantage may be seen for two close aromatic rings. It may be significant that the number of π electrons in the two rings is 10 or, including the electron pairs on N, 14, both 4n + 2 numbers. This system fails to follow Hückel's rule in that it is neither monocyclic nor coplaner. However, there are many examples which violate parts of the rule but still show relative electronic stability.[15]

Another advantage of the proton sandwich is that it would facilitate the reaction by bringing the two aromatic groups within 3.0 Å or less. In typical hydrogen bonds, the two groups sharing hydrogen are from 2.4 to 3.0 Å apart.[16] This is less than the distance between aromatic planes in ordinary π complexes (3.0-3.5 Å),[1] in ferrocene (3.32 Å),[17] in graphite (3.4 Å),[18] and in the smallest paracyclophane, /2,2/, (3.09 Å).[19]

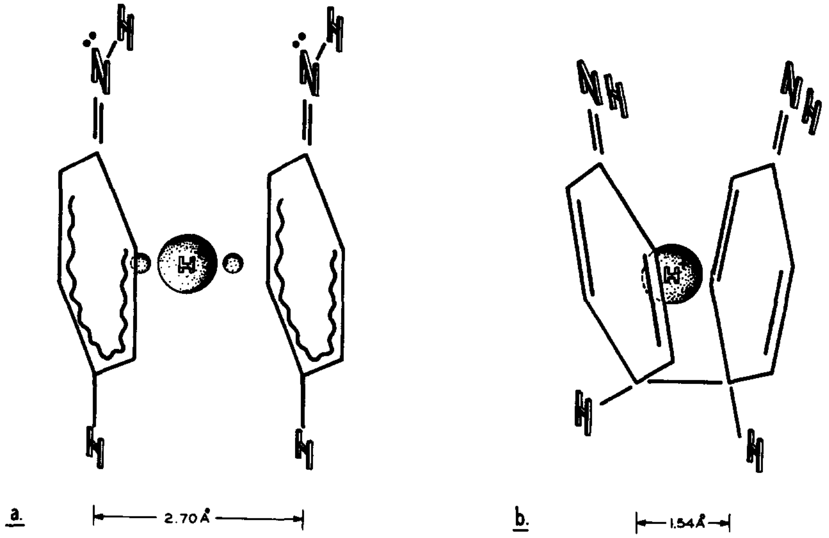

FIG 2. Drawn to scale using the dimensions taken from bond distances in Å: C-C, 1.40; C-H, 1.10; C=N, 1.29; N-H, 1.01; H^+ diameter, 0.74; C=N-H angle, 120°.

The proton sandwich, like ferrocene, should enjoy free rotation of the two aromatic planes around a centered perpendicular axis common to them. Rotation leads to o,p' benzidine products, while rotation and a slight horizontal sliding of the rings relative to each other gives semidine products.[20] None of these motions is untoward. The products normally found[8,20,21] for a variety of cases fit obvious geometric or electronic restrictions in rotations. Carlin[20] has shown the rearrangement, reduction and oxidation products have a common path; perhaps the sandwich.

A possible nonrotational reaction sequence may involve a simple proton-π complex first. Then this complex would draw the other aryl group in to form a sandwich. When the N-N bond breaks. the aryl planes may have sufficient momentum to continue moving until they touch at their other ends, forming a p,p' bond (Fig. 2b). An analogy is a breaking nutcracker with a proton for the nut. If the hinge (N-N bond) broke suddenly, the other ends would hit each other. The proton would be extruded out the newly opened end and be captured by a basic nitrogen. Tautomeric shifts and ionizations complete the reaction.

The rearrangement of m,m'-diaminohydrazobenzene[8], a substrate with high π electron density, fits the proton sandwich mechanism. The monoprotonated intermediate proposed in that paper differs from the proton sandwich only in placing the proton on N. With the proton on N it is more difficult to picture the driving force for N-N bond rupture than with the proton sandwich.

It is immaterial whether the proton is first or second order[21,22] in simple benzidine rearrangements. A second proton may be placed on N in the sandwich making a protonated imine. The positive isotope effect found with deuterated acids[23] is consistent with this mechanism as is the lack of effect of deuterium as a ring substituent.[21]

In summary, this work shows that a strong π hydrogen bond occurs in arylamines. Based on experimental work and theoretical reasons, a proton sandwich intermediate is proposed for the benzidine-semidine rearrangement. The sandwich is consistent with all the information on the rearrangement and it overcomes some spatial shortcomings of earlier mechanisms.*

*NOTE ADDED IN PROOF: A very recent paper by D. J. Cram and M. Goldstein (J. Am. Chem. Soc., 85, 1063 (1963)) suggests an intermediate similar to the proton sandwich to explain a neighboring group effect. Their intermediate is a proton sandwich between a double bond and a phenyl group.

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