Gas-Phase Basicities of Substituted Anilines. Inferences about the Role of Solvent in Dictating Site of Protonation

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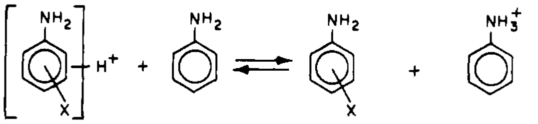
Abstract: The relative gas-phase base strengths of meta and para substituted aniline have been determined by pulsed ion cyclotron resonance spectroscopy and, with the exception of *m*-toluidine and *m*-anisidine, are found to correlate reasonably well with their corresponding aqueous-phase quantities. The deviations are interpreted in terms of protonation on the aromatic ring rather than at nitrogen as in the remaining compounds. Inferences are drawn about the influence of aqueous solvent in directing protonation at nitrogen.

Comparison of gas-phase acidities and basicities with those obtained in the condensed phase provides information about the role of differential solvation. Linear correlations have already been established between aqueous- and gas-phase acidities of meta and para substituted phenols[2] and between the base strengths of a variety of substituted pyridines[3,4] in the gas phase and in water. Successful correlations have also been drawn between the gas-phase acidities of substituted benzoic acids[5] and the basicities of monosubstituted benzenes[6] and their corresponding (solution phase) σ and σ^+ values. In all cases the aqueous media serves to attenuate, in varying degrees, the substituent effects observed for the gas-phase proton-transfer processes. The studies of Kebarle and co-workers[5,6] illustrate yet another benefit (as well as a caution) which may be drawn from attempted correlations and gas- and solution-phase acidities and basicities. In their investigation of substituted benzoic acids,[5] Yamdagni, McMahon, and Kebarle noted that the gas-phase acidity of the *p*-hydroxy compound was considerably higher than expected from its solution-based σ^0 value. The authors interpreted this deviation from the correlation line as evidence that, in the gas phase, proton removal from *p*-hydroxybenzoic acid occurs not from the carboxylate group but rather from the OH substituent. In a later study,[6] Lau and Kebarle noted that the gas-phase basicities of several substituted benzenes (notably, benzaldehyde, benzonitrile, and nitrobenzene) failed to properly correlate with solution-phase σ^+ values. Again such deviations were taken as evidence for alternative protonation sites in these compounds (i.e., on the substituent rather than on the aromatic ring). Correlation was achieved between the solution- and gas-phase basicities of a number of other substituted benzenes (i.e., the alkyl and halobenzenes, phenol, anisole, and aniline). It was concluded, therefore, that in the gas phase these compounds protonated on the aromatic ring, although it was also recognized that for aniline the ring and substituent affinities were probably very close.

The preceding paper[7] provided evidence indicating that, in the gas phase, aniline is, in fact, a nitrogen base. Protonation at carbon was found to be 1-3 kcal/mol less favorable, a difference small enough that selective substitution might be expected to effect a switch in the order of affinities. (Unfortunately this difference is too small for σ^+ correlations to be a reliable diagnostic of the site of protonation.) In this paper we present our results on the gas-phase proton affinities of a variety of meta and para substituted anilines. It will be seen that our data are best interpreted by concluding that the preferred site of protonation in each of these compounds (be it at nitrogen or on the aromatic ring) depends on the detailed nature of the substituent.

Method, Results and Discussion

Trapped cell ion cyclotron resonance spectroscopy[8] has been employed to measure the free energies for processes 1 in the

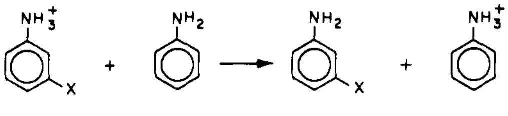


(1)

X = H; meta and para Me, OMe, Cl, F

gas phase. In Figure 1 these data are related to the corresponding solution-phase free energies.[9] With the exception of the points for *m*-methyl and *m*-methoxy substituents, relative gas-phase base strengths correlate reasonably well with those obtained in aqueous solution with an attenuation factor of 2.6. This result supports the assumption that in the gas phase as well as in aqueous solution all of the substituted anilines which correlate do react preferentially at nitrogen. Recall, however, in the gas phase the carbon basicity of aniline is only slightly lower than the preference to react at nitrogen.[7] Therefore, the noted deviations from linear correlation may be understood (in accord with the nature of the substituent) by assigning protonation in the gas phase to the aromatic ring in these systems, rather than to the amino substituent.

We have calculated by means of ab initio molecular orbital theory[10] the nitrogen proton affinities of a number of meta and para substituted anilines and, in addition, the carbon proton affinities of *m*-toluidine and *m*-anisidine. Nitrogen and ring proton affinities have not been arrived at by direct calculation[14] but rather via the use of *isodesmic* reactions.[15] ΔE for nitrogen protonation in a substituted aniline is obtained by combining the calculated STO-3G energy for the process



with the experimental proton affinity of aniline[3b,16] (ΔH° = 208.8 kcal/mol), which has been established to protonate preferentially at nitrogen.[7] Correspondingly, theoretical estimates of the ring affinities of meta substituted anilines are obtained by biasing ΔE for the *isodesmic* reactions by the experimental proton affinity of *m*-xylene[16,17] (194.6 kcal/mol), which must react on the aromatic ring. The theoretical nitrogen proton affinities, expressed relative to that of aniline, are plotted in Figure 1 alongside of our experimental data. In view of previous experiences with the levels of molecular orbital

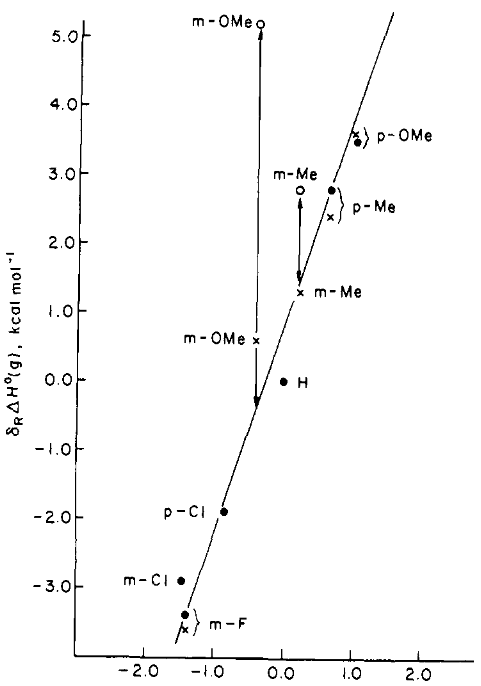
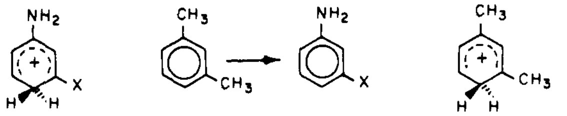
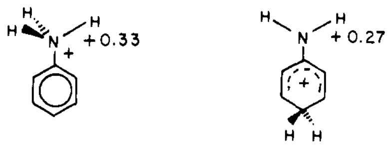


Figure 1. Enthalpies of *isodesmic* processes, $C_6H_5NH_3^+ + X\text{-}C_6H_4NH_2 \rightleftharpoons C_6H_5NH_2 + X\text{-}C_6H_4NH_3^+$, in the gas phase vs. free energies in aqueous solution (kcal/mol). Open and closed circles indicate gas-phase data from ion cyclotron resonance spectroscopy; crosses show theoretical STO-3G calculations. Open circles correspond to measurements on processes believed to involve carbon rather than nitrogen protonation. See text for explanation. Aqueous-phase data from ref 9.



theory[3b,13b,18] dealt with here, it is not surprising that the calculated nitrogen base strengths agree remarkably well with the gas-phase experimental data in those cases where nitrogen protonation is certain (all para substituted anilines and *m*-fluoroaniline) and exhibit a reasonable degree of correlation with the solution-phase measurements in all instances. Calculated carbon proton affinities for *m*-toluidine and *m*-anisidine (212.8 and 217.4 kcal/mol,[16] respectively) are in reasonable accord with the measured proton affinities for these compounds (211.6 and 214.0 kcal/mol),[16] providing further support for our assignment of the aromatic ring rather than the nitrogen as the reactive site.

Finally our data on the gas-phase proton affinities of the substituted anilines, when compared to the relative solution-phase basicities of these same compounds, allow comment on the magnitude of the difference in free energies of solvation between nitrogen and ring protonated forms. In particular, whereas in solution both *m*-toluidine and *m*-anisidine are nitrogen bases, in the gas phase, the affinities to react on the aromatic ring are greater by 1.3 and 5.8 kcal/mol, respectively. The latter quantity provides a lower limit to the differential solvation energy between nitrogen and carbon sites. We strongly suspect, however, that the actual differential solvation energy in these compounds is considerably larger. Thus, it is known that in aqueous media protonation in *m*-phenylenediamine occurs at nitrogen and not on the aromatic ring.[19,20] According to the theoretical STO-3G calculations, however, the carbon proton affinity of *m*-phenylenediamine is some 17 kcal/mol greater than that at nitrogen.[22] Such a value for the differential solvation energy is considerably larger than the figure of 7 kcal/mol[23] arrived at for alkyl substituted ammonium ions by simple consideration of the fact that the N-protonated form has one more protonic (N-H) hydrogen available for specific (hydrogen bonded) solvation than does the carbon protonated species. Calculated STO-3G charges[24] suggest that the reason for the apparent disparity is simply that each of the NH hydrogens in a molecule such as N-protonated aniline bear significantly more positive charge than those in the ring protonated form. This is consistent with the notion that the positive charge resides to a greater degree in the π system of the benzenium structure, where it is orthogonal to the plane occupied by the amino hydrogens.



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Effects of Electron Repulsion in Conjugated Hydrocarbon Diradicals

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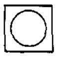
Abstract: It is shown that classification of conjugated diradicals into two types, according to whether their Hückel NBMO's can be confined to disjoint sets of atoms, provides a useful basis for understanding the electronic properties of such diradicals. If the Hückel NBMO's can be so confined, the lowest singlet and triplet states are nearly degenerate at the SCF level, and both SCF wave functions use a common set of MO's. On the other hand, if the Hückel NBMO's cannot be localized to disjoint groups of atoms, then the triplet lies well below the corresponding open shell singlet at the SCF level, and the MO's in the SCF wave functions for the two states differ. These general expectations, which emerge from previous theoretical work on cyclobutadiene (**1**) and trimethylenemethane (**2**), are applied to several other fully conjugated hydrocarbon diradicals. Ab initio SCF and full π space CI calculations on 1,3-dimethylenecyclobutadiene (**7**) and tetramethylenethane (**8**) are reported, which confirm the predictions for each of these molecules. It is demonstrated that PMO analysis of the mode of union of two odd AH's can be used to identify the class to which the resulting diradical belongs. The relationship between NBMO localizability to different sets of atoms in an AH diradical and the number of starred, compared to unstarred, atoms in the AH is also explored.

Diradicals are molecules possessing a pair of nonbonding molecular orbitals (NBMO's) that are occupied by a total of two electrons. One series of diradicals, in which the NBMO's occur in fully conjugated π systems, is comprised of the [4*n*]annulenes. Cyclobutadiene (**1**) is the first member of this series and the one that has received the most attention, both theoretical and experimental.[1] Another type of fully conjugated hydrocarbon diradical consists of those molecules for which no classical Kekulé structures can be written.[2] In this series trimethylenemethane (**2**) is the prototype and also the molecule that has been most studied.[3]



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In this paper we use a PMO approach[4] to show that conjugated diradicals result from the union of two odd alternant hydrocarbon (AH) fragments at a node in the NBMO of at least one of them. The PMO approach is a useful one for dividing diradicals into two classes. In one class the Hückel NBMO's can be chosen so that they are confined to different sets of carbon atoms, as is the case in the [4*n*]annulenes. In the other class, to which **2** belongs, the Hückel NBMO's cannot be so confined. This classification is shown to be of great utility for predicting the important differences in the effects of electron repulsion in the two classes of diradicals. These predictions are compared with the results of ab initio SCF and full π space CI calculations on one molecule from each class.

PMO Analysis of 1 and 2

The π systems of cyclobutadiene (**1**) and trimethylenemethane (**2**) can be analyzed as resulting from the union of an allyl radical (**3**) with a carbon bearing a p-π orbital (**4**), as shown in Figure 1. The existence of a pair of NBMO's in both **1** and **2** emerges clearly from this analysis. Since **3** and **4** are odd alternant hydrocarbons (AH's), each possesses an NBMO.[4] The union of these odd AH fragments to give both **1** and **2** takes place at a nodal plane of the NBMO of **3**. Consequently, the degeneracy of the NBMO's of **3** and **4** is not lifted by their mutual interaction in either mode of union. The noninteraction of the NBMO's of the fragments does not, however, by itself assure the survival of two NBMO's in **1** and **2**, for the p orbital of **4** does interact with the bonding and the antibonding MO of **3**. Nevertheless, the pairing theorem[4,5] guarantees, at least at the level of the Hückel theory, that these latter two MO's of **3** have coefficients of the same magnitude at each carbon and energies that are equally spaced about the energy (α) of the NBMO. This fact is sufficient to ensure that the interaction of the p orbital of **4** with these two MO's of **3**, while lowering the energy of the bonding MO and raising that of the antibonding MO, leaves an MO at the nonbonding level.[6] An orbital interaction diagram is shown in Figure 1.

Figure 1 shows that the π systems of **1** and **2** can both be analyzed in terms of interactions between the same MO's of **3** and **4** and that both **1** and **2** are diradicals. The diagram also illustrates a difference between **1** and **2** that results from the two modes of union of **3** and **4**. Union of **4** to the two terminal carbons of **3** results in a stronger interaction between the p orbital of **4** and the bonding and antibonding MO of **3** than does union of **4** to the central atom of **3**. Consequently, the bonding and antibonding MO's of cyclobutadiene lie respectively at lower and higher energies ($\alpha \pm 2\beta$) than the corresponding MO's in trimethylenemethane ($\alpha \pm 3^{1/2}\beta$).[7] However, a difference between **1** and **2** of much greater significance is in the form taken by the NBMO that arises from the three-orbital interaction in the two different modes of union.

In both **1** and **2** this NBMO results from the p orbital on **4** mixing in the bonding MO of **3** in an antibonding fashion and the antibonding MO in a bonding fashion. Application of the pairing theorem shows that the amount of mixing of these two MO's into the p AO is equal. Moreover, since the pairing theorem requires that the magnitudes of the coefficients of the AO's in these two MO's be the same, mixing of these two MO's into the p orbital of **4** results in a cancellation of their contributions at the carbon atom(s) in **3** where union with **4** occurs.