Inversion Barriers in *para*-Substituted Anilines from *ab initio* Molecular Orbital Theory

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Summary The effects of *para*-substituents (NO_2, CH_3, F, OH, NH_2) on the barrier to inversion and the geometry at the nitrogen atom in aniline have been studied using *ab initio* molecular orbital theory; substituents which are π-electron acceptors lower the barrier and lead to a slight flattening of the nitrogen pyramid while π-electron donors raise the barrier and increase the pyramidalization of the bonds at the nitrogen atom.

BOTH theory[1] and experiment[2,3] predict that the bonds at the nitrogen atom in aniline are pyramidal (I) and that there is a barrier to inversion through a planar transition state (II). Because the planar form of the molecule can be

orbital theory throughout, employing the STO-3G minimal basis set.[7] Geometries of the substituted anilines are taken as standard[8] except that the angle (α) between the NH_2 plane and the plane of the ring is optimized. The three bond angles at the nitrogen atom are constrained to be equal. Orbital and overlap electron populations are calculated using Mulliken's method.[9]

The results are quoted in the Table where the quantities listed have the following meanings. $\Delta\alpha$ is the change‡ in the angle α relative to its calculated value in aniline; ΔV is the corresponding change in the inversion barrier; $q_\pi(X)$ is the number of π electrons donated (positive) or accepted (negative) by the substituent (X) into the ring; and $\Delta_\pi n$–

TABLE. *Calculated quantities for* para-*substituted anilines* ($X-C_6H_4NH_2$)

X	$\Delta\alpha^a$ (degrees)	ΔV^a (kJ/mol)	$q_\pi(X)^{a,b}$	$\Delta q_\pi(NH_2)^{a,b}$	Interaction energy^a (kJ/mol) pyramidal	planar
NO_2	−3·4	−3·51	−0·041	+0·018	+9·2	+12·6
H	0	0	0	0	0	0
CH_3	+0·3	+0·59			−2·1	−2·5
F	+0·3	+0·59	+0·073	−0·003	−3·3	−3·8
OH	+1·2	+1·67	+0·095	−0·007	−6·3	−7·9
NH_2^c	+1·7	+2·38	+0·086	−0·009	−6·7	−9·2

^{a} Defined in text. Calculated values of α, V, and q_π (NH_2) for aniline are 47·7°, 11·38 kJ/mol, and +0·095, respectively.[1] ^{b} Values quoted for most stable (pyramidal) conformation. ^{c} The most stable conformation when $X=NH_2$ is one in which one NH_2 group is directed upwards and the other downwards.

stabilized through delocalization of the nitrogen lone pair into the π-system of the ring, one might expect a smaller angle of pyramidalization (shown as α in I) and a smaller barrier to nitrogen inversion in aniline than in aliphatic amines. These ideas are born out by experiment.[2-4]

Tyler and coworkers[2,5] investigated the effect of *para*-substitution on the pyramidal nature of the bonds at nitrogen in aniline. They found that a fluorine substituent considerably increases the pyramidalization and rationalized this result in terms of postulated electronic interactions, characteristic of the substituent. It is of interest to test and extend these observations by means of theoretical calculations on the molecules $XC_6H_4NH_2$ (X = NO_2, H, CH_3, F, OH, and NO_2).† In a closely related study,[6] theoretical and experimental descriptions of the effect of *para*-substitution on the torsional barrier in phenol were found to be in good agreement and could be readily interpreted in terms of the π-electron donating or accepting character of the substituent.

We have used single determinant *ab initio* molecular
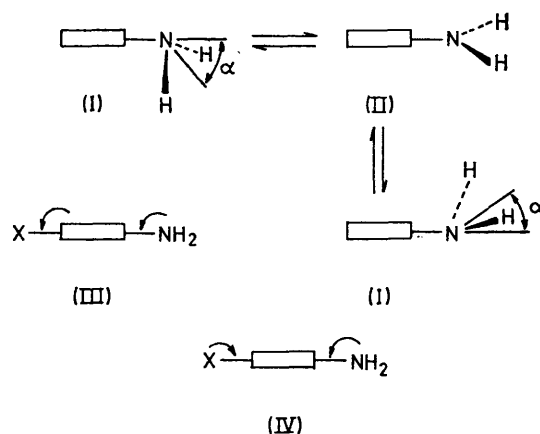
† For aniline,[1] both the angle α (47·7°) and inversion barrier V (11·38 kJ/mol) were calculated to be somewhat higher than experimental values[2,3] (37·7° and 6·74 kJ/mol, respectively).

‡ In all cases, we take the *change* in a calculated or experimental quantity to be the value in the substituted aniline less the value in aniline.

(NH$_2$) is the change in q_π(NH$_2$) relative to aniline.§ The interaction energy of the substituent X with the NH$_2$ group is defined as the energy change in reaction (1). Interaction energies for both pyramical and planar forms of the molecules are tabulated.

$$p\text{-NH}_2\text{C}_6\text{H}_4\text{X} + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5\text{NH}_2 + \text{C}_6\text{H}_5\text{X} \qquad (1)$$
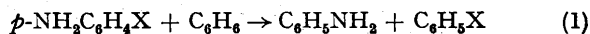
The following points are of special interest: (i)*Para*-substitution by the π-accepting NO$_2$ group lowers the barrier to nitrogen inversion in aniline. Conversely, substitution by π-electron donors (Me, NH$_2$, OH, F) increases the barrier. (ii) *Para*-substitution by the π-accepting NO$_2$ group leads to flattening of the nitrogen pyramid; substitution by π-electron donors has the opposite effect. The only experimental gas phase data on this point comes from a microwave determination of $\Delta\alpha$ for p-fluoroaniline.[5] Although theory and experiment agree that the *para*-fluoro-

substituent increases the pyramidalization, the theoretical value of $\Delta\alpha$ (0·3°) is much smaller than the experimental estimate (8·7°). Further gas phase data may explain this discrepancy. (iii) The calculated interaction energies suggest that aniline is stabilized by *para*-substituents which are π-electron acceptors and destabilized by π-electron donors. (iv) The values of q_π (X) and Δq_π (NH$_2$) in the Table suggest a rationalization of the above results in terms of the reinforcement (III) of, or opposition (IV) to, the delocalization of the nitrogen lone pair by the substituent X. Such interactions occur in both the planar transition state and the pyramidal ground state of these molecules but are more important in the planar conformation (see, for example, the calculated interaction energies for planar and pyramidal forms). This leads to the observed variation in geometry and inversion barriers.

§ The π-charge donated by NH$_2$ into a *planar* XC$_6$H$_4$ group is obtained from the increase in the number of π-electrons in this group in XC$_6$H$_4$NH$_2$ compared with XC$_6$H$_5$. For the special case X=NH$_2$, q_π(NH$_2$) is equal to half the increase in the number of π-electrons in the ring in NH$_2$C$_6$H$_4$NH$_2$ compared with C$_6$H$_6$. When X is non-planar and different from NH$_2$, q_π(X) and q_π(NH$_2$) cannot be uniquely defined.

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