Objectives

After completing this section, you should be able to

1. use the concept of resonance to explain why arylamines are less basic than their aliphatic counterparts.
2. arrange a given series of arylamines in order of increasing or decreasing basicity.
3. discuss, in terms of inductive and resonance effects, why a given arylamine is more or less basic than aniline.

Study Notes

With reference to the discussion of base strength, the traditional explanation for the base-strengthening effect of electron-releasing (I) substituents is that such substituents help to stabilize the positive charge on an arylammonium ion more than they stabilize the unprotonated compound, thereby lowering ΔG°.

The electron-withdrawing (i.e., deactivating) substituents decrease the stability of a positively charged arylammonium ion.

Note that the arylammonium ion derived from aniline, PhNH₃⁺, is commonly referred to as the anilinium ion.

Basicity of aniline

Aniline is substantially less basic than methylamine, as is evident by looking at the pKₐ values for their respective ammonium conjugate acids (remember that the lower the pKa of the conjugate acid, the weaker the base).

This difference in basicity can be explained by the observation that, in aniline, the basic lone pair on the nitrogen is to some extent tied up in – and stabilized by – the aromatic p system.
This effect is accentuated by the addition of an electron-withdrawing group such as a carbonyl, and reversed to some extent by the addition of an electron-donating group such as methoxide.

In the case of 4-methoxy aniline (the molecule on the left side of the figure above), the lone pair on the methoxy group donates electron density to the aromatic system, and a resonance contributor can be drawn in which a negative charge is placed on the carbon adjacent to the nitrogen, which makes the lone pair of the nitrogen more reactive. In effect, the methoxy group is ‘pushing’ electron density towards the nitrogen. Conversely, the aldehyde group on the right-side molecule is ‘pulling’ electron density away from the nitrogen, decreasing its basicity.

At this point, you should draw resonance structures to convince yourself that these resonance effects are possible when the substituent in question (methoxy or carbonyl) is located at the ortho or para position, but not at the meta position. An imine functional group is characterized by an sp\(^2\)-hybridized nitrogen double-bonded to a carbon. Imines are somewhat basic, with pK\(_a\) values for the protonated forms ranging around 7. Notice that this is significantly less basic than amine groups (eg. pK\(_a\) = 10.6 for methylammonium), in which the nitrogen is sp\(^3\)-hybridized. This phenomenon can be explained using orbital theory and the inductive effect: the sp\(^2\) orbitals of an imine nitrogen are one part s and two parts p, meaning that they have about 67% s character. The sp\(^3\) orbitals of an amine nitrogen, conversely, are only 25% s character (one part s, three parts p). Because the s atomic orbital holds electrons in a spherical shape, closer to the nucleus than a p orbital, sp\(^2\) hybridization implies greater electronegative than sp\(^3\) hybridization. Finally, recall the inductive effect from section 7.3C: more electronegative atoms absorb electron density more easily, and thus are more acidic. Moral of the story: protonated imine nitrogens are more acidic than protonated amines, thus imines are less basic than amines.

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