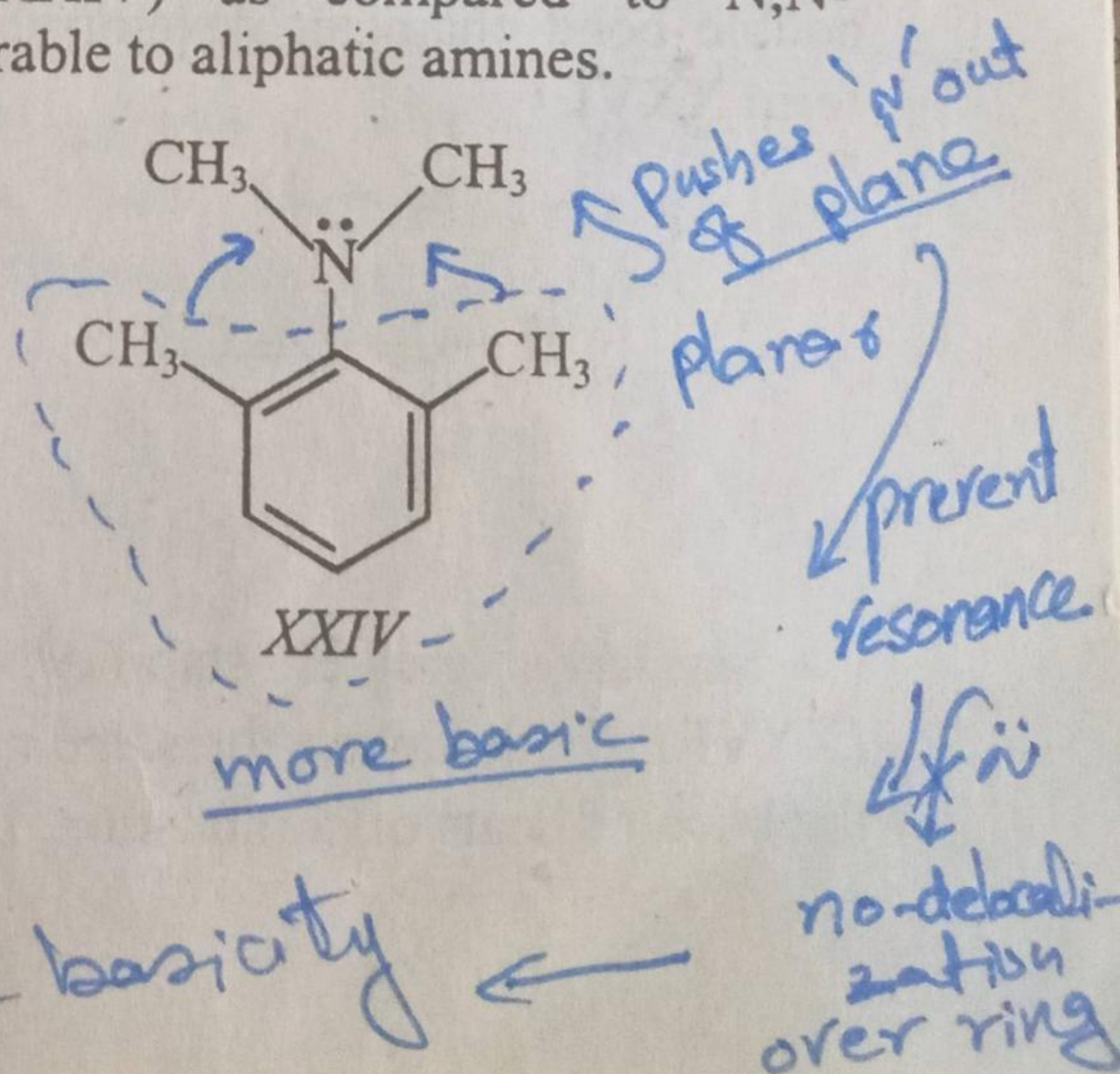
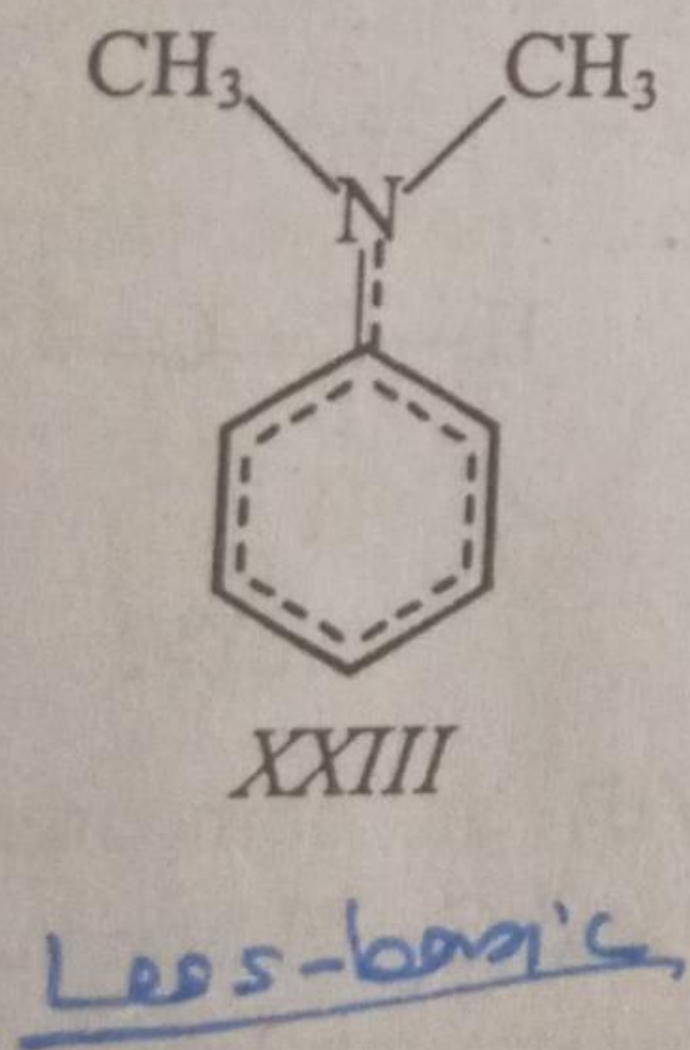


Steric Inhibition of Resonance

As has been seen earlier, it is necessary for all the atoms involved in resonance to be in the same plane to facilitate delocalization of electrons. If some atoms are forced out of planarity, resonance is prevented or reduced. Consider, for example, the effect of ortho substituents on the basicity of N,N-dimethylaniline (XXIII) which is less basic than aliphatic amines due to delocalization of the unshared pair of electrons of nitrogen over to the aromatic ring, dimethylamino- group being coplanar with the aromatic ring. However, substitution of methyl groups at the ortho positions pushes the dimethylamino- group out of the plane of the ring, to ease off overcrowding, i.e., it inhibits coplanarity and thus prevents resonance. The unshared electrons of nitrogen are no more delocalized to the ring. This phenomenon is called **steric inhibition of resonance** and results in the increased basicity of 2,6,N,N-tetramethylaniline (XXIV) as compared to N,N-dimethylaniline. The basicity of XXIV becomes comparable to aliphatic amines.



Increase basicity ←