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Evaluation of the Electron Donor Strength of Different Amino Groups

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Abstract: Knowledge of the electron donor strength of different amino groups, which can be affected by other substituents and bridges (rings) present in the molecule, is necessary to explain the properties of aromatic amines. The optimum conformation of aromatic amines is a compromise between the tendency of the nitrogen atom to be pyramidal and its tendency to assume planar configuration in order to maximize the resonance interaction with the aromatic part of the molecule. Numerous experimental techniques and theoretical calculations allow differentiate the substituent effect of the amino groups. Although spectroscopic methods (NMR, UV-VIS, IR/Raman, microwave, and photoelectron) are helpful to evaluate their donor strength, other data (dipole moment, basicity/reactivity, electron and X-ray diffraction) are complementary and have also been discussed in this review.

Keywords: Electron Donor Strength, Spectroscopic Methods

Introduction

With some minor exceptions amino groups are strong electron donors. Differentiation of their electronic effects has always been very important to physical organic chemists. Testing of different compounds shows that the amino groups affect significantly formation of the twisted intramolecular charge transfer state(Grabowski *et al.* 1979 and Zachariasse *et al.* 1994).

There are many different amino substituents known, *e.g.* NH_2, NHAlk, $NAlk_2$ and $N(CH_2)_n$. Some aromatic amines, *e.g.* indoline and julolidine contain the alkane bridges between the amine nitrogen and the ring *ortho*-carbon atoms. In consequence, their molecules are very rigid and reveal very interesting properties. There is a large number of papers published that deal with electronic effects of the amino groups, which emphasize the importance of the problem. It is noteworthy that some important aspects of the electronic effect of the amino groups were discussed thirty years ago (Chuchani, 1968) and recently (Shorter 1996). Some interesting less common substituents of that kind were, however, not included there.

Various experimental techniques and computational methods can be used to determine the substituent effects. Relations between the available experimental and calculated results and important geometrical parameters in the molecules of aromatic amines will be discussed in the present paper. Since basic nature of strong electron-donor amino substituents impedes application of the kinetic procedures to study their polar effects (Chuchani, 1968) spectroscopic methods will be emphasized.

Discussion

Any change in electronic effect of the substituent affects the whole molecule. Some of its properties, *e.g.* dipole moment, reactivity (basicity), ionization energy and extent of intramolecular charge transfer, are expected to reflect very properly the electron character of the substituent.

Due to its +M effect the parent amino group is a strong electron donor (σ_R = -0.76 (Taft and Lewis 1958: Charton 1964) -0.78 (Exner 1966). Inductive effect of NH_2 (σ_I = 0.10 (Taft *et al.* 1958), 0.11 (Exner 1966) slightly moderates its donating power (σ_p = -0.66 (McDaniel and Brown 1958). Amino group is much stronger electron donor (σ_p^+ = -1.3 (Brown and Okamoto 1958) when there is another substituent of -M type in the *para* position of the attached benzene ring. Due to inductive (+I) effect of N-alkyl groups, alkylamino substituents are even stronger electron donors((Exner 1966, McDaniel and Brown 1958, Brown and Okamoto 1958) . For amino groups the extent of conjugation with aromatic part of the molecule reflects facility of nitrogen to assume the sp^2 hybridization. In the Hückel theory this facility is shown by the overlap integral of the lone-pair orbital, n_N, and the π-orbital of benzene ring, π_{Ar}((Effenberger *et al* 1978). On the other hand, the coulomb integral reflects electro-negativity of the amino nitrogen atom. It has been found (Effenberger *et al* 1978) that different N,N-dialkylamino and polymethyleneimino, $N(CH_2)_n$, groups reveal similar inductive effects. Thus, donor strength of the amino group depends mainly on its resonance interactions with aromatic ring, which is related to the following geometrical parameters. Fig. 1:

1. C_{Ar}-N bond length;
2. R-N-R bond angle, α;
3. twist, *i.e.* torsion angle, ϕ;
4. bend angle, ψ;
5. pyramidalization, *i.e.* tilt or inversion angle, θ

It should be pointed out that some of these geometrical parameters, *e.g.* ψ and θ, are dependent on each other.

In most arylamines the angles α, ϕ, ψ and θ are intermediates of these in julolidine (2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline), I, and

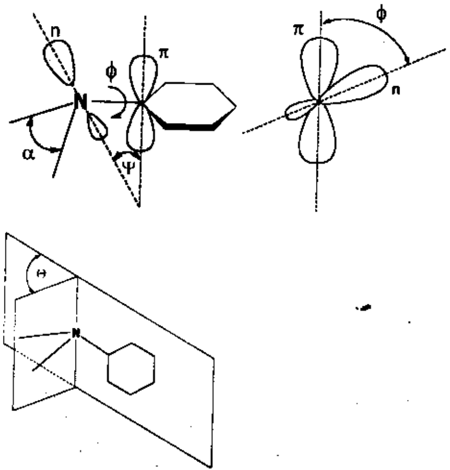
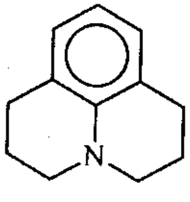
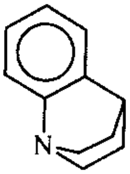


Fig. 1: Geometrical parameters of the aniline molecule

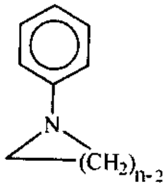


I

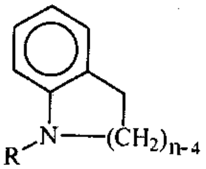


II

benzo-quinuclidine (3,4-dihydro-2*H*-1, 4-ethanoquinoline), II, both containing the Ar-N< fragments in extreme rigid conformations (Hoefnagel et al. 1981); (Kohler *et al.* 1997). However, it should be kept in mind that high barrier to change in hybridization of the nitrogen atom may be also expected in other bridged anilines (Butt *et al.* 1978). Little is known about the ground state conformation of cyclic amines III and IV. The available molecular geometries of the parent *aza*cycloalkanes, $(CH_2)_nNH$, may throw some light on this problem. Both experiment and theoretical (*ab initio*) calculations show that the strain energies in hexamethyleneimine (n = 6), piperidine (n = 5), pyrrolidine (n = 4), azetidine (n = 3) and aziridine (n = 2) are equal to 7, 0, 5, 25 and 27 kcal/mol, respectively (Dudav and Lim 1998).. This shows that the three- and four-membered rings in such compounds are much more strained than these in other cyclic amines. All substituents, including amino groups, affect geometry of the attached aromatic ring. It is noteworthy that valence angles $C_6C_1C_2$ and $C_3C_4C_5$ in mono-substituted benzenes (C_1 is the *ipso* carbon atom) were found related to σ_I and σ_R values of the substituent, respectively (Domenicano and Murray 1979). Changes in the bond lengths in such compounds are relatively less significant to the substituent because of the high force constants involved. It seems noteworthy that the idea of *n*-π conjugation in aromatic amines being discussed throughout the present paper is not commonly accepted. Thus, according to (Clark 1966) most interactions in aromatic amines arise from repulsion between the unshared electrons and the π system of the ring rather than from delocalization.



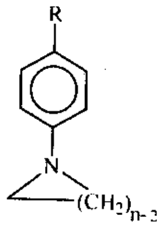
III/n



IV/n

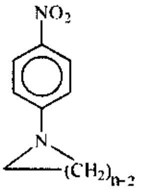
NMR spectral data

The nitrogen chemical shifts are influenced by the substituent polar (Axenord *et al* 1971) and steric effects (Sibi and Lichter 1979) and thus can be useful to estimate degree of *n*-π interaction in anilines (Crimaldi *et al* 1982). Shielding of the nitrogen in N,N-dimethylanilines upon 4-substitution by electron-donating groups is attributable to decreased electron delocalization. This is evidenced by correlation of the substituent chemical shifts (SCS) in ^{15}N NMR spectra for 4-substituted anilines and their N,N-dimethyl derivatives with σ_I and σ_R^- values in a dual-substituent-parameter (DSP) analysis (Crimaldi *et al* 1982). *Ortho*-substitution in N,N-dimethylaniline causes considerably large shift of its ^{15}N signal (Sibi and Litcher 1977). This has been attributed to the torsional distortion of NMe_2 group from the conformation defined by φ = 0° (Sibi and Litcher 1977) which results in a decreased electron delocalization (Sibi and Lichter 1979). The shift values correlate with ionization potentials of the aniline π electrons and thus also become a good measure of nitrogen-benzene ring delocalization, $n_{N-\pi_{Ar}}$ ° (Sibi and Litcher 1977). This relationship shows that the twist angles in 2,6-diethyl- and 2,6-diisopropyl-N,N-dimethylanilines are equal to 77 and 88°, respectively. The range of ^{15}N shifts in the spectra of N-(*p*-R-phenyl)aziridines, V/3, is substantially less than that for the corresponding N,N-dimethylanilines. This shows the lone-pair electrons of aziridine nitrogen to interact less effectively with benzene ring (Crimaldi *et al* 1982).

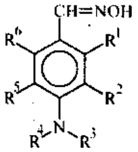


V/n

Steric effect of 2,6-dimethyl substitution in N-phenylaziridine on the ^{15}N resonance line position has been found to be much smaller than that in N,N-dimethyl-anilines (Crimaldi *et al* 1982). The analysis of these chemical shifts shows that the angle φ in N-phenylaziridine is equal to 0° but the benzene and aziridine rings in its molecule are not coplanar. The lack of correlation between ionization potentials of substituted N-arylaziridines and ^{15}N shifts has been attributed to direct interactions of the lone-pair orbitals with *para* substituents that are not reflected in the nitrogen shifts (Crimaldi *et al* 1982). ^{15}N chemical shifts and one-bond ^{15}N-H coupling constants in the spectra of anilines show that electron-acceptor substituents in the ring favour the sp^2 hybridization of amine nitrogen atom (Axenord *et al* 1971). The analysis of the chemical shift values for the ring protons in ^1H NMR spectra of aniline derivatives shows that donor strength of the amino substituents in the ground state of aromatic amines change in the following order (Effenberger *et al* 1978): 1-pyrrolidino > dimethylamino >1-piperidino. The amine nitrogen atom in N-(*p*-nitrophenyl)polymethyleneimines VI/>3 as well as in Ph-NR_2, where R = Me and Et, was found to be nearly-sp^2 hybridized (Eastes. *et al* 1971). However, it is not the case for n = 3. Decreased n_N-π_{Ar} interaction in VI/6, which reflects the relative rigidity of the chair form of six-membered ring, is also consistent with the downfield shift for the signals of protons *2* and *6* in the spectra of VI/5, VI/7 and Ph-NR_2, where R = Me, Et [30]. Nearly-sp^2 and nearly-sp^3 hybridization of the amino nitrogen atom in VI/4-6 and VI/3, respectively, has also been proved by the solvent-dependent ^1H NMR chemical shifts (Kamlet *et al* 1971). The ^1H NMR spectrum of 1-phenylaziridine, III/3, was found to be strongly temperature dependent (Bottini and Roberts 1958). This means that the $C_{Ar}NCC$ fragment in this compound is not planar and that inversion in its molecule occurs rather slowly (the coalescence temperature is less than -77°C (Bottini and Roberts 1958). Other authors (Bystrov *et al* 1965) show the methylene protons in this compound to be chemically equivalent. This observation negates low frequency of aziridine ring inversion. Moreover, it proves that n_N electrons in 1-phenylaziridine are not delocalized into benzene ring (Bystrov *et al* 1965). Good quality correlations between ^1H chemical shifts of methylene protons and σ^- constants for *p*-substituted N-phenylaziridines indicate that resonance interaction of the amine nitrogen atom with the aromatic ring is important (Severson *et al* 1972). It is additionally confirmed by the correlations of the ring breathing frequencies with the σ^- values (Severson *et al* 1972). ^{13}C NMR chemical shifts for aniline were found to be quite sensitive to the orientation of NH_2 group: both theoretical (GIAO, *i.e.* Gauge Including Atomic Orbitals) and experimental results show that amino group is tilted away from the ring plane by 42° (Barfield and Fagerness 1997). Calculations show that chemical shift values increase (downfield effect) as the amino group is moved away from the planar orientation with the largest changes appearing at the *ipso*, *ortho* and *para* positions (Barfield and Fagerness 1997). The chemical shifts of *para* carbon atom in the spectra N,N-dimethyl- and N,N-diethylanilines and 1-phenylaziridine, III/3, 1-phenylpyrrolidine-, III/5, and 1-phenylpiperidine, III/6, correlate well with other known measures of benzene ring-nitrogen resonance such as oscillator strength of the UV bands, $\cos^2\phi$ values and exaltation of molar refraction (Nash 1964: Lauterbur 1963). Moderate quality correlation has also been found between these δ values and pK_a's for various aminobenzenes except N,N-diethylaniline which exhibits an abnormal (high) base strength in hydroxyl solvents arising from steric inhibition to hydrogen bonding in the free base (Nash 1964). Although large differences in basicities were found for N,N-diethylaniline and N-phenyl-pyrrolidine, close similarity of their ^{13}C NMR spectra shows that electron distributions in the benzene rings are nearly the same in these two compounds (Nash 1964). The chemical shifts of *para* carbon atom with respect to the amino substituent in ^{13}C NMR spectra of respective *p*-aminobenzaldoximes, VII, was used to calculate the σ_R^O values for different amino groups (Gawinecki *et al* 1998). The data presented in Table 1 show that 1-pyrrolidino group is the most powerful electron-donor among all amino groups studied.



VI/n

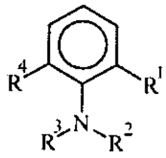


VII

Table 1: σ_R^O substituent constants for different amino groups (Gawinecki 1998). Formula VII.

R^1	R^2	R^3	R^4	R^5	R^6	σ_R^O
H	H	H	H	H	H	-0.48
H	H	Me	H	H	H	-0.52
H	H	Me	Me	H	H	-0.53
H	H	Me	Et	H	H	-0.57
H	H	Et	Et	H	H	-0.57
Me	H	Me	Me	H	H	-0.64
Me	H	Me	Me	H	Me	-0.67
H	Me	Me	Me	H	H	-0.24
H	H	$(CH_2)_4$		H	H	-0.63
H	H	$(CH_2)_5$		H	H	-0.47
H	H	$(CH_2)_6$		H	H	-0.59
H	$(CH_2)_2$		Me	H	H	-0.47
H	$(CH_2)_3$		Me	H	H	-0.48
H	$(CH_2)_4$		Me	H	H	-0.33
H	$(CH_2)_2$		$(CH_2)_3$	H	H	-0.43
H	$(CH_2)_3$		$(CH_2)_3$	H	H	-0.59

π-Electron density at the *para* carbon atom in aromatic compounds depends on twist angle of the substituent (McRae and Goodman 1966) and thus, its chemical shift can be used to calculate these angles for the amino groups in anilines. This has been done for compounds of formula VIII (Ahlbrecht *et al* 1984) The effect of *ortho*-methyl group in N,N-dimethylanilines on ^{13}C chemical shift has also been found useful to evaluate the angle ϕ and barrier to



VIII

Table 2: Twist angles of the amino group in anilines VIII (Ahlbrecht et al 1984)

R^1	R^2	R^3	R^4	ϕ [deg]
H	H	H	H	12
Me	H	H	H	19
Me	H	H	Me	0
H	H	Me	H	16
Me	H	Me	H	18
Me	H	Me	Me	61
H	Me	Me	H	19
Me	Me	Me	H	68
Me	Me	Me	Me	80
H	Et	Me	H	16
H	Et	Et	H	0
$(CH_2)_2$		H	H	33
$(CH_2)_3$		H	H	0
$(CH_2)_4$		H	H	53
$(CH_2)_5$		H	H	64
$(CH_2)_2$		Me	H	32
$(CH_2)_3$		Me	H	13
$(CH_2)_4$		Me	H	58
$(CH_2)_5$		Me	H	80
$CH(CH_2CH_2)_2$			H	90[a]

[a] Benzoquinuclidine, II.

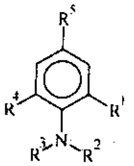
^{13}C NMR spectra (Nash 1964) show that N-phenylaziridine is least conjugated of N-phenyl cyclic amines. It has been found that the substituent in *p*-substituted N-phenyl-aziridines only slightly affects the electron distribution in aziridine ring (Liepinsh *et al* 1978). This proves that n_N-π_{Ar} conjugation in these compounds is insignificant, which has been additionally confirmed by the minor temperature effect on ^{19}F NMR spectrum of 1-(*p*-fluorophenyl)aziridine (Liepinsh *et al* 1978). ^{19}F chemical shifts are very sensitive to very small perturbations in the π-charge density at the fluorine atom produced by substituent (Taft *et al* 1963). ^{19}F NMR spectra of *p*-fluoroanilines, *p*-F-C_6H_4-NR^1R^2, were found useful in evaluation of the extent of n_N-π_{Ar} conjugation (Bystrov *et al* 1962). Substituent constants for amino, dimethylamino and 1-aziridino groups, based on fluorine chemical shift in the spectra of proper fluoroanilines, are equal to -0.486, -0.530 and -0.290, respectively (Bystrov *et al* 1962). Analysis of ^{19}F chemical shifts show that 1-aziridinyl group is not as conjugatively electron-donating as either NH_2 or NMe_2 group (Pews 1967). The inductive and resonance substituent constants based on ^{19}F chemical shifts of the respective *p*-substituted fluorobenzenes are given in Table 3 (Pews 1967).

Table 3: Inductive and resonance substituent constants of amino groups based on ^{19}F chemical shift in the spectra of *p*-R-C_6H_4-F (Pews 1967)

R	σ_I	σ_R^O
$N(CH_2)_2$	0.07	- 0.29
NH_2	0.01	- 0.48

^{19}F chemical shifts in the NMR spectrum of N,N,2-trimethyl-4-fluoroaniline show *ortho*-methyl group to produce a 56 % steric inhibition to resonance effect (Taft *et al* 1963). In consequence, σ_R^O constant for the twisted *p*-dimethylamino substituent is equal to -0.24 (it was -0.52 for non-twisted NMe_2 group) (Taft *et al* 1963). ^{19}F chemical shifts of 4-amino-3,5-dimethylfluorobenzene and of its N,N-dimethyl derivative were interpreted in terms of steric inhibition to resonance: two *ortho*-methyl groups are insufficient to push the NH_2 group out of conjugation with the benzene ring (Dewar and Takeuchi 1967). Although N,N-di-methylamino group in N,N,3,5-tetramethyl-4-aminofluorobenzene is much twisted respect to the ring plane, there is still a significant resonance interaction between those two parts of the molecule (Dewar and Takeuchi 1967). Analysis of ^1H, ^{13}C and ^{15}N NMR chemical shifts in aminobenzenes and aminopyridines shows that the amine groups are tilted away from the ring plane by 25-45° (Barfield and Fagerness 1997). Comparison of the calculated and experimental shift values indicates that pyramidalization of the amine nitrogen causes a downfield effect of ^1H, ^{13}C and ^{15}N resonances(Barfield and Fagerness 1997). It was found that two *ortho* methyl groups in N-methyl- and N,N-dimethyl-anilines cause a diminution of the N-methyl ^{13}C-^1H coupling constant by about 0.5 and 1.5 Hz, respectively (Yoder *et al* 1970). It is partly attributed to the inductive effect of these groups. Steric inhibition to resonance between the amino group and the benzene ring is responsible for the remainder of this decrease (Yoder *et al* 1970).

UV-VIS spectral data: Substitution at the *ortho* carbon in N,N-dimethylaniline causes NMe_2 group to twist out of the ring plane, so the nitrogen valences become more pyramidal (Jaffe and Orchin 1970). The calculations based on the band intensities show *ortho*-methyl group in ethyl N,N,3-trimethyl-4-aminobenzoate to produce a 56 % steric inhibition to the resonance (Taft and Evans 1957). It is obvious that less twist is required in the pyramidal than in planar conformation to relieve steric repulsion (Jaffe and Orchin 1970). The angle of twist of the NMe_2 group in *ortho*-substituted N,N-dimethyl-anilines is linearly dependent on both van der Waals radius of the substituent and on the total oscillator strength of the UV absorption band (Klevens and Platt 1949). The size and number of *ortho* alkyl substituents (Me, Et, *i*-Pr, *t*-Bu) has almost no effect on intensity of the UV absorption band of anilines (Wepster 1957; Burgers *et al* 1958). However, only the number of such groups affects the spectra of N-methylanilines, intensity of the UV absorption bands, ε, for N,N-dimethylanilines depends both on their number, and especially on their size (Wepster 1957). There is no n_N-π_{Ar} conjugation in 2,N,N-trimethyl-6-*tert*butylaniline (Burgers *et al* 1958). The twist angles of the NMe_2 group in substituted N,N-dimethylanilines calculated by means of the equation $\cos^2\phi = \varepsilon/\varepsilon_o$ are compiled in Table 4. It should be mentioned, however, that using this relationship for nearly planar molecules is contraindicated (Retting *et al* 1984), so very low ϕ values in Table 3 should be treated as less accurate.



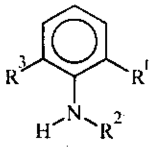
A

However, reactivity of 2,6-di(*tert*butyl)aniline is quite different from that of un-substituted aniline the UV

Table 4: The twist angles of amino group in substituted anilines (Taft and Evans 1957; Wepster 1957; Burgers *et al* 1958; Van *et al* 1954).

R^1	R^2	R^3	R^4	R^5	φ [deg]
H	H	Me	H	H	0
H	H	Et	H	H	0
Me	H	Me	Me	Me	46
Me	H	Et	Me	Me	47
t-Bu	H	Me	*t*-Bu	*t*-Bu	52
t-Bu	H	Et	*t*-Bu	*t*-Bu	51
H	Me	Me	H	H	0
Me	Me	Me	H	H	50
Et	Me	Me	H	H	56
i-Pr	Me	Me	H	H	58
t-Bu	Me	Me	H	H	78
Me	Me	Me	Me	H	68
Me	Me	Me	Me	Me	66
i-Pr	Me	Me	*i*-Pr	*i*-Pr	72
Me	Me	Me	*t*-Bu	Me	77
H	Me	Me	H	NO_2	0
Me	Me	Me	H	NO_2	44
t-Bu	Me	Me	H	NO_2	77
Me	Me	Me	Me	NO_2	52
H	Me	Me	H	CO_2Et	0
Me	Me	Me	H	CO_2Et	48(47)
Me	Me	Me	Me	CO_2Et	64(62)

spectrum shows that n-π conjugation in its molecule was not affected by the *tert*butyl groups present (Van *et al* 1954). On the other hand, there is no resonance interaction between the amino nitrogen atom and the benzene ring in benzoquinuclidine, II, which is also an aromatic amine (Wepster 1952). UV absorption spectra for some substituted anilines collected in Table 5 seem worth analyzing in order to show the difference between the N- and *ortho*-substitution and N-*ortho* annulation. Both *ortho*-substituents and the bridges between C_{ortho} and N have almost no effect on position of the π→π* band. On the other hand, *ortho*-substituents diminish its intensity (one *tert*butyl more than two methyls). The effect of the bridge on ε_{max} is less distinct but it becomes more apparent for longer bridges. However, it is obvious that *ortho* alkyl groups decrease the band intensity in the spectra of N,N-dialkylanilines, the question arises why the N-C_{ortho} bridges affect the spectra in the similar way. In the efforts undertaken to clear out this problem (Retting *et al* 1984;McRae and Goodman 1958) it was assumed that both molecules of N,N-dimethylaniline and N-methylindoline are almost planar. Nevertheless, the N atom in these compounds can still have some minor sp^3 character. Moreover, some valence angles in these compounds may slightly differ from each other. Thus, due to the angle strain of the five-membered ring, conformational distribution is much broader in N,N-dimethylaniline derivatives than in N-methylindolines, and hence, these bridged amines have lower oscillator strength and higher experimental resonance stabilization although both compounds may posses a nearly planar ground state minimum geometry (Retting *et al* 1984). Although both ε_{max} values shown in Table 4 and the results of semiempirical quantum-chemical calculations (MO LCAO SCF) (McRae and Goodman 1958) indicate the twist angle in N,N-dimethylaniline to be smaller as compared to that in N-methylindoline (and its homologons), numerous physico-chemical data do not support this conclusion (Retting *et al* 1984). Molecular models show that due to the angle strain in the five-membered ring the C_{Ar}-C_{Ar}-N valence angle in indoline and its N-methyl derivative is expected to be much smaller than 120°. It is also seen in Table 4 that *ortho*-substituents affect markedly intensity of the n →π* band (steric inhibition to resonance). Length of the bridge between C_{ortho} and N on ε_{max} of this band is less apparent than that for the π→π* band. UV absorption spectra of *p*-aminonitrobenzenes show the following order of electron-donor strength of substituents (Kamlet and Taft 1977): $NEt_2 > N(CH_2)_4 > N(CH_2)_5 > NMe_2 > NHPr\text{-}i > NHEt > NHMe > NH_2 > N(CH_2)_2$. This conclusion is supported by the E_{HOMO} values and the position of the CT bands in the spectra of complexes of mono-, 1,3-bis- and 1,3,5-tris (dialkylamino)benzenes with 1,3,5-trinitrobenzene (Effenberger *et al* 1978). The UV spectra show that of all N-phenyl cyclic amines, N-phenylaziridine is the least conjugated one (Baddeley *et al* 1956).



B

Table 5: The UV absorption spectra[a] of anilines in isoöctane (Remington 1945)

			$\lambda_{max}(\varepsilon_{max})^b$	
R^1	R^2	R^3	π→π* band	n →π* band
H	Me	H	250 (13600)	298 (2400)
Me	Me	H	250 (6400)	282 (1000)
Me	Me	Me	250sh (2000)	282sh (500)
t-Bu	Me	H	250sh (700)	c
H	Me	H	250 (13600)	298 (2400)
H	$(CH_2)_2$		253 (10100)	303 (2800)
H	$(CH_2)_3$		257 (10100)	303 (2700)
H	$(CH_2)_4$		252 (8500)	286sh (2000)

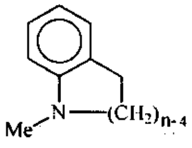
[a] Approximated values taken directly from the absorption curves.

[b] λ_{max} in nm, ε_{max} in $mol^{-1}dm^3cm^{-1}$.

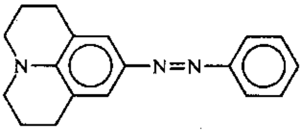
[c] No band was observed.

It has been found that the nitrogen atom in the ground state of aniline has a sp^3 hybridization (Brand *et al* 1966). This atom is also nearly-sp^3 hybridized in N-(*p*-nitrophenyl)aziridine, VI/3 (Baddeley *et al* 1956). On the other hand, in other N-(*p*-nitrophenyl)poly-methyleneimines VI as well as in Ph-NR_2, where R = Me, Et, it is nearly-sp^2 hybridized. Low ε_{max} value of the band at 425 nm in the spectrum of VI/6, as compared to the spectra of VI/5 and VI/7, proves there is a serious steric inhibition to resonance in its molecule. The angle of twist, φ, in N-(*p*-nitrophenyl)piperidine, calculated by means of equation $\cos^2 \phi = \varepsilon/\varepsilon_o$, is equal to 33° (Baddeley et al 1956). Sharply diminished absorption intensity of the spectrum of N-phenylpiperidine, as compared to N-phenylpyrrolidine, shows the φ angle to be about 45° in the former compound. The analysis of the UV spectra of N-aryl cyclic amines III indicates conclusion that the ψ angle in N-phenylaziridine is large. Due to interaction between the nitrogen atom and the phenyl ring, the resonance energy in III changes in the following order of ring size: n = 3 < 6 < 4 < 5 (Baddeley *et al* 1956).

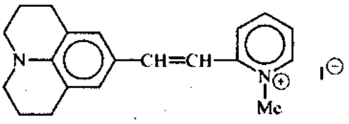
The spectra of N,N-dimethylaniline and of the benzo derivatives of cyclic amines IX/5 and IX/6 are quite similar (Jaffe and Orchin 1970). However, the spectrum of N-methyl- *homo*tetrahydroquinoline, IX/7, shows considerable difference from the spectra of two lower homologons, and this difference is certainly due to the noncoplanarity of the seven-membered ring. It seems noteworthy that intensity of the primary absorption band in the spectra of 2-R,6-R'-disubstituted 4-(N,N-dimethylamino)nitrobenzenes and ethyl 4-(N,N-dimethylamino)benzoates change in the following order (Wepster 1957): R/R' = H/H > H/Me > Me/Me > H/*t*-Bu. Thus, one *ortho-tert*butyl group shows more serious steric effect than two methyl groups in both *ortho* positions.Nearly-sp^2 hybridization of the amine nitrogen atom in VI/4-6 and nearly-sp^3 in VI/3 has also been proved by the solvent shift of the UV absorption bands (Kamlet *et al* 1971). Solvatochromic effects show hybridization of the amino nitrogen atom in *m*-R_2N-nitroaniline to be intermediate between sp^2 and sp^3 for R=H and very near sp^2 for R=Me (Kamket *et al* 1979). The analysis of λ_{max} values for different 4-aminoazobenzenes, *p*-R_2N-C_6H_4-N=N-C_6H_5, reveals that electron-donor power of the amino groups increases in the following order (Hallas *et al* 1984): $(CH_2)_4N$ > Et_2N > Me_2N > $(CH_2)_5N$. The amino nitrogen atom in VI is much stronger donor than that in 4-(1-pyrrolidino)azobenzene (Castelino and Hallas 1971). The spectra of stilbazole dyes VII and VIII in water show that alkane bridges between C_{ortho} and N affect mainly the position of the absorption band (Smith 1982).



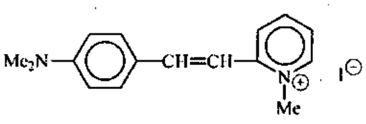
IX/n



X



XI



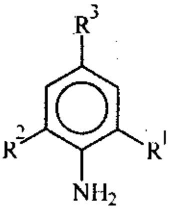
XII

λ_{max}[nm](ε_{max}) = 478(26100)
λ_{max} [nm](ε_{max}) = 437(25300)

The vibrational analysis of the UV spectrum of aniline shows that the angle α in this compound is ~46° (Brand *et al* 1966).

IR and Raman spectral data: IR and Raman spectra of aromatic amines were found to be also indicative of their geometries. Especially bond angles in these compounds can be easily determined by these methods.The angle α, barrier to rotation about the C-N bond, and barrier to inversion at the nitrogen atom in aniline (gas phase), studied by the Raman and IR spectroscopies, were found to be equal to 112°, 3.54 kcal/mol (1238 cm^{-1}) and 4.5 kcal/mol (1574 cm^{-1}), respectively (Evans 1960). Similar value of α (111°) has been found for aniline in THF solution (Krueger 1962). It is noteworthy that hybridization of the N atom in *p*-phenylenediamine was proved to be exactly sp^3 (α = 109.4°). On the other hand, electron withdrawing substituents in the ring increase the angle α: e.g. for *p*-nitroaniline it is equal to 113.6° (Krueger 1962). The correlation of symmetric *vs.* asymmetric NH_2 frequencies shows that sp^2 hybridization of the nitrogen atom in ring-substituted anilines becomes more favoured when electron-acceptor substituents are present in the ring (Krueger 1962).

Frequencies of the symmetric NH_2 stretching vibrations (in CCl_4) were used to determine the angles α in some alkyl derivatives of aniline shown in Table 6. It may be seen, that there is no simple relation between the angle α and the size and number of substituents in the *ortho* positions.



C

Table 6: The angles α in some alkyl anilines (Krueger 1962)

R^1	R^2	R^3	α [deg]
H	H	H	111.7
Me	H	H	111.5
Et	H	H	110.8
i-Pr	H	H	111.2
t-Bu	H	H	113.5
Me	Me	H	110.9
Me	Me	Me	110.3
i-Pr	*i*-Pr	*i*-Pr	109.3
t-Bu	*t*-Bu	*t*-Bu	115.8

The square roots of integrated absorbancies of the skeletal vibrations, involving the carbon-carbon stretching within the ring, in the 1600-1585 and 1500-1400 cm^{-1} regions, are a good measure of the extent of resonance interaction between benzene ring and unsaturated substituent (Eleksanyan *et al* 1966). These bands are less intense in the spectrum of N-phenylaziridine as compared to N,N-dimethylaniline. The extent of n_N-π_{Ar} interaction in former compound was found to be less than that in aniline and its N,N-dimethyl derivative (Eleksanyan *et al* 1966 and Brownlee *et al* 1968). Moreover, its IR spectrum (Brownlee *et al* 1968) proves that N-phenylaziridine is least conjugated in the series of N-phenyl cyclic amines. The calculated substituent constants for different amino groups are shown in Table 7 (Katritzky and Topsom 1970 and Brownlee *et al.* 1966). This data show that resonance interactions between the N atom and benzene ring change in the following order: $N(CH_2)_2 < N(CH_2)_5 < NMe_2 < N(CH_2)_3 < NEt_2 < N(CH_2)_4$. The steric hindrance causes NMe_2 group in N,N-dimethylaminodurene to be twisted by 65° (Katritzky and Topsom 1970). The far infrared spectra show that the angles θ in aniline and its *p*-fluoro derivative are equal to ~ 42° and ~ 43°, respectively (Larsen *et al.* 1998). Barriers to inversion are 524.4 ± 5 cm^{-1} and 596 ± 5 cm^{-1} and barriers to rotation are 2005 ± 40 cm^{-1} and 1568 ± 40 cm^{-1} in these compounds, respectively (Larsen *et al.* 1998).

Table 7: Substituent constants of the amino groups (evaluation based on intensity of the IR bands).(Katritzky and Topsom 1970: Brownlee *et al.* 1966)

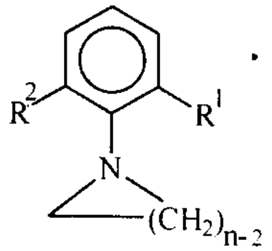
R	σ_R^O
NHMe	-0.522 (-0.52)
NMe_2	-0.533 (-0.53)[a]
NHEt	-0.520 (-0.52)
NHBu-*n*	-0.536 (-0.54)
NHPr-*i*	-0.533 (-0.53)
NEt_2	-0.571 (-0.57)
$N(CH_2)_2$	-0.382 (-0.38)
$N(CH_2)_3$	-0.552 (-0.55)
$N(CH_2)_4$	-0.628 (-0.63)
$N(CH_2)_5$	-0.474 (-0.47)

[a] Other σ_R^O values: -0.54 (based on ^{19}F NMR spectra) (Taft *et al* 1963), -0.52 (based on reactivity measurements) (Taft *et al* 1963), -0.50 (evaluated by means of equation $\sigma_R^O = 2.0\sigma_R'''$) (Taft *et al* 1959).

It is noteworthy that rotational barriers in aniline and its N-alkyl derivatives correlate with the extent of resonance interaction between the amino group and benzene ring (Grindley *et al.* 1974). The strain energies in $Ph\text{-}NH_2$ and $Ph\text{-}NMe_2$ were found to be 3.2, 5.5 and 8.1 $kcal/mol^{-1}$, respectively (Cervellati and Borgo 1981).

Microwave spectral data : The microwave spectral data indicate that amino group in aniline is pyramidal: α = 112.3-113.5° (Lister and Tyler 1966 and Hastie *et al.* 1970). The C_{Ar}-N bond length and the tilt angle, θ, in this compound were found to be equal to ~140 pm (Lister and Tyler 1966 :Lister *et al.* 1974) and 37.5-39.4° (Lister and Tyler 1966 :Lister *et al.* 1974), respectively. Similar spectral data show that angles α and θ in *p*-floroaniline (gas phase) are ~112° and ~46.4°, respectively (Hastie *et al.* 1970). It is noteworthy that much lower value of θ (~20°) has been found for its N-methyl derivative (Cervellati and Borgo 1981).

Photoelectron spectral data: ionization energies Photoelectron spectroscopy is a sensitive probe for the extent of n_X-π_{Ar} conjugation and thus enables prediction of the Ar-X conformation (Kobayashi and Nagakura 1974). Differences between ionization potentials in the photoelectron spectra of N-aryl cyclic amines XIII were used to determine the twist angles in these compounds (Table 8). In *p*-dimethyl-amino-, *p*-diethylamino-, *p*-(N-pyrrolidino)- and *p*-(N-piperidino)benzonitriles ϕ = 4, 21, 0 and 33°, respectively (Retting and Gleiter 1985).



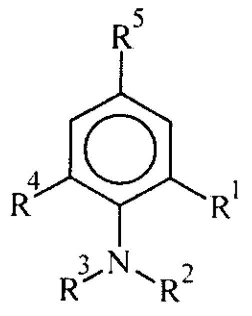
XIII/n

Table 8: Angles ϕ [deg] in the spectra of N-aryl cyclic amines XIII (Rozeboom *et al* 1982)

R^1	R^2	n: 3	4	5	6
H	H	0	0	0	48
H	Me	0	28	52	68
Me	Me	0	34	83	86

CNDO/S3 supported analysis of the UV photoelectron spectrum of N,N-di-methylaniline shows the twist angle of NMe_2 group with respect to the ring plane to be equal to 30° (LaFamina *et al* 1973). This is at variance with the earlier data based on the same experimental method that shows ϕ = 0° (Maier and Turner 1973). According to the same source (Maier and Turner 1973), ϕ = 55° and 69° in 2,N,N-trimethyl- and 2,6,N,N-tetramethylanilines, respectively. It is noteworthy that photoelectron spectra show N atom to have the sp^3 hybridization not only in N,N-dimethylanilines but also in indoline.

UV spectra of the charge-transfer complexes of anilines with tetracyano-ethylene were found to be useful for determination of ionization energies, I_D, in those amines (Farrell and Newton 1965), (Table 9). These data show both N- and ring alkyl substituents cause



D

Table 9: Ionization energies in anilines (Farrell and Newton)

R^1	R^2	R^3	R^4	R^5	I_D [eV]
H	H	H	H	H	7.76
H	H	Me	H	H	7.58
H	H	Et	H	H	7.56
H	H	*n*-Pr	H	H	7.54
H	H	*n*-Bu	H	H	7.53
H	Me	Me	H	H	7.44
H	Et	Me	H	H	7.37
H	Et	Et	H	H	6.99
H	*n*-Pr	*n*-Pr	H	H	6.96
H	*n*-Bu	*n*-Bu	H	H	6.95
Me	Me	Me	H	H	7.37
H	Me	Me	H	Me	7.33
H	Et	Et	H	Me	6.93
Me	Me	Me	Me	H	7.22
Me	Me	Me	H	Me	7.17

I_D to decrease. Moreover, comparison of the effect of *ortho*- and *para*-methyl groups on I_D shows that its steric influence is insignificant.

The gas-phase basicities of N-phenyl*aza*cycloalkanes III/n were found to increase with *n* values (Cauletti *et al* 1988). On the other hand, their ionization energies change in the following order: n = 3 > 6 > 4 > 5. The relationship between ionization energies and proton affinities shows that in N-phenylpyrrolidine the angle $\phi = 0°$. This explains why N-phenylpyrrolidine is of the same type as Ph–NR_2 (R = H, Me, Et, *n*-Pr), at least from the point of view of the observed changes in ionization energies (Cauletti *et al* 1988). The values of proton affinities and ionization energies for N-phenyl*aza*cycloalkanes III/n, where n = 3, 4 and 6, show ϕ angle in these compounds to be quite different from 0°, as it is for n = 6, or, perhaps, it is equal to 0° but the angle ψ is large, which reflects the serious strain in 3- and 4-membered rings (Cauletti *et al* 1988).

Dipole moments: Dipole moment of aniline (1.15 D (Hatta *et al* 1973) was found to be only slightly affected by the *ortho*- and N-methyl groups: its value is appreciably diminished only in 2,6,N-trimethylaniline and especially in 2,N,N-trimethyl- and 2,6,N,N-tetramethylanilines (Fischer 1950). Charge distribution in the molecules of aromatic amines shows order of electron-donor strength of the amino groups to be $(CH_2)_4N > Et_2N > (CH_2)_5N$ (Beach *et al* 1984: Mazet *et al* 1970)

and $NEt_2 > N(CH_2)_4 > NMe_2 > N(CH_2)_5$ (Mazet *et al* 1970). The calculated and measured dipole moments confirm considerable twist of NMe_2 group in *ortho*-methyl substituted N,N-dimethylanilines (Hallas *et al* 1977). Thus, there is a strong steric inhibition to resonance in these molecules (Smith 1961). Comparison of the experimentally observed and theoretically calculated dipole moments of 2,N,N-trimethylaniline shows hybridization of the nitrogen atom to be close to sp^3 (McRae and Goodman 1966).

Basicity: Nitrogen atom is the predominant site of proton attachment in aniline (Smith *et al* 1995). Delocalization of its *n* electrons causes aromatic to be weaker bases than aliphatic amines (Smith 1968). Thus, the more near-sp^2 is hybridization of the N atom, the lower should be pK_a of aniline derivative.

pK_a values of N,N-dialkylanilines and cyclic aromatic amines III/n in 50 % aqueous ethanol change in the following order (Baddeley *et al* 1979): C_6H_5-NEt_2 > *o*-Me-C_6H_4-$N(CH_2)_5$ > *o*-Me-C_6H_4-$N(CH_2)_4$ > C_6H_5-$N(CH_2)_5$ > C_6H_5-NMe_2 > C_6H_5-$N(CH_2)_4$. Sequence of the base strength of anilines of formula *p*-R-C_6H_4-NR^1R^2 in water only slightly depends on the *para* substituent (Eastes *et al* 1969):

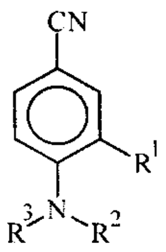
for R = H, Me: R^1/R^2 = H/H < H/Me < Me/Me < H/Et < H/*i*-Pr < Et/Et

for R = NO_2: R^1/R^2 = H/Me < Me/Me < H/Et < H/H < H/*i*-Pr < Et/Et

These results confirm that N-alkyl groups cause an increase in basicity of aniline due to their +I effect. On the other hand, N-alkylation may significantly change effectiveness of solvation of both amine and its conjugate acid. It was concluded that the amine nitrogen atom is nearly-sp^3 hybridized in anilines and *p*-toluidines, and nearly-sp^2 hybridized in *p*-nitroanilines (Eastes *et al* 1969).

Alkyl groups in the *ortho* positions in aniline always decrease its pK_a (Smith 1968). On the other hand, substitution of the amino hydrogen atom(s) by alkyl(s) causes an increase of the base strength of aromatic amines. *Ortho* alkyl groups in N,N-dialkyl-anilines prevent dialkylamino group from assuming the coplanarity with the ring and hence decrease its resonance effect and increase basicity of the compound. On the other hand, 2,N-dimethylaniline is weaker and 2,N,N-trimethylaniline is stronger base than N-methylaniline. Unexpectedly, 2,6,N,N-tetramethylaniline has lower pK_a than 2,N,N-trimethylaniline (Smith 1968). Benzoquinuclidine II is a particular aromatic amine (Chapter 8). As expected, it is relatively strong base. Its pK_a value seems worth comparing with these for selected anilines measured in 50 % aqueous ethanol at 25°C (Hoefnagel *et al* 1976):

pK_a: C_6H_5-NH_2 < C_6H_5-NMe_2 < *o*-Me-C_6H_4-NMe_2 < C_6H_5-NHBu-*t* < < C_6H_5-N(Me)Bu-*t* < benzoquinuclidine. The term "steric inhibition to resonance" refers to nonplanar sterically hindered molecule while the unhindered reference molecule is planar (Bohm *et al* 1994). Thus, it is necessary for the molecule to take particular conformation due to the hindrance alone. When estimating the steric hindrance one should consider some additional contributing effects. Thus, basicities of *ortho*-methyl substituted N,N-dimethyl-anilines in solution reflect not only the perturbation in n_N-π_{Ar} conjugation but also the steric hindrance to solvation in the anilnium cation (Van *et al* 1954:Brown 1950). It is why the gas phase measurements should be more simple to interpret and should answer the question about the conformation of N-C_{Ar} bond and hybridization of the amine nitrogen atom. The gas phase basicities show that of two *ortho* methyl groups in N,N,2,6-tetra-methylaniline the second reveals less distinct effect (Bohm *et al* 1994). pK_a values of aniline derivatives IV/n change in the following order depending on R and *n* (Baddeley *et al* 1956): H,n=7 > Me,n=7 ≈ H,n=6 > H,n=5 ≈ Ph-NMe_2 > Me,n=6 > Me,n=5. 1,2,4,5-Tetrahydropyrrolo[3,2,1-*hi*]indole, XIV, was unexpectedly found to be stronger base (pK_a = 4.1, in 50 % aqueous ethanol) than julolidine, I, (pK_a~3.6) (Anet *et al.* 1961).



XIV

Perhaps, in this case the pK_a value also reflects both the conformational changes in the molecule and differences in steric hindrance to solvation (Van *et al* 1954).

It has been found that linear correlation between the twist angle and pK_a values of aniline derivatives VIII is very rough due to peculiar solvation effects (Ahlbrecht *et al* 1984). Thus, the anomalies in the base strength attributed to steric hindrance of solvation (Van *et al* 1954) also enable evaluation of the conformation of aromatic amines (Wepster 1957).

Reactivity: Acidities of *p*-aminobenzoic acids, R_2N-C_6H_4-CO_2H, and the rates of reduction of *p*-nitroanilines, R_2N-C_6H_4-NO_2, show the following order of the electron donating effect for different amino substituents (Weringa and Janssen 1968):

$N(CH_2)_5 < NMe_2 < N(CH_2)_4 < NEt_2 < N(i\text{-}Pr)_2$

Decreased mesomerism that results from the twisting of the NCC plane out of the benzene ring plane is illustrated by the pK_a value for *p*-(N-piperidino)benzoic acid, which is lower as compared to other *p*-aminobenzoic acids, *p*-R_2N-C_6H_4-CO_2H (Eastes *et al* 1971: Weringa and Janssen 1968): pK_a: $Et_2N > (CH_2)_4N > Me_2N > (CH_2)_5N$. Comparison of the pK_a values for III/n, *p*-R_2N-C_6H_4-CO_2H and Ph-NR_2 also confirms that amine nitrogen atom in N-arylaziridines is sp^3 hybridized (Eastes *et al* 1971).

Table 10 shows the substituent constants for some amino groups defined on the basis of dissociation constants of *p*-aminobenzoic acids, *p*-R_2N-C_6H_4-CO_2H (Van de Graaf *et al* 1981).

Table 10: The substituent constants of amino groups based on dissociation data for *p*-R_2N-C_6H_4-CO_2H (Van de Graaf *et al* 1981)

NR_2	σ
NH_2	-0.62
NMe_2	-0.69[a]
NEt_2	-0.71
$N(CH_2)_4$	-0.69
$N(CH_2)_5$	-0.41

[a] This value is different from that commonly used (-0.83 (McDaniel and Brown 1958).

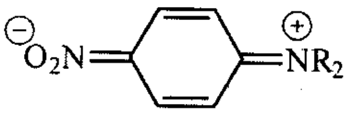
The pK_a values of 4-amino-3,5-dimethylbenzoic acid and its N,N-dimethyl derivative, as well as saponification rates for the respective ethyl esters, have been interpreted in terms of steric inhibition to resonance (Schaefer and Miraglia 1964). NMe_2 group has been found to be much twisted with respect to the benzene ring while the NH_2 group seems to be only slightly affected by the neighbourhood of two methyl groups. The rate of saponification of ethyl 3,5-dimethyl-4-aminobenzoate is almost eleven times lower than that of its N,N-dimethyl derivative which results from the twisting of NMe_2 group in the latter compound (Westheimer and Metcalf 1941).

Ortho substituents affect the rate of hydrogen exchange in N,N-dimethyl-anilines (Brown *et al* 1939). Examination shows that bicyclic structures in N-methylindoline and N-methyl-1,2,3,4-tetrahydroquinoline are planar (Brown *et al* 1939). On the other hand, the seven-membered ring in IV/7 (R = Me) is highly puckered, so the rate of hydrogen exchange in this compound is comparable to that in *ortho*-methyl- and 2,6-dimethylanilines (Brown *et al* 1939). Although benzoquinuclidine, II, is an aromatic amine, there is no resonance interaction between the amino nitrogen and the benzene ring in its molecule. It has been proved by its unsuccessful coupling with *p*-nitrobenzenediazonium salts (Wepster 1952). The σ_R^O for the twisted -N< group in benzoquinuclidine is equal to -0.134 (Cutress 1972) (as compared to -0.53 for NMe_2 group (Brownlee *et al* 1968). On the other hand, another hindered amine, *i.e.* 2,6-di-(*tert*butyl)aniline, can be readily coupled with arenediazonium salts to give the respective *p*-aminoazobenzenes (Wepster 1952: Burgers *et al* 1958: Van *et al* 1954). Due to steric inhibition to resonance in N-*t*-butyl,N-methylaniline, this compound does not react with nitrous acid nor with ethyl nitrite to give the *para*-nitroso derivative (Van Hoek *et al* 1958). The formation of 4'-nitro-4-(N-*t*-butyl,N-methylamino)azobenzene from this compound and *p*-nitrobenzenedi-azonium chloride proceeds extremely slowly with only 10 % yield (Van Hoek *et al* 1958). None of N,N-dimethylanilines containing 2-*t*-butyl and 2,6-dimethyl groups can be nitrosated (Van Hoek *et al* 1958). Moreover, these amines are resistant to oxidation, even when exposed to the air and to the sunlight for a long time (Van Hoek *et al* 1958).

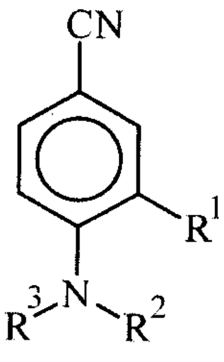
Electron and X-ray diffraction: Electron diffraction data show the C_{Ar}-N distance and the angle α in aniline (gas phase) to be 143 pm and 116°, respectively (Vilkov and Timasheva 1965). X-Ray diffraction studies (Fukuyo *et al* 1982) indicate that amino group in this compound is pyramidal. Moreover, the angles α and θ, and C_{Ar}-N distance in aniline are equal to ~119° or ~104° (there are two different molecules in the unit cell) and 38°, and 139 pm, respectively (Fukuyo *et al* 1982). It is also known from X-ray studies [(Fukuyo *et al* 1982) that the amino nitrogen atom in the aniline molecule is displaced by 12 pm from the ring plane. Although intermolecular N-H···N hydrogen bonding has been found only in the crystal state, the molecular structure of this compound is similar to that in the gas phase (Fukuyo *et al* 1982:Brand *et al* 1966).

Electron diffraction studies (Naumov 1966) point exclusively to the conformation of N-phenylaziridine, in which the lone-pair orbital is effectively perpendicular to the plane of benzene ring. Other geometrical parameters of the molecule are as follows: θ = 54.5°, ϕ = 0° and C_{Ar}-N = 146 pm (Naumov 1966). X-Ray diffraction studies show the C_{Ar}-N distance and the angles α and θ in *m*-nitroaniline are equal to 140.4 pm, 121.0° and 8.26°, respectively (Delugeard and Messager 1975). The CNH_2 fragment in *p*-nitroaniline is planar and C_{Ar}-N,

α and ϕ are equal to 137.1 pm, 112° and 16°, respectively (Trueblood *et al.* 1961). The amino nitrogen atom is displaced by 2 pm from the ring plane. There are intermolecular hydrogen bonds, -NH-H···O-NO-, in the crystal of this compound (Trueblood *et al* 1961). Small but significant contribution of the quinoid resonance form to the molecular structure was also confirmed (Trueblood *et al* 1961). X-Ray studies for *p*-nitro-N,N-dialkylanilines show NR_2 groups to be only slightly twisted out of the ring plane (Mak *et al* 1965: Maurin *et al* 1988). Angle ϕ = 7.3° has been found in dimethylamino derivative (Mak *et al* 1965). The C_{Ar}-N distance and the angles θ and α are equal to 135.8 pm, -6.35° and 118.2°, respectively, for *p*-nitro-N,N-dimethylaniline and 135.7 pm (135.1 pm), -9.40° (7.49°) and 116.2°(114.4°), respectively, for *p*-nitro-N,N-diethylaniline (there are two molecules in the unit cell of the latter). Quinoid structure XV makes slighter (for *p*-nitro-N,N-dimethylaniline) (Mak *et al* 1965) or considerably larger (for *p*-nitro-N,N-diethylaniline) (Maurin *et al* 1988) contribution to the hybrid molecule than the corresponding structure in *p*-nitroaniline. Thus, *p*-nitroanilines presents the structural evidence against classical concept of *through-resonance* (*cross-conjugation*): the weights of the canonical structure XV are 12.7 and 9.3 % for N,N-diethyl-*p*-nitroaniline and 2,6,N,N-tetramethyl-4-nitroaniline, respectively (Krygowski and Maurin 1989). Table 11 presents the X-ray data for some *p*-aminobenzonitriles (Heine *et al* 1994: Gornitzka *et al* 1994). It may be seen that C_{Ar}-N distance is the same for *p*-aminobenzonitrile and its N,N- and 2,6-dimethyl derivatives, as well as for N,3,5-trimethyl-4-aminobenzonitrile but this bond is much longer in N,N,3,5-tetramethyl-4-aminobenzonitrile. N- and *ortho*-methyl groups have some effect on θ but this angle is largest in N,N,3,5-tetramethyl derivative. Methyl groups in the position *ortho* with respect to the amino group in 4-(N,N-dimethylamino)benzonitrile have no effect on angle α. The nitrogen atom is only slightly displaced from the ring plane in N,N-dimethylamino derivative (its displacement is most distinct in N,N,3,5-tetramethyl-4-aminobenzonitrile). Of the last three compounds in Table 11 it is *p*-(N-pyrrolidine) derivative which is most similar to *p*-(N,N-dimethylamino)benzonitrile that contain an sp^2 hybridized nitrogen atom. Molecular structures of benzoquinuclidine, II, and of its 6-cyano derivative, XVI, in the crystal state were also studied.[21] These data confirm that there is no n_N-π_{Ar} conjugation in these compounds (aromatic π and amino lone pair orbitals are orthogonal). X-Ray diffraction studies show that angles α in *p*-dimethylaminobenzoic acid and α-*p*-dimethylaminobenzaldoxime are equal to 116.9° (Anulewicz *et al* 1994) and 115.5° (Bachechi and Zambonelli 1972), respectively.



XV

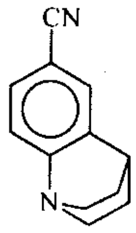


E

Table 11: X-Ray structural data of *p*-aminobenzonitriles (Heine *et al.* 1994: Gornitzka *et al.* 1994)

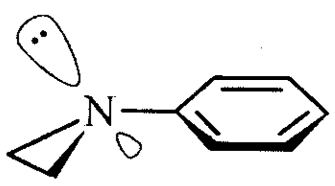
R^1	R^2	R^3	C_{Ar}-N [pm]	θ [deg]	α [deg]	z [pm]^a
H	H	H	137	34	114	6
H	Me	Me	137	~11	116.5	~1
Me	H	H	137	~16.5	~114	~6
Me	H	Me	136	12	120	5
Me	Me	Me	141	59.3	116.2	12
H	$(CH_2)_4$		136	25.7	94	-
H	$(CH_2)_5$		136	11	112.5	-
H	$(CH_2)_6$		138	26.7	116	-

^{a} Displacement of amine nitrogen atom from the plane of benzene ring.



XVI

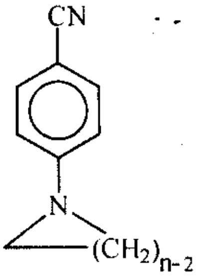
Electron diffraction studies point exclusively to the conformation of N-phenylaziridine in which the pyramidalization and twist angles are equal to 125.5° and 0°, respectively (Naumov *et al.* 1966):



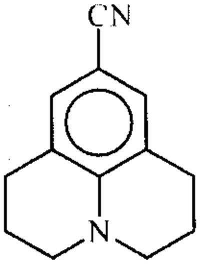
F

Quantum-chemical calculations: *Ab initio* calculations (Adams 1993) show that amino group in aniline is pyramidal (unless the very strong π-electron withdrawing group appears in the ring) and that C_{Ar}-N bond is bent out of the ring plane by about 2°. The results of MNDO treatment are similar (Adams 1987). Semiempirical and *ab initio* calculations show that NMe_2 group and aromatic part of the molecule in most N,N-dimethylarylamines are coplanar in the ground state (Barbieri *et al*). The only exceptions are the compounds where steric effects appear (Barbieri *et al*). PM3 calculations (Vaschetto and Retamal 1997) show that (i) the amino N atom in anilines is tetra-hedral with inclination to become more sp^2 hybridized (trigonal) in molecules that carry electron-withdrawing substituents in the ring, and (ii) the angle between the ring plane and the C-N bond in unsubstituted aniline is equal to be 5.37°. It is known from the INDO calculations (Strametz and Schmidtke 1976) that barriers to nitrogen inversion, internal nitrogen rotation and pyramidalization angle, θ, in aniline are equal to 1.2 kcal/mol, 7.5 kcal/mol (2623 cm^{-1}) and 39.35°, respectively. The following data for aniline were obtained by use of the MINDO/3 method (Parr and Wasylishen 1977): C_{Ar}-N = 135.9 pm, $\theta = 8.65°$, $\alpha = 111.38°$ and dipole moment $\mu = 1.360$ D. In general, electron-acceptor substituents in the ring decrease the C_{Ar}-N distance and θ, and increase α. There is a linear dependence between the calculated θ's and observed chemical shifts of the carbon atom bound to the NH_2 group as well as between θ and $^1J(^{15}N,H)$ coupling constants in the NMR spectra of aromatic amines (Parr and Wasylishen 1977).

Ab initio calculations show the angle θ in aniline to be 38-39° (Wolf *et al* 1980), 42.3° (Bock *et al* 1986) and 47.7° (Hehre *et al* 1972). The calculated dipole moment of aniline, 1.48-1.49 D, agrees with the experimental value (Wolf *et al* 1980), The inversion barriers of the nitrogen atom were estimated to be 0.9-1.1 kcal/mol (315-385 cm^{-1}) (Wolf *et al* 1980), and 1.59 kcal/mol (556 cm^{-1}) (Bock *et al* 1986). *Ab initio* calculations show that π-electron-donor substituents in the benzene ring of aniline molecule stabilize the planar transition state and thus lower the inversion barrier of the nitrogen atom (Hehre *et al* 1972). The calculated geometries of aniline and *p*-substituted anilines were found to be in reasonable agreement with experimental data in the gas phase (Von Nagy *et al* 1982). *Ab initio* and semiempirical calculations parametrized by the vibrational spectrum show the angle θ in aniline to be ~42° (Castella and Kassab 1994). The analysis of the resonance interactions between benzene ring and substituent in some dialkylaminobenzenes by the Hückel method leads to the conclusion that donor strength of amino substituent in the ground state of studied aromatic amines change in the following order (Effenberger *et al* 1978): 1-pyrrolidino > dimethylamino > 1-piperidino. CNDO/S3 calculations parametrized by the photoelectron spectra (gas phase) show the twist angle of the amine group, ϕ, to be ~ 35, ~15 and ~10° in *p*-(N-pyrrolidino)-, XVII/5, *p*-(N-piperidino)benzonitrile, XVII/6, and 9-cyanojulolidine, XVIII, respectively (LaFemina *et al* 1988). The angles ϕ in N,N,2-trimethyl- and N,N,2,6-tetramethyl- aniline, calculated by the same method, are equal to ~55 and 70°, respectively. Moreover, it has been found that conformation of the *ortho*-methyl group(s) in these compounds has no effect on ϕ (LaFemina *et al* 1988). The calculated (*ab initio*) weight of the structure XV(R=H) of *p*-nitroaniline is only 2-11 % (Hiberty and Ohanessian 1984). This is in coincidence with the results of X-ray studies for similar compounds (Chapter 9). It is noteworthy that bending of the dimethylamino group in *p*-N,N-dimethyl-aminobenzonitrile by 20° towards the benzene ring causes only slight changes in position and intensity of the absorption band (Retting *et al* 1984). Semiempirical (AM1) calculations show that aromatic π and nitrogen lone pair orbitals in benzoquinuclidine and its 6-cyano derivative are orthogonal (Kohler *et al* 1997)



XVII/n

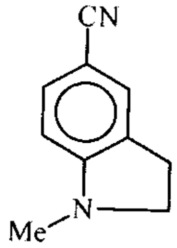


XVIII

Other data: Polarographic half-wave potentials for aniline derivatives were also used as a measure of the electron donor strength of amino groups (Weringa and Janssen 1968: Bent *et al* 1951). The following order of electron-donating effect of the substituents has been found: $NR_2 = N(CH_2)_5 < NMe_2 < N(CH_2)_4 < NEt_2 < N(i\text{-}Pr)_2$ (Weringa and Janssen 1968). Oxidation potentials of mono-, 1,3-di- and 1,3,5-triaminobenzenes show the order of electron-donating properties of amino groups to be as follows (Effenberger *et al* 1978): 1-pyrrolidino > dimethylamino > 1-piperidino.

The Kerr constant for N-phenylaziridine (solutions in cyclohexane and benzene) points exclusively to ϕ being equal to 0° in this compound (Armstrong *et al* 1971). Low barrier to nitrogen inversion proves that conjugative n_N-π_{Ar} interaction appears in its molecule (Armstrong *et al* 1971).

Fluorescence spectra show that both molecules of 1-methyl-5-cyanoindoline, XIX, and 6-cyanobenzoquinuclidine, XVI, are rigid.



XIX

The former is planar and the latter contains an sp^3 amino nitrogen atom precluding the n_N-π_{Ar} conjugation to appear (Grabowski *et al* 1979: Rotkiewicz *et al* 1976). Equilibrium angle between NH_2 group and the ring plane, and barrier to inversion in aniline have been found to be equal to 42° and 454 ± 70 cm^{-1}, respectively (Quack and Stockburger 1972).

Conclusions

The optimum conformation of aromatic amines is a compromise between the tendency of trivalent nitrogen to be pyramidal and its tendency to assume planar configuration in order to maximize the resonance interaction with the aromatic nucleus. Thus, the amino moiety is pyramidal or coplanar with aromatic part of the molecule, depending on nature of the substituent(s) attached to nitrogen atom and/or to the aromatic ring.

Literature search shows that there are many different methods that can be used to evaluate the electron-donor strength of the amino groups. The ^{19}F, ^{14}N, ^{15}N, ^{13}C and ^{1}H NMR spectral data are influenced by the substituent polar and steric effects and thus are very useful to estimate the degree of n-π interaction in anilines. Especially ^{19}F chemical shifts are very sensitive to perturbations in the π-charge density at the fluorine atom produced by substituents. Shielding of the nitrogen in anilines upon substitution by electron-donating groups is attributable to decreased electron delocalization. *Ortho*-substitution in N,N-dimethylaniline causes considerably large shift of its ^{15}N signal, which is attributed to torsional distortion of the NMe2 group, and to decreased electron delocalization in such a molecule. ^{13}C NMR chemical shifts for aniline were found to be quite sensitive to the orientation of NH_2 group which is tilted away from the ring plane in this compound. ^{15}N chemical shifts and one-bond ^{15}N-^{1}H coupling constants in the spectra of anilines show that electron-acceptor substituents in the ring extort from the amine nitrogen atom to be sp^2 hybridized.

UV-VIS, IR and Raman spectra of aromatic amines were found to be also indicative of their geometries. Especially bond angles in these compounds can be easily determined by last two methods. The square roots of integrated absorbancies of the skeletal vibrations, involving carbon-carbon stretching within the ring, in the 1600-1585 and 1500-1400 cm^{-1} regions, are a good measure of the extent of resonance interaction between benzene ring and substituent. The microwave spectral data indicate hybridization of the amino nitrogen atom in anilines as well as the C_{Ar}-N bond length and the tilt angle in these compounds. Photoelectron spectroscopy is a sensitive probe for the extent of n_X-π_{Ar} conjugation and thus also enables prediction of the Ar-X conformation. On the other hand, dipole moment of aniline is only slightly affected by the *ortho*- and N-methyl groups. Basicities of *ortho*-methyl substituted N,N-dimethylanilines in solution reflect not only the perturbation in n_N-π_{Ar} conjugation but also the steric hindrance to solvation in the anilinium cation. It is why the gas phase measurements are simpler to interpret and answer the question about conformation of the N-C_{Ar} bond and hybridization of the amine nitrogen atom. The HNH bond angle in aniline in solid, gas phase or in solution proves the nitrogen atom to be sp^3 hybridized. Pyramidalization angle in this compound is equal to ~40°. The ring electron-acceptor substituents in aniline favour the sp^2 hybridization of the nitrogen atom. In general, such groups in the ring decrease the C_{Ar}-N distance and pyramidalization angle, and increase the HNH bond angle. UV spectra prove that the size and number of *ortho* alkyl substituents have almost no effect on the bond, twist, bend and pyramidalization angles in anilines. The *tert*butyl groups do not affect the n-π conjugation in 2,6-di(*tert*butyl)aniline.

However, only the number of alkyl groups affects the spectra of N-methylanilines, intensity of the UV absorption bands for N,N-dimethylanilines depends both on their number, and especially on their size. There is no n_N-π_{Ar} conjugation in 2,N,N-tri-methyl-6-*tert*butylaniline. *Ortho*-methyl group in N,N,2-trimethylanilines causes serious steric hindrance to resonance. In consequence, σ_R^O constant for such twisted *p*-dimethylamino substituent is equal to -0.24 (it was -0.52 for non-twisted NMe_2 group). There is still a significant resonance interaction between the amino group and benzene ring in N,N,2,6-tetramethylanilines. UV spectra show that steric interaction between one *ortho-tert*butyl and N,N-dimethylamino groups in aromatic amines is stronger than that between two *ortho*-methyl and the N,N-dimethylamino groups in these compounds.

The twist angle in N-phenylaziridine is equal to 0° but benzene and aziridine rings in its molecule are not coplanar (the bend angle in this compound is large). The amine nitrogen atom in N-(*p*-nitrophenyl)aziridine is nearly-sp^3 hybridized. It has been found that substituent in *p*-substituted N-phenylaziridines only slightly affects electron distribution in the aziridine ring. This proves that n_N-π_{Ar} conjugation in these compounds is insignificant. Substituent resonance constant for 1-aziridino groups is equal to -0.29 (-0.38). The twist angle in N-phenylaziridine and its *ortho*-methyl and 2,6-dimethyl derivatives is also equal to 0°. Pyramidalization angle in N-phenyl-aziridine is large (54.5°). N-Phenylaziridine is least conjugated of N-phenyl cyclic amines. Hybridization of the amino nitrogen atom in N-phenylazetidine, N-phenylpyrrolidine and N-phenylpiperidine is nearly-sp^2. The twist angle in first two compounds is equal to 0° but this angle is equal to 48° in N-phenylhexamethyleneimine. Moreover, it is known that twist angle in this compound is increased by introduction of the methyl groups into *ortho* positions. The donor strength of "cyclic" amino substituents change in the following order: 1-pyrrolidino > 1-azetidino > 1-piperidino.

The respective substituent constants are equal to -0.63 (-0.69), -0.55 and –0.47 (-0.41). The electron-donor strength was found to change as follows: $N(CH_2)_2 < NH_2 < N(CH_2)_5 < NMe_2 < N(CH_2)_3 < NEt_2 < N(CH_2)_4$. Thus, 1-pyrrolidine is the most powerful electron-donor among different amino groups.

Molecules of N-methylindoline and N-methyl-1,2,3,4-tetrahydroquinoline are planar. On the other hand, the seven-membered ring in N-methyl-*homo*-tetrahydro-quinoline is highly puckered. The amino nitrogen atom in first two compounds is much stronger electron-donor as compared to that in the third compound. It has been proved that the n_N-π_{Ar} conjugation in julolidine is much stronger than that in lilolidine. Although benzoquinuclidine is an aromatic amine, there is no resonance interaction between the amino nitrogen atom and the benzene ring in its molecule. $\sigma_R{}^O$ for the twisted -N< group in this compound is equal to -0.13

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