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Photochemistry of Aliphatic and Aromatic Amines

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The luminescence spectroscopic properties and photochemical reactions of aliphatic and aromatic amines in liquid and solid solutions are examined. Attention is concentrated on the photochemical reactions of aromatic amines derived from aniline in liquid solutions. The mechanism of the photodissociation of the nitrogen-hydrogen and carbon-nitrogen bonds and the dependence of the luminescence spectroscopic properties of amines on their structure and on the positions of their energy levels in the lowest electronically excited states are discussed.
The bibliography includes 151 references.

CONTENTS

I.	Introduction	1041
II.	Aliphatic amines	1042
III.	Aromatic amines	1045

I. INTRODUCTION

Much attention has been devoted recently to the study of the mechanisms of the photochemical processes involving aliphatic and aromatic amines not only because of the vigorous development of fundamental photochemical studies but also because of numerous investigations in adjacent branches of science and engineering (photobiology, photodegradation, and photostabilisation of polymers, theory of photographic processes, lasers based on organic compounds). The absorption bands of amines are as a rule located in the ultraviolet and in addition amines have low oxidation potentials. In view of these properties, aliphatic and aromatic amines are convenient models for the investigation of the mechanisms of photochemical processes and, in particular, of the quenching of fluorescence via electron transfer and for the investigation of donor–acceptor interactions in exciplexes.

The need for a detailed description of the reactivities of organic compounds in terms of different classes arises from the fact that photochemical behaviour is usually classified in terms of types of reactions: photodissociation (photocleavage), photosubstitution, photoaddition, photoisomerisation, and photorearrangements, as well as oxidation-reduction reactions (electron phototransfer). However, such studies are insufficient for the understanding of the reactivities of compounds of different types, particularly since in practice the converse problem frequently arises: it is necessary to know the photochemical properties of compounds of a definite class in order to foresee all the reactions possible under the given conditions.

The aim of the present review was to examine and summarise the results of studies of the photochemical and luminescence spectroscopic properties of aromatic and aliphatic amines. For this purpose, a classification of the photochemical properties of amines is proposed on the basis of ideas concerning the elementary photochemical processes and a scheme for the disposition of the lowest electronically excited states in specific systems has been constructed. The nature of the electronically excited state through which a photochemical reaction proceeds is discussed on the basis of kinetic data for the elementary processes.

The formation of exciplexes in the degradation of the electronic excitation energy has been studied in extremely great detail.[1-3] This review deals only with the mechanisms of the photochemical reactions of amine molecules in solutions (the mechanisms of the solid-phase reactions of these compounds have been studied fairly completely[4-13]). The data on the photolysis and, in particular, the luminescence of amines in the gas phase, which have been described systematically in a monograph,[7] are invoked only insofar as they are needed for the understanding of the photoprocesses in the condensed phase.

Table 1. The luminescence spectroscopic properties of aliphatic amines.

Amine	Solvent	λ_{abs}^{max}, nm	ϵ_{max}, litre mol^{-1} cm^{-1}	λ_{fl}^{max}, nm	φ_{fl}	τ_{fl}, ns	Refs.
Trimethylamine	—	198	3720	287	0.97	45	[31]
Diethylmethylamine	hexane	—	—	292	0.64	26.0	[33]
"	tetrahydrofuran	—	—	308	0.44	42	[33]
"	ether	—	—	340	0.14	48	[33]
Triethylamine	hexane	—	—	286	0.69	--	[33]
"	tetrahydrofuran	—	—	340	—	--	[38]
"	ether	—	—	310	—	—	[38]
4-Methylpiperidine	—	207	5500	290	0.95	60	[37]
4,*N*-Dimethylpiperidine	—	—	—	—	1.0	50	[37]
N-Methylmorpholine	—	204	4150	274	0.78	66	[37]

Notation: λ_{abs}^{max} and ε_{max} are the wavelength of the maximum in the absorption spectrum and the extinction coefficient and λ_{fl}^{max}, ϕ_{fl}, and τ_{fl} are the wavelength of the maximum in the fluorescence spectrum, the quantum yield, and the fluorescence lifetime.

II. ALIPHATIC AMINES

1. Absorption Spectra

Bands of moderate intensity with a maximum at ~200 nm (Table 1) are observed in the ultraviolet absorption spectra of the simplest aliphatic amines (methyl- and ethyl-amines). Previously it was regarded as an established fact that the long-wavelength absorption band of aliphatic amines corresponds to the $n \rightarrow \sigma^*$ transition and is therefore absent from the spectra of acid solutions since the nitrogen atom in the cation has no non-bonding n electrons.[14-21] Within the framework of this type of explanation and on the basis of quantum-chemical calculations, it has been suggested[14] that the unshared electron pair in the molecules of ammonia and alkylamines is located in the *sp*-hybrid atomic orbital (AO) located along the symmetry axis of the molecule. The band corresponding to the $n \rightarrow \sigma^*$ transition in the absorption spectra of such molecules should be fairly intense.[22-31] Recent calculations[19-23] have shown that all the lowest electronically excited states of ammonia and primary amines are of the Rydberg type (Table 2) (the assignment of the long-wavelength absorption bands to the $\sigma \rightarrow \sigma^*$ and $n \rightarrow \sigma^*$ transitions in alkylamines is erroneous[31]). The simplest primary amines (methylamine and ethylamine) have a lowest Rydberg n, 3*s* state in which the predissociative decomposition of the N–H bond takes place.[23]

Table 2. The transitions for ABCO and ABCU.[39]

Transition	n	Orbital*
ABCU		
$S_1 \leftarrow S_0$	3	3*s*
$S_2 \leftarrow S_0$	3	3*p*
$S_3 \leftarrow S_0$	3	3*d*
$S_3 \leftarrow S_0$	4	4*s*
$S_4 \leftarrow S_0$	4	4*p*
ABCO		
$S_1 \leftarrow S_0$	3	3*s*
$S_2 \leftarrow S_0$	3	3*p*
$S_3 \leftarrow S_0$	4	4*s*

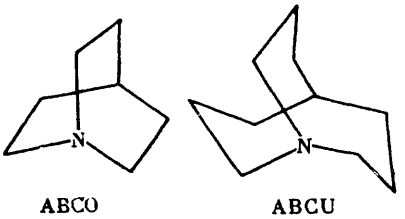
*Only the Rydberg orbitals are presented.

2. Luminescence Properties

Tertiary aliphatic amines fluoresce in the gas phase and in solution,[12,32,33] while primary and secondary amines do not. The fluorescence of the simplest tertiary amines (trimethylamine and tri-n-propylamine) under the influence of light at a wavelength of 206.2 nm takes place either in the σ^* or Rydberg state.[32] The absence of fluorescence in primary and secondary amines in the gas phase is associated with their effective deactivation via predissociation, which takes place only in compounds where hydrogen (or deuterium) is bonded directly to the nitrogen.[32-42]

In the absence of steric perturbations, the configuration of the molecules of saturated tertiary amines (in which the unshared electron pair of the nitrogen plays the role of the chromophore) in the equilibrium excited singlet state is planar (and not tetrahedral as in the ground state).[39]

The nature of the atomic orbitals in which n electrons are excited on irradiation has been determined for symmetrical amines derived from 1-azabicyclo[2,2,2]octane (ABCO) and 1-azabicyclo[3,3,3]undecane (ABCU) on the basis of the magnitude of the quantum defect (Table 2); it was found that all three long-wavelength bands are of the Rydberg type for these substances.[39-42]



ABCO ABCU

An intense bathochromic shift of the fluorescence spectra with increasing solvent polarity is characteristic of all aliphatic amines (Table 2); the long-wavelength bands of the fluorescence excitation and absorption spectra then remain

unaltered (at 77 K a shift of the above type is not observed in a frozen matrix).[42] The shift is associated, according to Muto et al.,[42] with the change in the nature of the lowest electronically excited state of amines from the Franck–Condon state, corresponding to the first absorption band of the σ* type, to the Rydberg 3s state, which is significantly stabilised under the influence of the solvent as a result of the ion–dipole interaction of the nucleus of the cation in the Rydberg 3s state with a solvent molecule. A model of the solvated Rydberg state,[42] in which the orbital of the excited amine electron passes through the closest solvent molecules has in fact been developed on the basis of the fluorescence data for aliphatic amines. Thus the solvated Rydberg state consists, according to Nakato et al.,[43] of a cation–electron pair linked by Coulombic forces.

The role of the solvated Rydberg state in the bathochromic shift of the fluorescence spectrum of diethylmethylamine in a polar solvent has been noted in a recently published communication.[33]

An *ab initio* quantum-chemical calculation of the energies of the lowest electronic transitions in trimethylamine, ABCO, and diazabicyclo[2,2,2]octane (DABCO) showed[34] that all these states are fully of the Rydberg type (no valence states with energies below 6.4 eV have been found), although it had been assumed earlier[41] that two long-wavelength bands in the absorption spectra of dialkylamines are associated with the $n \rightarrow \sigma^*$ transition. It has also been noted that in the case of saturated amines there can be no mixing of the excited valence states with the Rydberg states (at least for the amines in which excitation entails an insignificant alteration of the molecular geometry[34]).

3. Photochemical Properties

(a) Primary amines

The photochemical properties of all the aliphatic amines, except tertiary amines, are determined by the lability of their N–H bonds. Under the influence of light with $\lambda < 240$ nm, aliphatic amines in hexane decompose with formation of gaseous products and hex-1-ene. The primary step in the photolysis is the dissociation of the N–H bond:[15]

$$RNH_2 + h\nu \rightarrow R\dot{N}H + H. \quad (1)$$

The quantum yields in the photodecomposition of amines in hexane are listed in Table 3; they depend only slightly on the concentration of the amines and increase insignificantly with increased temperature.

In polar solvents (for example, in water) the dissociation of the C–N bond becomes possible because the homolytic dissociation of the N–H bond is hindered owing to the considerable solvation of the amine molecules:[16,17]

$$RNH_2 + h\nu \rightarrow \dot{R} + \dot{N}H_2. \quad (2)$$

The photodecomposition quantum yield is then found to be less than in hexane (Table 4) and the photolysis products are ammonia and alcohols. In water the yield in the photodecomposition of amines increases sharply with increasing pH.

The mechanism of the liquid-phase photolysis of aliphatic amines has been studied in greatest detail for solutions of cyclohexyl- and cyclopentyl-amines in cyclohexane and cyclopentane and also of n-hexylamine in hexane.[18] The products of the photolysis of cyclohexylamine are cyclohexylcyclohexane and ammonia and those of the photolysis of cyclopentylamine are cyclopentylcyclopentane, *N*-cyclopentylidenecyclopentylamine, and dicyclopentylamine. The primary processes occurring under these conditions can be illustrated schematically in the following manner:

$$RR'CHNH_2 \xrightarrow{h\nu} \begin{cases} \rightarrow RR'CH\dot{N}H + H; & (3) \\ \rightarrow RR'\dot{C}H + \dot{N}H_2; & (4) \\ \rightarrow RR'\dot{C}NH_2 + H; & (5) \\ \rightarrow RR'C{=}NH + H_2. & (6) \end{cases}$$

Table 3. The quantum yields in the photochemical decomposition of amines in hexane (ϕ_1) and water (ϕ_2)*.

Amine	φ_1	φ_2	Amine	φ_1	φ_2
Isopropylamine	0.100	0.049	n-Pentylamine	0.052	0.037
n-Propylamine	0.079	0.039	n-Hexylamine	0.064	0.038
Isobutylamine	0.092	0.046	n-Heptylamine	0.036	0.025
n-Butylamine	0.082	0.042	n-Octylamine	0.039	0.027
Isopentylamine	0.086	0.050			

*The amine concentration was 10^{-3} M; the irradiation was carried out at a wavelength of 230–240 nm.

Table 4. The energy levels (E, eV), the oscillator strengths (f), and the wave functions for the aniline molecule (according to the data of Kimura et al.[47]

Level	E_{calc} (gas phase)	E_{exp} (gas phase)	E_{exp} (in hexane)	f_{calc}	f^*_{exp} (in hexane)
W_1	4.72	4.40	4.32	0.021	0.028
W_2	5.42	5.39	5.31	0.174	0.144
W_3	6.42	6.40	6.32	0.416	0.510
W_4	6.86	6.88	7.06	0.505	0.570
W_5	8.04	7.87	—	0.745	0.68
W_6	8.05	7.87	—	0.416	0.68

*Data of Kimura and Nagakura.[55]

The relative contributions of reactions (3)–(6) for each compound are determined by the stability of the corresponding alkyl radicals. For cyclohexylamine, the principal primary photochemical process is the dissociation of the C–NH_2 bond [reaction (4)], which is followed by the interaction with the solvent:

$$NH_2 + C_6H_{12} \rightarrow \dot{C}_6H_{11} + NH_3;$$

$$2C_6H_{11} \rightarrow C_{12}H_{22}. \quad (7)$$

In the case of cyclopentylamine dissociation of the N–H bond [reaction (3)] plays the main role. On photoirradiation of n-hexylamine in cyclohexane the main product is *N*-(1-hexylidene)-n-hexylamine together with bicyclohexyl and cyclohexylamine; here too the primary photochemical process is reaction (3) involving the elimination of a hydrogen atom.[18]

The almost complete lack of data on the quantum yields of the primary photochemical processes in the photolysis of aliphatic amines in the liquid phase is noteworthy. It is

apparently due to the difficulty of the quantitative determination of the yields of the aminyl radical formed.

In contrast to the processes in the gas phase, the nature of the primary process in solutions has been little investigated: for example, it has not been established for virtually any system which of the bonds in the molecule is dissociated and what is the probability of the process; the extent of other radiative and non-radiative pathways leading to the dissipation of the electronic excitation energy in solutions of aliphatic amines are also unknown. The secondary photochemical reactions, i.e. the further reactions of the compounds arising in reactions (3)–(6) with formation of stable final products, have not been investigated in extremely great detail for aliphatic amines. The present level of knowledge is such that the nature of the final photoproducts and the relative yields can be predicted for any aliphatic amines in the usual solvents.

In the photolysis of amines in the gas phase the quantum yields in the formation of products have been measured for a series of primary photochemical processes[44–46] (one should bear in mind that only the yields in the formation of the final products were measured and the efficiency of the primary photochemical processes was inferred only from indirect data).

For example, it has been suggested[44] that methylamine undergoes photodissociation under the influence of radiation with $\lambda = 184.9$ nm:

$$CH_3NH_2 + h\nu \rightarrow CH_3\dot{N}H^* + H.$$

The quantum yield is unity and the aminyl radical formed is in an electronically excited state, decomposing further in accordance with the scheme

$$CH_3NH^* \longrightarrow H + H_2C{=}NH.$$

As a result, the quantum yield for the formation of hydrogen in the photolysis of gaseous CH_3NH_2 exceeds unity.

The quantum yields of the photochemical reaction of CH_3NH_2 in the gas phase depend strongly on the excitation wavelength[44] and the excitation of the methylamine molecule to the S_3 state entails the formation of CN and HCN via the mechanism

$$CH_3NH_2 \xrightarrow{h\nu} \begin{cases} \xrightarrow{\alpha} CH_3\dot{N}H^* + H \rightarrow H + H_2C{=}NH; \\ \xrightarrow{1-\alpha} CH_2NH^* + H_2 \rightarrow H_2 + HCN^*; \end{cases}$$

$$HCN^* \longrightarrow \begin{cases} \xrightarrow{\beta} H + \dot{C}N; \\ \xrightarrow{1-\beta} HCN, \end{cases}$$

where $\alpha = 0.59$ and $\beta = 0.44$.

As regards the photolysis of amines in the solid phase, there has been only one communication[40] stating that hydrogen atoms are ejected into the gas phase in the photolysis of frozen methylamine.

The first attempts to interpret theoretically the accumulated experimental data on the photochemical reactions of aliphatic amines and to answer the important question why the dissociation of the N–H bond in gaseous amines and not the C–N bond is most likely have been made only recently.[23] By means of non-empirical calculations, it has been possible to show[23] that the lowest excited singlet state of methylamine (the Rydberg n, $3s$ state) is capable of an adiabatic transition to the valence states of the radical products (CH_3NH + H or CH_3 + NH_2). As for NH_2, the $3s$ orbitals then lose their Rydberg character and are localised at the H atom (which leads to the dissociation of the N–H bond). In general, the transition to the Rydberg states takes place as follows: $3s \rightarrow 3s$, $\sigma^* \rightarrow 1s$.

The bond dissociation in systems of this kind thus proceeds in such a way that n, $3s$ states are converted into n, σ^* states (here σ^* refers to N–H or C–N bonds) at a certain point on moving along the reaction coordinate (i.e. on "extension" of the N–H or C–N bond). The potential energy surface of the molecule in the n, $3s$ state has a shallow minimum corresponding to such dissociation or has none at all. However, higher Rydberg states (for example, n, $3p$) have deeper minima and should be correlated with higher (usually Rydberg) states of the products. The behaviour of the molecules in the n, $3s$ state in the bond dissociation process should therefore differ from their behaviour in higher Rydberg states for which the H_2 elimination process is possible.

The potential energy surfaces for the dissociation of the N–H and C–N bonds in the n, $3s$ state for CH_3NH_2 have a minimum in the region of the Franck–Condon geometry; the dissociation of the N–H bond therefore takes place in the state to which the system is excited.

The C–N bond dissociation energy in methylamine is twice as high as the N–H bond dissociation energy.[13] However, even when the energy barrier is the same, the N–H bond should have been ruptured much more readily because this process can take place fairly effectively via tunnelling (which is feasible precisely for shallow minima of the kind which obtain in the n,$3s$ state). This in fact explains the finding that the primary photochemical process involving methylamine (and many other primary amines) in the gas phase is the dissociation of the N–H bond and this is why triethylamine (and other tertiary amines) are relatively stable on excitation by radiation with a wavelength in the region of the 0–0 band in the absorption spectrum.

(b) Secondary amines

The main products of the photolysis of ethylmethylamine in hydrocarbon solvents are hydrogen, unsaturated compounds, small amounts of methane, and a nitrogen-containing polymer.[59]

Photolysis of pure liquid diethylamine by the radiation emitted by a high-pressure mercury lamp in the absence of oxygen leads to the formation of mainly *N*-butenylidene(2-ethyl-2-butyl)ethylamine (yield in excess of 70%) and also a mixture of the *meso*-racemates of *NN*-diethyl-2,3-butylenediamine, tetraethylhydrazine and 1,3-diethyl-2,4,5-trimethylimidazoline.[20,21] The reaction mechanism involves the photodissociation of the α-hydrogen atom and the formation of the radical $CH_3\dot{C}HCNC_2H_5$. The disproportionation of this radical leads to the formation of *N*-ethylideneamine, while dimerisation produces *NN*-diethyl-2,3-butylenediamine; the interaction of these two products affords 1,3-diethyl-2,4,5-trimethylimidazoline:

$$2CH_3CHNHC_2H_5 \longrightarrow \begin{cases} \rightarrow CH_3CH{=}NC_2H_5 + (C_2H_5)_2NH; \\ \rightarrow CH_3\underset{\displaystyle CH_3CHNHC_2H_5}{CHNHC_2H_5}; \end{cases}$$

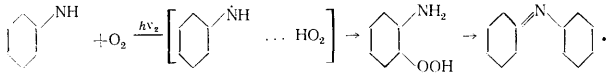
$$2CH_3CH{=}NC_2H_5 \rightarrow \underset{\displaystyle CH_2CH{=}NC_2H_5}{CH_3CHNHC_2H_5} \rightarrow CH_3CH{=}CHCH{-}NC_2H_5.$$

The presence of hydrazine among the reaction products means that the primary step in the photolysis is the abstraction of a hydrogen atom from the nitrogen, i.e. the dissociation of the N–H bond.

It is noteworthy that one cannot postulate the photodissociation of the pure compound on photoirradiation, as was done by Allan and Swan,[20] because at the given concentration

of the test substance it is in principle impossible to distinguish true photodissociation from the processes occurring on self-quenching.

The photoirradiation of solutions of amines in the presence of oxygen leads to a variety of products, which are obtained on decomposition of the hydroperoxide formed initially.[21] The excited state of the contact charge-transfer complex between the amine and oxygen arises in the first stage of photolysis[24-28] and then decomposes with formation of a hydroperoxide, which is converted into the final products:



The photoirradiation of solutions of di-n-hexylamine, dicyclohexylamine, and cyclohexyl-n-hexylamine in cyclohexane (10^{-2} M) in the absence of oxygen at 18 °C leads to the formation of the corresponding imines in preparative yields of 89–91%[28,29] (for the first compound, the product is *N*-n-hexylidene-n-hexylamine together with cyclohexylcyclohexane and n-hexylamine, while for the second compound the product is *N*-cyclohexylidenecylcohexylamine together with cyclohexylcyclohexane and cyclohexylamine). The entire photochemical reaction includes the following processes:

$$R_2NH + h\nu \rightarrow [R_2\dot{N} + H];$$
$$[R_2\dot{N} + H] \rightarrow R'CH{=}NR + H_2;$$
$$R_2NH + H \rightarrow R_2\dot{N} + H_2;$$
$$2R_2\dot{N} \rightarrow R'CH{=}NR + R_2NH.$$

In the review of von Sonntag and Schueman[12] the formation of hydrogen and imines in the photolysis of dihexylamines has been erroneously attributed to the H_2 elimination reaction.

The photoirradiation of a solution of dimethylamine in n-nonane (at a concentration in excess of 1 M) at 35 °C in the absence of oxygen leads to the formation of mainly *NNN'N'*-tetramethyldiaminomethane.[23] In addition, a small amount of methylamine and microamounts of *NNN*-triemthyldiaminomethane as well as tetramethylhydrazine are produced. The overall process mechanism includes the following stages:

$$\begin{gathered}(CH_3)_2NH \xrightarrow{h\nu} [(CH_3)_2\dot{N} + H];\\ [(CH_3)_2\dot{N} + H] \rightarrow H_2 + CH_3N{=}CH_2;\\ 2(CH_3)_2\dot{N} \rightarrow (CH_3)_2NCH_2N(CH_3)_2 + CH_3N{=}CH_2;\\ (CH_3)_2NH + H_2C{=}NCH_3 \rightarrow (CH_3)_2NCH_2NHCH_3.\end{gathered} \quad (8)$$

Photoirradiation of solutions of dimethylamine in chloroform and other organochlorine solvents also leads to the formation of aminyl radicals, but as a result of the photodissociation of the intermediate charge-transfer complex and not as a result of direct photodissociation:[24-26]

$$(CH_3)_2NH \cdot CCl_4 \xrightarrow{h\nu} Cl_3\dot{C} + [(CH_3)_2NH^+]Cl^-;$$
$$[(CH_3)_2NH^+] + (CH_3)_2NH \rightarrow (CH_3)_2NH \cdot HCl + (CH_3)_2\dot{N}.$$

The aminium radical-cation abstracts a hydrogen atom from the initial compound with formation of $(CH_3)_2\dot{N}$. This results in the formation of the dimer $(CH_3)_2NCH_2N(CH_3)_2$ and methylamine in this case too, but via different mechanisms.

Thus, in contrast to the photolysis of dimethylamine in the gas phase,[17,24-26] in organic solvents the recombination of aminyl radicals with formation of hydrazine derivatives takes place to an extremely significant extent. The almost complete absence of *NN*-dimethyldiaminomethane among the photolysis products means, according to the authors,[24] that the mechanism of the photolysis of dimethylamine is different to that postulated by Allan and Swan[20] and does not include the stage involving the formation of a C-centred radical (in addition, the α-aminoalkyl radical formed shows a tendency to recombine but not disproportionate). It is noteworthy that, according to the data of Kassab et al.,[23] obtained in the photolysis of a 1 M solution of dimethylamine, the photolysis products do not contain an imine having the structure R'HC = NR, while according to Hadley and Volman[30] precisely these amines are the main final photolysis products.

This discrepancy is apparently associated with the fact that at fairly high temperatures the imines are effectively converted into other products as a result of the reaction with the initial amine [reaction (8)] and also the fact that the imines investigated by Hadley and Volman[30] are less reactive in the nucleophilic addition of amines owing to the steric hindrance introduced by the bulky hexyl substituent.

The photodissociation of the N–H bond and the formation of the aminyl radical $(CH_3)_2\dot{N}$ in the photolysis of dimethylamine have been confirmed by the direct detection of this radical by EPR at 77 K[31,32] (the $CH_3NH\dot{C}H_2$ radical was not then detected).

In the photolysis of solutions of primary and secondary amines in non-polar solvents, the dissociation of the N–H bond is the main process for n-alkyl derivatives; the composition of the stable products is then determined by the reactivity of the aminyl radical formed and the concentration of the amine (i.e. the ratio of the rates of radical disproportionation and recombination) and also by the interaction of the radicals with the amine itself. In the photolysis of cyclic amines in more polar solvents, the probability of the dissociation of the C–N bond is greater, which leads to the appearance of products such as ammonia and bicyclohexyl (for cyclohexylamine).

(c) Tertiary amines

The photolysis of pure triethylamine by the light of a moderate pressure mercury lamp in the absence of oxygen leads to the formation of the *meso*-racemic mixture of *NNN'N'*-tetraethyl-2,3-butylenediamine and *NN*-diethyl-2,3-butylenediamine,[20] as well as small amounts of 1,3-diethyl-2,4,5-trimethylimidazoline and tetraethylhydrazine. The authors believe that the primary photochemical steps in this case are both the dissociation of the C–H bond with formation of the radical $CH_3\dot{C}HN(C_2H_5)_2$ and the dissociation of the C–N bond with formation of the radical $(C_2H_5)_2\dot{N}$, which is converted into diethylamine by abstracting hydrogen; diethylamine undergoes in its turn the photochemical decomposition described above.

III. AROMATIC AMINES

1. Absorption Spectra

The ultraviolet absorption spectra of the simplest aromatic amines (aniline and its derivatives) both in the gas phase and in solution have been investigated in fair detail.[47-55] The ultraviolet absorption spectra of aniline vapour clearly manifest five bands, three of which correspond to benzene absorption bands; at least two of the five bands are due to intramolecular charge transfer from the amino-group to the ring.[47]

Quantum-chemical calculations make it possible to interpret in detail the absorption spectra of aniline (Table 4). The wave functions for the excited states of aniline in the CNDO/S method were set up using singly excited electronic configurations of the π,π* aromati ccomponent of the aniline molecule and configurations with charge transfer from the orbitals of the unshared electron pair of the nitrogen atom to the antibonding orbitals of the aromatic ring (these configurations

correspond to the $l \rightarrow a_\pi$ transitions in Kasha's terminology [47,50]

Seven electronic configurations have been used to construct the wave functions $\Psi_0 - \Psi_b$: thsoe of the ground state, two charge-transfer states, and four locally excited states corresponding to the $A_{1g} \rightarrow B_{2u}$, $A_{1g} \rightarrow B_{1u}$, and $A_{1g} \rightarrow E_{1u}$ transitions in the benzene molecule. It follows from these calculations that the transition to the S_1 state in aniline corresponds to the transition to the B_{2u} state of the benzene ring; the contributions of charge-transfer configurations to this S_1 state are 22% for aniline and 36% for *NN*-dimethylaniline. The contribution of the charge-transfer configurations to the W_2 state of aniline is more than 50% (Table 4); thus the transitions in the aniline molecule cannot be regarded as simply the benzene transitions perturbed by the presence of the attached amino-group.[56]

Table 5. The calculated and experimental energies (E) and oscillator strengths (f) for the long-wavelength transitions of aniline derivatives.[47,55]

Transition	E, eV		f	
	calc.	expt.	calc.	expt.
		N-Methylaniline		
$W_0 \rightarrow W_1$	4.66	4.37	0.024	0.031
$W_0 \rightarrow W_2$	5.28	5.20	0.179	0.190
$W_0 \rightarrow W_3$	6.32	6.31	0.330	0.478
$W_0 \rightarrow W_4$	6.85	6.88	0.440	0.556
$W_0 \rightarrow W_5$	7.95	7.80	0.826	0.71
$W_0 \rightarrow W_6$	7.97		0.472	
		N-Ethylaniline		
$W_0 \rightarrow W_1$	4.63	4.34	0.025	0.048
$W_0 \rightarrow W_2$	5.22	5.17	0.181	0.230
$W_0 \rightarrow W_3$	6.28	6.28	0.3 4	0.450
$W_0 \rightarrow W_4$	6.85	6.88	0.426	0.530
$W_0 \rightarrow W_5$	7.92	7.75	0.850	0 77
$W_0 \rightarrow W_6$	7.95		0.475	
		NN-Dimethylaniline		
$W_0 \rightarrow W_1$	4.61	4.30	0.026	0.044
$W_0 \rightarrow W_2$	5.17	5.15	0.182	0.256
$W_0 \rightarrow W_3$	6.25	6.25	0.279	0.350
$W_0 \rightarrow W_4$	6.85	6.88	0.409	0.575
$W_0 \rightarrow W_5$	7.90	7.68	0.875	0.81
$W_0 \rightarrow W_6$	7.93		0.497	
		NN-Diethylaniline		
$W_0 \rightarrow W_1$	4.55	4.21	0.027	0.051
$W_0 \rightarrow W_2$	5.06	5.00	0.186	0.280
$W_0 \rightarrow W_3$	6.18	6.25	0.233	0.318
$W_0 \rightarrow W_4$	6.84	6.88	0.377	0.535
$W_0 \rightarrow W_5$	7.86	7.62	0.920	0.88
$W_0 \rightarrow W_6$	7.89		0.525	

It is believed[47-49,55] that all the intense absorption bands of aniline and its simplest derivatives (*N*-methylaniline, *N*-ethylaniline, *NN*-dimethylaniline, *NN*-diethylaniline, and *N*,n-butylaniline) with energies below 6.2 eV are due to $\pi-\pi^*$ transitions (Table 5). The additional bands in the region of 230 nm in the spectra of *N*-methyl-, *N*-ethyl-, and *N*-butyl-anilines have been tentatively assigned[99] to the $n \rightarrow \sigma^*$ transition, because the bands corresponding to the $n \rightarrow \sigma^*$ transitions are characteristic of saturated aliphatic amines precisely in the region of ~200 nm[57] (see the discussion of this problem below). Despite the convincing agreement between the calculated and measured transition energies[47,55] (Tables 4 and 5), an unambiguous interpretation of the electronic states of amines remains unattainable because of the necessity for the complete separation of the contributions by the σ and π orbitals, since the amine molecules are nonplanar.[58]

On the basis of calculations[49] by the PPP method taking into account the configuration interaction (in relation to aniline, β-naphthylamine, β-aminoanthracene, vinylamine, and butadienylamine), it has been shown that the excited states of many aromatic and unsaturated amines cannot be classified as "pure" π,π^* or l,a_π states but are mixed [it has been suggested that they be designated by $S(\pi l,\ \pi^*)$ and $T(\pi l\pi)$]. With increase of the Ar–NH_2 bond length, "pure" l,a_π states can appear among the excited states of these amines†.

The increase in the size of the π system is accompanied by a decrease of the contribution of the l,a_π state to the wave functions of the lowest excited states because the vibrational structure is revealed more clearly in the absorption spectra of amines with an extensive system of π-bonds.

Furthermore, comparison of the rotational constants for the S_1 state of aniline and other benzene derivatives[68] makes it possible to establish precisely that the C–N bond in the molecule of aniline in the S_1 state is shorter by 0.08 Å than in the S_0 state, because the conjugation between the unshared electron pair in the $2p_x$ orbital and the π electrons of the ring is stronger in the S_1 state.

By measuring the absorption and magnetic circular dichroism spectra of aniline and *NN*-diethylaniline in solution in the gas phase, it has been possible to establish[52] that the absorption bands of these compounds in the range 46000 to 60000 cm^{-1} correspond to the Rydberg transitions.

The absorption spectrum of aniline vapour contains a 0–0 band, corresponding to the $S_1 \leftarrow S_0$ transition and located at 46530 cm^{-1}, as well as a vibrational progression at 490 cm^{-1}. These bands are absent from the spectra of the solutions and films at 77 K; on these grounds, there are attributed to Rydberg transitions, like the bands at 53270 and 56660 cm^{-1}. All these bands are described by the Rydberg formula

$$h\nu = 62\,170 - R/(n-\delta)^2,$$

where 62170 cm^{-1} is the first (adiabatic) ionisation potential of aniline. The quantum defect, which amounts to $\delta = 0.53$, shows that the bands belong to the *np* series.

In contrast to aniline, Rydberg transitions not only of the *p* type but also of the *s* type (corresponding to the first ionisation potential) can be clearly observed for *NN*-diethylaniline, which is associated with the fact that the highest occupied orbital in *NN*-diethylaniline has a different character—this is predominantly the *n* orbital of the substituent (the amino-group).

Thus Rydberg transitions appear at 47180 cm^{-1} in the spectrum of aniline and at ~36520, 38880, and 42000 cm^{-1} for *NN*-diethylaniline;[52] consequently the appearance of low-lying Rydberg states, due to the change in the nature of the highest occupied molecular orbitals, may be expected for aniline derivatives with electron-donating substituents (particularly in solution).

Previously it was thought to be established that the oscillator strengths of dialkylanilines,[59] corresponding to the four long-wavelength absorption bands, are proportional to

† Precisely the involvement of the l,a_π state in the establishment of the excited states explains the spreading of the absorption bands of the amines (compared with the bands in the spectra of hydrocarbons having a vibrational structure), because the change in the C = N bond length on excitation is in fact associated with these states.

$\cos^2\alpha$, where α is the angle between the plane of the amino-group and that of the benzene ring (the so-called "$\cos^2$ law"). This was deduced by Platt on the basis of the hypothesis that the dipole moment of the transition is proportional to the resonance energy, which is in its turn proportional to the overlap integral of the orbitals of the amino-group and the ring and hence to the angle α. However, the resonance energy for 5-cyano-*N*-methylindoline and all other indoline derivatives investigated is much higher than for methyl- or diethyl-aniline, although the oscillator strength of the long-wavelength transition is much lower for indoline derivatives.[59-61]

It is believed[62] that this discrepancy is caused by the mixing of the lowest charge-transfer states of these compounds with locally excited states: it has been shown that the energy of the lowest state of aniline hardly changes when the molecule is "twisted"[63] and the observed bathochromic shift of the absorption band is a consequence of the decreased energies of charge-transfer transitions. For low values of α, the mixing is slight and the usual $f \propto \cos^2\alpha$ relation is observed; for high values of α, there is a deviation from the relation caused by the contribution of the charge-transfer state.

According to Frolen and Goodman,[63] the $f \propto \cos^2\alpha$ law is valid only in the range of values of α amounting to ~30–90°; for smaller angles, one must use the formula

$$(\epsilon_{corr} - \epsilon_{min})/(\epsilon_0 - \epsilon_{min}) = \cos^2\alpha,$$

where ε_{corr} is the extinction coefficient at the maximum corrected for the non-steric influence of the substituents and ε_0 and ε_{min} are the maximum and the minimum values of ε respectively.

2. Luminescence Properties

All aromatic amines fluoresce in liquid solutions and hardly phosphoresce in frozen matrices;[62-91] examples are presented in Table 6.

The dependence of the fluorescence spectra of aniline on solvent polarity has been studied in detail and it has been shown that, with increased solvent polarity, the maximum of the fluorescence spectrum shifts from 315 nm in cyclohexane to 342 nm in water.[53] In hydroxylated solvents 1:1 complexes are formed with a hydrogen bond between the hydrogen of the hydroxyl and the unshared electron pair of aniline; an increase of solvent polarity leads to the "blocking" of the unshared electron pair of nitrogen, as a result of which the luminescence transition becomes close to the $n \rightarrow \pi^*$ type and the fluorescence quantum yield is correspondingly reduced.[65]

The fluorescent state of the β-naphthylamine molecule corresponds to the $'L_b$ state of naphthalene. The absorption band corresponding to this transition lies 6000 cm^{-1} below the band corresponding to the $'L_a$ state[148] (Table 6).

The first absorption band in the spectrum of α-naphthylamine consists of two unresolved components corresponding to transitions to the modified $'L_a$ and $'L_b$ states of naphthalene. The shoulder in the region of 30000 cm^{-1} in the absorption spectrum of its solution in cyclohexane corresponds to the transition to the $'L_b$ state.

Two features are characteristic of the luminescence properties of naphthylamines: an appreciable bathochromic shift of the fluorescence spectra in polar solvents while the fluorescence excitation spectrum remains unchanged and a significant discrepancy between the calculated and experimental fluorescence lifetimes.[148] It has been observed that the excitation of β-naphthylamine entails an increase of the dipole moment by 3.5 D, while the dipole moment of α-naphthylamine increases by 1.9–2.5 D. The increase of the dipole moment on excitation is caused by charge transfer from the nitrogen of the amino-group to the ring; the amino-group then undergoes a change in its conformation from the tetrahedral sp^3 conformation in the ground state to the trigonal sp^2 conformation in the excited state.[148] The equilibrium excited state is characterised by a greater degree of charge transfer than the Franck–Condon state, and the probability of a transition from this state is therefore greater than the probability calculated from the absorption spectra. This is why the experimental fluorescence lifetimes $\tau = \tau_{fl}/\phi$ are smaller than those calculated from the absorption spectrum.

Analogous results for α-naphthylamine have been again obtained recently and quite independently.[147] The authors investigated the kinetics of the quenching of the fluorescence and the shift of the fluorescence band as a function of solvent polarity and concluded that the $'L_a$ and $'L_b$ states of α-naphthylamine undergo an inversion in polar solvents. According to the authors,[147] the anomalous bathochromic shift of the fluorescence spectra of α-naphthylamine in polar solvents (even in frozen glasses) is associated with two mechanisms for relaxation of the Franck–Condon state: a change in the conformation of the amino-group and the relaxation of the solvent dipole relative to the increased amine dipole in the excited state, which leads to an increase of the contribution of the $'L_a$ charge-transfer state in polar solvents. The observed dependence of the bathochromic shift on solvent viscosity and temperature can be explained by the operation of the solvent dipole relaxation mechanism.

A characteristic feature of all aromatic amines, which leads to a change in their absorption spectra and to the quenching of their fluorescence, is the formation of hydrogen bonds with proton acceptors.[67] In the ground state the hydrogen bond between amines and proton acceptors is frequently very weak (for example, the equilibrium constant for the hydrogen-bonded complex between 1-aminopyrene and pyridine in hexane is 3 litre mol^{-1}); in polar solvents the hydrogen bonds are even weaker by virtue of the solvation of the amine and acceptor molecules. In the S_1 state amines form hydrogen bonds much more vigorously; the formation of a complex is manifested by the bathochromic shift of the absorption spectra.

It has been established by picosecond laser photolysis[114] that the excitation of such hydrogen-bonded complexes leads to charge transfer between the donor and acceptor and equilibrium between the locally excited donor and the charge-transfer complex (CTC) (D – H...A and $D^+ - H...A^-$) is established over a period shorter than 6 ps.

It is believed[114] that the fluorescence of amines in hydrogen-bonded complexes with pyridine is quenched as a result of the formation of short-lived non-fluorescent CTC on excitation of the hydrogen-bonded donor (amine)–acceptor (pyridine) pair.

(a) Acid–base properties in the ground and excited states

The luminescence properties of aromatic amines are closely related to their acid–base properties, namely all aromatic amines are weak bases. When aniline and aminoanthracenes are protonated, the perturbing influence of the amino-groups on the aromatic ring is reduced to a minimum and the absorption spectrum of the $C_6H_5NH_3^+$ ion in alcohol is therefore almost identical with the benzene spectrum,[69] while the spectra of the cations of aminoanthracenes are almost identical with the spectrum of anthracene.

The anilinium ion fluoresces and phosphoresces in the ether–isopentane–ethanol mixture (EPA) at 80 K and at room temperature;[22] the positions of the maxima of the 0–0 band at 80 K in EPA are illustrated below:

	Aniline	Anilinium ion
Absorption	35502	37497
Fluorescence	29620	37580
Phosphorescence	24535	29470

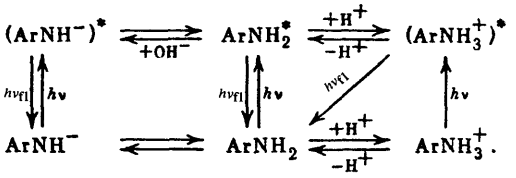
Table 6. The luminescence spectroscopic properties of amines.

Amine	Solvent	ν_{abs}, cm^{-1}	ϵ_{max}	ν_{fl}, cm^{-1}	φ_{fl}	τ_{fl}, ns	E_{0-0}, cm^{-1}	φ_{ISC}	Refs.
Aniline	hexane	34 800	1 760	31 750	0.17	3.9	32 937	0.75	[64]
"	"	34 602	1 800	30 580	0.14	—	—	—	[64]
"	ethanol	35 210	1 480	29 411	0.10	2.7	32 062	0.90	[64]
N-Methylaniline	cyclohexane	33 900	—	—	—	—	—	—	[99]
NN-Dimethylaniline	"	33 444	—	—	—	—	—	—	[99]
β-Naphthylamine	"	—	5 600	—	0 33	6.9	—	—	[148]
"	ethanol	—	—	—	0.46	16.6	—	—	[148]
α-Naphthylamine	cyclohexane	31 250	2 000	26 670	0.46	6	—	—	[148]
"	ethanol	—	—	—	0 57	19.5	—	—	[148]
1-Aminoaphthalene-sulphonic acid	DMF	28 490	—	21 690	0.82	27.3	—	—	[148]
"	acetonitrile	20 070	—	21 690	0.82	28.5	—	—	[148]
"	methanol	29 325	—	20 620	0.24	17.3	—	—	[148]
1-Aminoanthracene	water–ethanol	—	4 000	—	—	—	21 650	—	[87]
2-Aminoanthracene	"	—	4 000	—	—	14	22 100	—	[87]
9-Aminoanthracene	"	—	4 000	—	—	—	21 500	—	[87]
2-Aminonaphthalene-1-sulphonic acid	methanol	29 000	—	25 060	0.39	4.46	—	—	[87]
Ditto	water	29 411	—	24 900	0.21	2.03	—	—	[87]
o-Aminobenzoic acid	cyclohexane	29 800	—	25 800	—	—	—	—	[151]
Ditto	benzene	29 600	—	25 200	—	—	—	—	[151]
"	ethanol	29 800	—	24 200	—	—	—	—	[151]
m-Aminobenzoic acid	cyclohexane	31 000	—	26 000	—	—	—	—	[151]
Ditto	ethanol	31 300	—	22 700	—	—	—	—	[151]
"	acetonitrile	31 000	—	24 600	—	—	—	—	[151]
p-Aminobenzoic acid	benzene	35 100	—	30 700	—	—	—	—	[151]
Ditto	ethanol	34 600	—	29 000	—	—	—	—	[151]
"	acetonitrile	35 100	—	29 900	—	—	—	—	[151]
Methyldiphenyl-amine	cyclohexane	34 245	12 500	—	0.042	—	24 600	0.89	[136]
Diphenylamine	"	35 460	17 400	—	0.05	3.2	25 200	0.38	[136]
Triphenylamine	"	33 333	23 700	—	0.072	—	24 500	0.88	[136]
"	toluene	—	—	—	0.045	—	—	1.05	[111]
1-(*NN*-Dimethylamino)-naphthalene	cyclohexane	31 850	—	26 320	0.011	0.13	—	—	[147]
"	acetonitrile	31 850	—	23 670	—	—	—	—	[147]
"	THF	32 050	—	24 540	0.12	1.58	—	—	[147]
2,2,4-Trimethyl-1,2-dihydroquinoline	cyclohexane	29 070	3 200	—	0.31	6.78	—	0.02	[123]
6-Ethoxy-DHQ	"	27 030	3 000	—	0.33	8.44	—	0.014	[123]
6-Hydroxy-DHQ	"	28 090	3 600	—	0.39	8.80	—	0.017	[123]
N-Acetoxy-2,2,4-trimethyldihydro-quinoline	"	32 258	5 000	—	—	—	—	—	[120]
2,2,4-Trimethyl-THQ	"	—	—	—	0.17	2.79	—	—	[53]
4-Phenyl-THQ	benzene	—	—	—	0.09	2.33	—	—	[53]
6-Aminochrysene	cyclohexane	29 600	21 880	25 100	0.28	—	—	—	[150]
"	ethanol	29 500	19 050	22 935	0.25	—	—	—	[150]
"	water	29 410	—	21 280	0.16	—	—	—	[150]

Notation: ν_{abs}, ϵ_{max}, and ν_{fl} are the long-wavelength maximum in the absorption spectrum, the extinction coefficient at the maximum, and the maximum in the fluorescence spectrum respectively, ϕ_{ISC} is the intersystem conversion quantum yield, and DHQ and THQ represent 1,2-dihydroquinoline and 1,2,3,4-tetrahydroquinoline respectively; for the significance of the remaining notation, see the footnote to Table 1.

In the S_1 state the principal properties of aniline are weakened and the anilinium ion dissociates adiabatically in the excited state at room temperature; the fluorescence of aniline itself is then observed.[69]

Aminoanthracenes and 1,2-dihydroquinolines in the excited state undergo acid dissociation: a longer-wavelength fluorescence band, corresponding to emission by the anthramide anion[87] or the corresponding anion derived from 1,2-dihydroquinolines,[88] appears in the spectrum in highly alkaline solutions.



Thus, a common feature of all aromatic amines is the weakening of the basic and intensification of the acid properties when they are excited to the S_1 state, which leads to the effective quenching of the fluorescence of amines by proton donors.[70–74]

The mechanism of the dissipation of the electronic excitation energy in the phototransfer of a proton has been studied in detail.[70–72] It has been shown in relation to aqueous and alcoholic solutions of β-naphthylamine, 3-aminopyrene, and 2-aminoanthracene that in highly acid solutions of the amines the excited states of the latter undergo effective induced deactivation by protons.[70,71] This process apparently involves the protonation of aromatic amines in the aromatic ring. At acid concentrations of 2–5 M, the appearance of a third emission band of amines (apart from the fluorescence bands of the neutral amine and the cation), which is due to the fluorescence of a carbonium ion, has been observed[71] in the range 550–580 nm. This means that the protonation process is adiabatic without loss of excitation.

The possibility of the induced deactivation by the proton of the excited states of 1- and 2-naphthylamines, formed as a result of the dissociation of their cations in the excited state, has also been noted[74] but it has been attributed to adiabatic deactivation.

The p*K* of the amines in the ground and excited states have been listed in another review[73] and will not be quoted here.

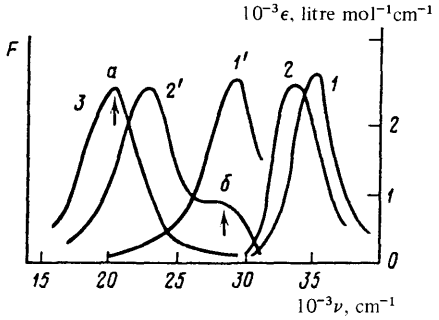


Figure 1. Absorption and fluorescence spectra of *p*-cyano-3-methyl-*NN*-dimethylaniline:[75,81] 1) and 1') in methylcyclohexane; 2) and 2') in dichloromethane; 3) in acetonitrile (the absorption spectrum in acetonitrile is close to that in methylcyclohexane and is not presented here).

(b) The luminescence properties of amine molecules with a "twisted intramolecular charge transfer state"

NN-Dialkyl-*p*-cyanoanilines (and in general anilines with electron-donating and electron-accepting substituents in the *para*-position) occupy a special place among aniline

derivatives.[62,75-86] A characteristic feature of these compounds is the two-component fluorescence of their solutions in polar solvents (Fig.1).[75] In a non-polar solvent (methylcyclohexane) there is only one "normal" fluorescence band of *NN*-dialkyl-*p*-cyanoanilines, while in more polar solvents there are two components *a* and *b*, the intensity and bathochromic shift of the long-wavelength component *a* increasing with solvent polarity.

Detailed studies of the luminescence,[76-78] luminescence spectroscopic,[79,80] and photochemical[85] properties of the above compounds led to the conclusion that a type of excited states (Fig.2), hitherto unknown, exists for these compounds—"states with twisted intramolecular charge transfer" (TICT) in the terminology adopted by Grabowski et al.[75] Quantum-chemical calculations showed that complete intramolecular charge transfer from the unshared electron pair of the $N(CH_3)_2$ group to the π^* orbital of the CN substituent[81] is possible for these compounds in the conformation where the angle α between the planes of the donor and acceptor is 90°.

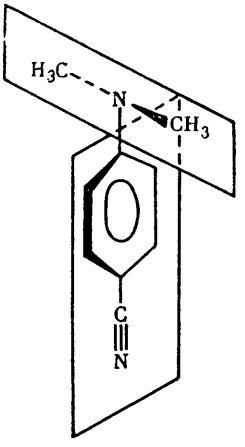
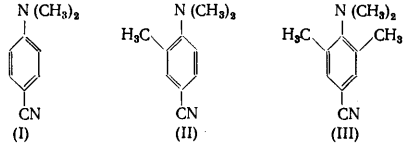
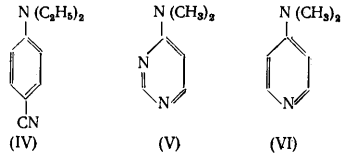
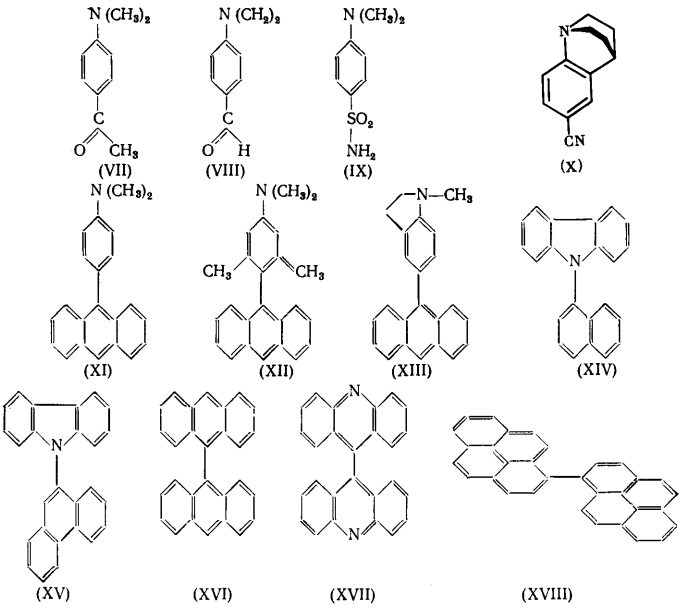


Figure 2. The "twisted state" of *p*-cyano-*NN*-dimethylaniline.

The formulae of all the compounds for which TICT has been postulated are given below.[75]







Thus, when *NN*-dialkyl-*p*-cyanoanilines are irradiated, the usual delocalised π,π^* state is initially excited, as in all other aniline derivatives. In non-polar solvents this state exhibits the usual fluorescence (the *b* band); but in polar solvents rapid $b^* \rightarrow a^*$ relaxation takes place and radiation is emitted from this TICT state (the *a* band). In solvents of moderate polarity the $b^* \rightleftarrows a^*$ equilibrium obtains and both fluorescence bands are shown.

The kinetics of the solvation by alcohol of the TICT state of *p*-dimethylaminobenzonitrile have been followed directly by the method of picosecond laser photolysis.[82] It follows from the results of these measurements that the equilibrium between the planar and TICT states in propanol is established after ~20 ps; the constant of this equilibrium has been estimated (not less than 30 in propanol and not less than 25 in butanol). A second value of the formation time of TICT state, amounting to 11 ps, has been determined from the kinetics of the quenching of the two-component fluorescence of *p*-dimethylaminobenzonitrile by oxygen[75,81] and, according to these data, the rate of formation of the TICT state does not depend significantly on the viscosity.

The most convincing proof of the role of the TICT states in the emission of the anomalous fluorescence band has been provided by structural studies.[75,81] The authors studied in detail the luminescence spectroscopic properties of various sterically hindered anilines and showed that, for compounds (II) and (III) whose *ortho*-positions relative to the amino-group contain methyl groups (in which the twisted structure is as it were "fixed"), only the *a* band is observed, while compound (I) emits both bands.

The fluorescence of compounds (I)–(III) in the TICT state must be rigorously prohibited both by steric factors (owing to the minimum overlap of the orbitals involved in the transition for the "twisted" conformation) and by the symmetry ($A_2 \leftarrow A_1$ transition in the C_{2v} point group). However, extremely low activation energies have been obtained from the temperature variation of the emission rate constant: $k_B = k_0 + k_1 \exp(-hcE/kT)$, $E \approx 120$–200 cm^{-1}. Such low values of E are associated with the occurrence of torsional vibrations, which increase the overlap between the donor and acceptor orbitals and thus increase the probability of the radiative transition.

The luminescence properties of *p*-dimethylaminobenzaldehyde (VII) and its derivatives (XVI) are even more complex.[77] Apart from the emission bands *a* and *b* associated with the TICT, the spectra of these compounds show bands due to aggregates and excimers.

In non-polar solvents the monomer of *p*-dimethylaminobenzaldehyde does not fluoresce at all in the lowest $S_1(n\pi^*)$ state and only phosphorescence in the $T_1(\pi,\pi^*)$ state is observed; in polar solvents a band *b* due to the fluorescence in the $S_1(\pi,\pi^*)$ state is observed. With increase of solvent polarity, there is a bathochromic shift of the band corresponding to the emission from the TICT state.

The fluorescence quantum yield of *p*-dimethylaminobenzaldehyde and *p*-dimethylaminoacetophenone in methyltetrahydrofuran depends on the excitation wavelength (Table 7).[84]

Table 7. The fluorescence (ϕ_{fl}) and phosphorescence (ϕ_{phosph}) quantum yields for *p*-dimethylaminobenzaldehyde (DAB) and *p*-dimethylaminoacetophenone (DAA).[84]

Amine	Solvent	φ_{fl}		φ_{phosph}
		λ_{exc} = 338 nm	λ_{exc} = 357 nm	
DAB	methyl-THF	—	0.09	0.20±0.015
DAB	propanol	0.56	0.93	0.07±0.017
DAB	methanol-water	0.98	—	0.014
DAA	methyl-THF	<0.01	—	0.44±0.05
DAA	propanol	0.32	—	0.04

The existence of several conformers of compounds (I) and (II) in the ground state follows from the discrepancy between the fluorescence excitation spectra of the two compounds and their absorption spectra. The fluorescence quantum yield of compounds (I) and (II) increases appreciably with decrease of temperature: at 77 K it is greater by two orders of magnitude than at room temperature, which is associated, according to the authors,[84] with the presence of conformers also in the TICT state, the relaxation of the initially populated planar state to form the TICT state being controlled by diffusion.

Calculations by the CNDO/S method have confirmed the existence of a whole series of conformers of compounds (I) in the ground and excited states, which are characterised by different angles of rotation of the $-N(CH_3)_2$ and $-CHO$ goups relative to the plane of the ring and by different degrees of hybridisation of the nitrogen atom, which is also responsible for the dependence of the fluorescence and phosphorescence spectra on the excitation wavelength.[86]

3. Photochemical Properties

The photochemical properties of aromatic amines are classified in this Section in terms of the type of the primary processes undergone by the amines. Four possible processes are examined: photodissociation of the N–H bond, photoionisation and formation of exciplexes, photodissociation of the C–N bond, and photorearrangements in the aromatic rings.

(a) Photodissociation of the N–H bond

Photoirradiation of solutions of primary and secondary aromatic amines in non-polar solvents leads to the rupture of the N–H bond and the formation of hydrogen atoms and aminyl radicals:

$$RNH + h\nu \rightarrow R\dot{N} + H \cdot$$

Aminyl radicals have been detected by flash photolysis in the photoirradiation of aniline and *N*-methylaniline,[89,94] 1,2-dihydroquinolines,[90–92] 1,2,3,4-tetrahydroquinolines (Fig. 3),[93] indoles,[94,96] 7-azaindolines,[97,98] and indolines.[100] The formation of hydrogen on photolysis of aniline and 1,2-dihydroquinolines has also been demonstrated mass-spectrometrically and chromatographically.[89,101]

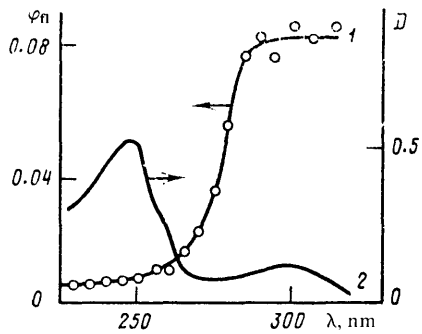


Figure 3. Dependence of the fluorescence quantum yield for a solution of 1,2,3,4- tetrahydroquinoline on the excitation wavelength (curve *1*) and the absorption spectrum of its solution in heptane (curve *2*).

The photodissociation quantum yields and the extinction coefficients of the aminyl radicals formed are presented in Table 8.

In non-polar solvents the neutral aminyl radicals are as a rule destroyed via a second order reaction in the absence of oxygen as a result of disproportionation or recombination:

$$2RN \rightarrow \text{products.}$$

The rate constants for this process are 1.5×10^9 litre $mol^{-1}s^{-1}$ for anilino-radicals in hexane[89] and 8.9×10^7 litre $mol^{-1}s^{-1}$ for 1,2-dihydroquinoline radicals.[101]

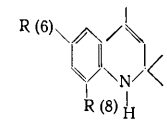
It has been shown[88,102] both experimentally and by quantum-chemical calculations that aminyl radicals are much stronger bases than the initial amines.

In aqueous and aqueous alcoholic solutions radical-cations are therefore formed in the photolysis of amines even at neutral pH:

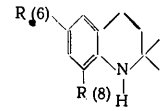
$$RNH + h\nu \rightarrow R\dot{N} + H \underset{-H^+}{\overset{+H^+}{\rightleftarrows}} RNH^+.$$

For example, the p*K* for the equilibrium $C_6H_5\dot{N}H + H^+ \rightleftarrows C_6H_5NH_2^+$ is 7.0 ± 0.1;[88] for 1,2-dihydroquinolines, the p*K*

are as a rule higher (Table 9).



(XIX): R (6)=R (8)=H
(XX): R (6)=H, R (8)=OH
(XXI): R (6)=CH_3, R (8)=H
(XXII): R (6)=H, R (8)=CH_3



(XXIII): R (6)=R (8)=H
(XXIV): R (6)=OH, R (8)=H

Table 8. The quantum yields in the photodissociation of the N–H bond and the extinction coefficients of the aminyl radicals formed.

Amine	Solvent	Radical		λ_{exc}, nm	Φ	Refs.
		λ_{max}, nm	ϵ, litre $mol^{-1}s^{-1}$			
Aniline	cyclohexane	400	670*	276	10^{-3}	[89]
"	"	308	4700**	254	0.07±0.02	[99]
N-Methylaniline	"	314	—	—	—	—
"	"	400	—	254	0.0054	[99]
Phenylethylamine	"	—	—	254	0.01	[99]
"	"	—	—	214	0.045	[99]
2,2,4-Trimethyl-1,2-dihydroquinoline	benzene	420	7500**	340—360	0.011	[123]
"	"	—	—	200—280	0.030	[123]
6-Hydroxy-DHQ	"	—	—	200—280	0.42	[123]
6-Methyl-DHQ	"	400	5000**	200—280	0.016	[123]
8-Methyl-DHQ	"	400	3000**	200—280	0.17	[123]
"	"	—	—	340—360	0.012	[123]
4-Methyl-7-azaindoline	hexane	400	457***	340—360	0.24	[97]
4,6-Dimethyl-7-azaindoline	hexane	400	457***	340—360	0.36	[97]
4,6-Dichloro-7-azaindoline	hexane	400	457***	340—360	0.22	[97]

*The extinction coefficient was determined by comparison with the spectrum of stable 2,4,6-di-t-butylanilino-radical.
**The extinction coefficient was determined by the simultaneous measurement of the absorption spectra of the anilino-radicals at 77 K in 3-methylpentane and the determination of the amount of radicals in this spectrum with the aid of EPR spectra.[123]
***The extinction coefficient was determined by the method of Malkin et al.[98] involving the comparison of the amount of aminyl radicals formed in the direct and benzophenone-sensitised photolysis.

The aniline radical-cations formed on photolysis are destroyed in water via a second-order reaction with a rate constant of 1.5×10^9 litre $mol^{-1}s^{-1}$ apparently as a result of the formation of dimeric complexes.[89]

So far little is known about the mechanism of the photodissociation of aromatic amines, particularly about the nature of the electronically excited state in which photodissociation takes place. The main source of the difficulty in determining the mechanism is the lack of quantitative information about the efficiency of the photodissociation due to the complexity of the quantitative determination of the aminyl radicals and hydrogen atoms formed on photolysis of amines.

The nature of the photochemically active excited state in such reactions was investigated for the first time only recently: for anilines, 1,2-dihydroquinolines, and 1,2,3,4-tetrahydroquinolines, we observed[90,93,99] the dependence of the fluorescence (Fig. 4) and photodissociation quantum yields on the excitation wavelength, which permitted the conclusion that, on excitation at the wavelength corresponding to the long-wavelength band in the absorption spectrum, the photodissociation takes place in the lowest singlet state (the lowest triplet state for tetrahydroquinolines) and that, with increase of the excitation energy, a new photodissociation channel is opened—via the highest excited states.

Table 9. The excess electron density at the nitrogen atom in the amine or in the aminyl radical (q_N) and the pK of the radical-cation (according to Pirogov and Malkin.[88,102]

Amine	q_N		pK	
	molecule	radical	molecule	radical*
(XIX)	−0.2089	−0.2141	4.7	10.8
(XX)	−0.2021	−0.2026	4.8	—
(XXI)	−0.2087	−0.2156	3.6	10.3
(XXII)	—	—	3.7	9.4
(XXIII)	−0.2140	−0.2091	4.55	13.0
(XXIV)	−0.2101	−0.1992	4.8	—
Aniline	—	—	4.58	7.0

*The pK were determined in an aqueous solution of ethanol at the point where the absorption spectrum of the neutral radical appeared.

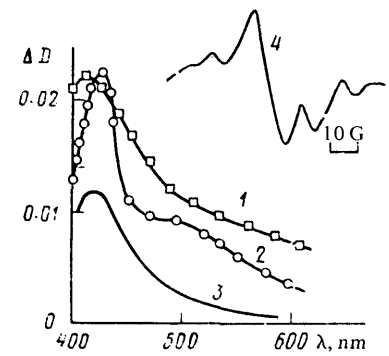


Figure 4. Absorption spectra of heptane solutions of the short-lived intermediates formed on photolysis of 1,2,3,4-tetrahydroquinoline [1) compound (XIX); 2) compound (XX)] and the absorption (curve 3) and EPR (curve 4) spectra of the aminyl radicals formed on photolysis of compounds (XIX) in vitreous 3-methylpentane matrix at 77 K.

The yield in the photochemical decomposition of aniline on photoexcitation with light at $\lambda = 254$ nm is 0.1, which is close to the quantum yield in the evolution of H_2. This shows that processes other than the dissociation of the N–H bond hardly occur in the photolysis of aniline in cyclohexane.[99]

At the present time the only question that remain obscure is whether the dissociation of the N–H bond in the highest excited states is responsible for the observed dependence on wavelength of the fluorescence quantum yields of aniline and other amines. Evidently, other photochemical processes (for example, reversible photoisomerisation of the benzene ring with formation of Dewar benzene) cannot induce this

process, because the fluorescence quantum yield of *NN*-dimethylaniline is almost independent of the excitation wavelength.[99] The dependence of the fluorescence and photochemical decomposition quantum yields of anilines and hydrogenated quinolines on the excitation wavelength is observed only in non-polar solvents and in water, while in alcohol there is no such dependence, which is apparently due to the recently observed formation of complexes between amines and alcohols.[103]

According to Köhler and Getoff[99] and Robin,[104] many amines exhibit low-lying Rydberg $n,3s$ states in the region of 40000 cm^{-1}. It appears probable that on excitation to the S_2 state, aniline (an in general all primary and secondary amines) undergo a transition onto the Rydberg potential surface, where bond dissociation takes place. A calculation[105] of the energies of the excited states of 1,2-dihydroquinolines by the CNDO/S method taking into account 40 excited configurations showed that a sharp increase of the photodissociation quantum yield takes place in the region of the $T_8(\sigma,\pi^*)$ state localised at the NH fragment (Fig.5).

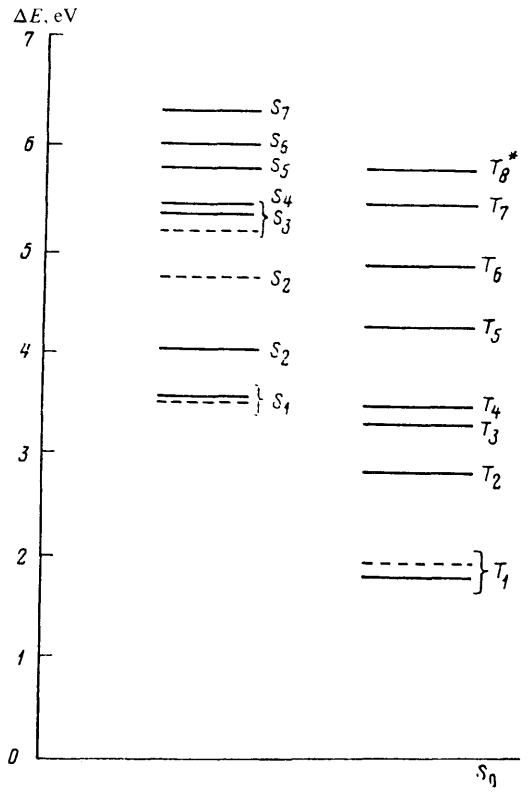


Figure 5. Energy level diagram for the electronically excited states of 2,2,4-trimethyl-1,2-dihydroquinoline (continuous line—calculation; dashed line—experiment). The σ,π^* states are marked by an asterisk; the others are π,π^* states.

The calculation demonstrated that all the electronically excited states of dihydroquinolines with energies less than 56000 cm^{-1} are delocalised over the entire molecule. The question therefore arises in what way the excitation energy of the entire π-system leads to the dissociation of the N–H bond.

There exist two different mechanisms of such a process which can be achieved, in principle, for the molecules of aromatic amines:[106,107] photodissociation in a bound state (adiabatic photodissociation) and predissociation. In the former case the electronic excitation energy, delocalised over the entire molecule, is converted into the vibrational energy of an individual N–H bond, while in the latter case it is converted into the electron ic energy of this bond. Convincing evidence for the particular photodissociation pathway in the condensed phase is at present lacking for any complex molecules (with the exception of the photodissociation of triphenylmethane[107]). For dihydroquinoline molecules, one can postulate that, when the excitation energies are below 42000 cm^{-1}, the N–H bond dissociates in a bound state via a non-adiabatic mechanism (Fig.6). Since the N–H bond dissociation energy is 3.46 eV (27890 cm^{-1}) (aniline), the rate of photodissociation via the adiabatic mechanism should be fairly low (the rate constant for the photodissociation of a C–H bond with the same strength by radiation with an energy of 54000 cm^{-1} does not exceed 10^6),[106] which is confirmed by the low dissociation yield on excitation at the wavelength corresponding to the long-wavelength absorption band (Table 10).

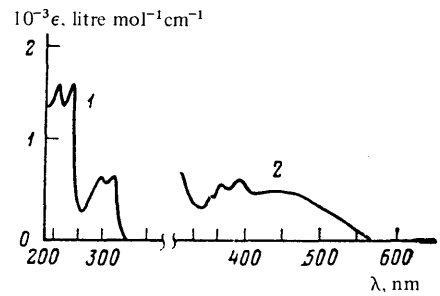


Figure 6. Absorption spectra of 1-cyano-2-hydroxy-1,2-dihydroquinoline in EPA at 77 K: 1) before irradiation with ultraviolet light; 2) after irradiation with ultraviolet light.

Table 10. The ionisation energies in vacuo (I_g) of the commonest amines.

Amine	I_g, eV	Refs.
Triphenylamine	6.68	[4]
Diphenylamine	7.25	[4]
Tetramethylphenylenediamine	6.2	[4]
Aniline	6.60	[4]
Indole	7.44	[6]
Carbazole	7.20	[151]

When the excitation energy exceeds 42000 cm^{-1}, the transition of the molecule to the repulsion state of the N–H bond and the occurrence of photodissociation via the predissociation mechanism become possible. It has been shown[106] that the repulsion state of the C–H bond (and in general the

R–H bond) is of the triplet type, i.e. the dissociation of the N–H bond can take place with an appreciable yield only in the triplet state.

Thus, for low excitation energies (less than 42000 cm^{-1}), the photodissociation of the N–H bond proceeds via the adiabatic mechanism with a low quantum yield (<0.01). When the energies are in excess of 42000 cm^{-1}, a new channel appears, leading to the dissociation of the N–H bond via predissociation, which increases the efficiency of the overall process. The nature of the increased quantum yield in the dissociation of the N–H and O–H bonds in the photoirradiation of indoles and phenols observed in a series of studies,[94,95,99,109] which involves the operation of two photodissociation mechanisms, is analogous.

(b) Photoionisation

By photoionisation we understand the direct transfer of an electron under the influence of light to the condensed phase with formation of a solvated electron.[4] Photoionisation is characteristic of compounds with a low ionisation potential (*p*-phenylenediamine and its methyl derivatives), while photodissociation predominates for amines with a relatively high ionisation potential (virtually all the remaining amines). The ionisation energy threshold J is defined by the expression

$$J = J_g - P_+ - V_0,$$

where J_g is the ionisation energy in the gas, P_+ the energy of the ionisation of the medium by the cation (radical-cation), and V_0 the energy of the interaction of the excess electron with the medium.

It follows from the data in Table 10 that the photoionisation of aromatic amines in the liquid phase can proceed via both one-quantum and two-quantum mechanisms. In non-polar solvents the differences between the energies of the one-quantum photoionisation of tetramethylphenylenediamine (TMPD) are determined by the quantity V_0 (V_0 for non-polar liquids varies from +0.6 eV for tetramethylsilane to −0.1 eV for n-hexane),[4–6] while the absolute value of the photoionisation threshold of TMPD is in the range from 4.3 eV in tetramethylsilane to 4.99 eV in n-hexane.[4] On photoexcitation of aromatic amines in non-polar solvents (other than TMPD) at the wavelength corresponding to the long-wavelength absorption band, photoionisation should therefore proceed extremely ineffectively.

It has been recently observed[113] that the photoionisation of TMPD on irradiation with light having energies in the range 42000–62000 cm^{-1} in weakly polar solvents (tetramethylsilane, 2,2-dimethylbutane, isoctane, cyclohexane, and n-hexane) leads to the formation of an electron–cation geminal ion pair, which either dissociates into the free ions or (with a significantly higher proabability) recombines to form excited TMPD, which emits recombination fluorescence.

In polar solvents the photoionisation is in general much more effective. The photoionisation of 2,7-bis(dimethylamino)-4,5,9,10-dihydropyrene in acetonitrile takes place in the fluorescent S_1 state, which is destroyed with formation of a radical-ion pair comprising the radical-cation of the amine and the radical-anion of acetonitrile; this pair subsequently dissociates into the free radical-ions (after 9 ns).[114] In benzonitrile the same compound forms an exciplex with the solvent and in this case the ionic photodissociation takes place directly in the exciplex.[115]

On the other hand, it has been shown[116] that the one-quantum ionisation of 1,6-bis(*NN*-dimethylamine)pyrene in acetonitrile proceeds via the intermediate formation of a long-lived (several microseconds) ion pair comprising the amine radical-cation and the solvated electron, which subsequently dissociates into the free ions.

In a detailed study[117] it was observed that the photodissociation of *NNN'N'*-tetramethylbenzidine (TMB) in acetonitrile, benzonitrile, and pyridine proceeds via an exciplex with the solvent, from which a radical-ion pair is formed (in the case of acetonitrile this ion pair comprises the amine radical-cation and the radical-anion derived from the acetonitrile dimer) and, in contrast to the ion pairs formed by 2,7-bis(*NN*-dimethylamine)-4,5,9,10-dihydropyrene, this ion pair is so long-lived that before dissociation it has sufficient time to react with acetonitrile to form the polymeric ion pair $TMB^+...(CH_3CN)^-$. Thus the formation of exciplexes with the solvent is a fairly general mechanism of the one-quantum photoionisation of aromatic amines in polar solvents such as acetonitrile, benzonitrile, dimethylformamide, and pyridine.

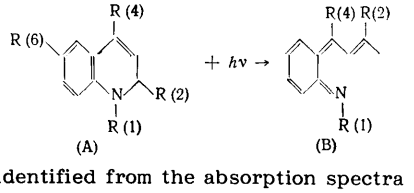
(c) Dissociation of the C–N bond in aromatic amines

In contrast to aliphatic amines, where the dissociation of the C–N bond takes place fairly frequently and has been reliably identified, there is very little reliable evidence for the dissociation of the C–N bond in aromatic amines. It has been observed[118] by EPR that the photoirradiation of TMPD in perdeuterio-3-methylpentane at 77 K leads to the formation of only one product, namely the methyl radical, as a result of the two-quantum C–N bond dissociation reaction in TMPD.

It has been demonstrated spectrophotometrically[119] that ultraviolet irradiation of frozen solutions of *NN*-dimethylaniline in EPA and 3-methylpentane at 77 K results in the formation of the anilino-radical $C_6H_5\dot{N}CH_3$ (the maxima in the absorption spectrum are at 314.0 and 400.0 nm). These bands usually overlap with the absorption bands of the dimethylaniline radical-cation. However, infrared irradiation of a solution subjected to preliminary irradiation with ultraviolet light at 77 K makes it possible to eliminate the radical-cations (as a consequence of the liberation of solvated electrons from traps and their recombination with the radical-cations) and to obtain the absorption spectrum of the anilino-radical. Thus the homolytic photodissociation of the C–N bond has been suggested as the primary photochemical reaction of *NN*-dimethylaniline.

The dissociation of the C–N bond with formation of the anilino-radical is possible also in the liquid phase;[89] thus anilino-radicals appear in the photolysis of *NN*-dimethylaniline in benzene, although the probability of this process is much less than the probability of the dissociation of the N–H bond.[89]

The photodissociation of the C–N bond has been studied in greatest detail in aromatic amines in relation to the opening of the ring of 1,2-dihydroquinolines.[120–126] The photoirradiation of solutions of 1,2-dihydroquinolines in EPA at 77 K entails the ruputre of the C–N bond and the formation of brightly coloured products with a quinonaldine structure:



(A) (B)

which were identified from the absorption spectra (Fig.6). The reverse thermal reaction takes place in the dark.

The mechanism of the formation of the quinonaldine form is apparently analogous to the mechanism of the opening of the pyran ring in pyrans, chromenes, and spiropyrans,[127–129] i.e. the excitation involves the ruputre of the C–N bond, a change in the hybridisation of the nitrogen atom, and the

rotation of both parts of the molecule about the C(3)–C(4) bond with formation of an almost planar quinonaldine structure. The probability of the dissociation of the C–N bond is determined by the nature of the substituents in the R(1) and R(2) positions and occurs only for dihydroquinolines with electron-accepting groups at the nitrogen atom.

In vitreous solutions at 77 K all the dihydroquinolines are photochemically stable. It has been observed[122] that the opening of the ring in dihydroquinolines is sensitised by triplet energy donors, which proceeds via the lowest state $T_1(\pi,\pi^*)$ having a closed or cyclic form. In contrast to the photochromic chromenes and spiropyrans, there exist no quantitative data concerning the effectiveness of the opening of the ring in dihydroquinolines on irradiation with ultraviolet light.

It is noteworthy that dihydroquinolines containing only a hydrogen atom as the substituent at the nitrogen do not undergo the ring opening reaction on photoirradiation and only the dissociation of the N–H bond takes place.[120,121] The energy level diagrams for the initial compound and the products of the N–H and C–N bond dissociation reactions of dihydroquinolines have been constructed on the basis of quantum-chemical calculations by the PPP method[126] and have made it possible to put forward the following reaction scheme:

$$(A) \xrightarrow{h\nu} (A(S_1)) \rightarrow (A(T_1)) \begin{cases} \rightarrow (B(T_1)) \rightarrow (B(S_0)); \\ \rightarrow R\dot{N}(S_0). \end{cases}$$

Calculations of the transition energies, atomic charges, and Viberg indices for the lowest singlet and triplet transitions of the *N*-acyl-substituted and unsubstituted dihydroquinolines have shown that an electron-accepting substituent at the nitrogen atom weakens the C–N bond; the photoexcitation of dihydroquinoline molecules leads to the same effect. For dihydroquinolines without substituents at the nitrogen atom, a new channel leading to the degradation of the excitation energy appears, namely the dissociation of the N–H bond, which occurs much more effectively than the dissociation of the C–N bond.

The luminescence properties of 1,2-dihydroquinolines and 1,2,3,4-tetrahydroquinolines containing hydrogen as the substituent at the nitrogen atom have been investigated in detail.[129–135] It has been observed that the first and second absorption bands in the spectra of dihydroquinolines shift in different directions under the influence of the solvent,[133] which indicates their different nature.

It has been shown by infrared spectroscopy that di- and tetra-hydroquinolines form complexes with chlorine-containing solvents in the ground state. In aqueous alcoholic solutions bands due to the $T_1 \leftarrow S_0$ transitions are observed after the introduction of KI.[129] The energies of the T_1 states of dihydroquinolines determined from these spectra are consistent with the values obtained from the phosphorescence spectra.[123]

4. Photorearrangements

The most important and most thoroughly investigated reaction of aromatic amines, which involves the benzene ring, is the photocyclisation of diphenylamines to carbazoles.[136–142]

It is known that the photoirradiation of derivatives of diphenylamine leads to the almost quantitative formation of carbazoles in almost all solvents (Fig. 7).[136–138]

It follows from the experiments on the quenching of fluorescence and the sensitisation of the photocyclisation of diphenylamine and triphenylamine in hexane that the cyclisation takes place in the T_1 states of the amines via the intermediate formation of a short-lived product (E) (Table 11). Carbazole is formed from (E) as a result of the thermal elimination of two hydrogen atoms (it has been specially demonstrated that the amount of H_2 evolved is consistent with the amount of carbazole formed[139]).

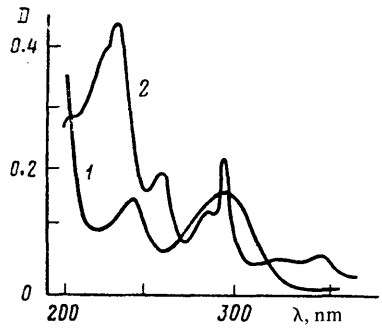


Figure 7. The conversion of *N*-methyldiphenylamine into carbazole: 1) absorption spectrum of a 2.6×10^{-5} M solution in hexane before irradiation; 2) after irradiation with ultraviolet light.

Table 11. The quantum yields in the formation of carbazole (ϕ_1) and the consumption of diphenylamine (ϕ_2) on irradiation with light at $\lambda = 253.7$ nm.[138,139]

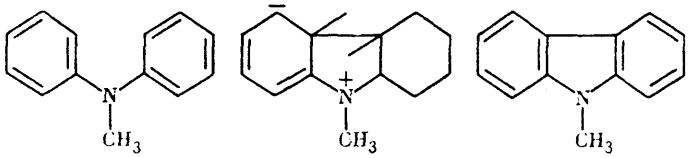
Solvent	Presence of oxygen*	φ_1	φ_2
Methyldiphenylamine			
Cyclohexane	+	0.67	0.67
Cyclohexane	–	0.06	0.06
Methylcyclohexane	+	0.67	0.67
Methylcyclohexane	–	0.06	—
n-Hexane	+	0.62	0.62
n-Hexane	–	0.06	—
Ethanol	+	0.57	—
Diphenylamine			
Cyclohexane	+	0.06	0.07
Cyclohexane	–	0.10	—
Methylcyclohexane	+	0.06	—
n-Hexane	–	0.05	—
Ethanol	–	0.10	—
Triphenylamine			
Cyclohexane	+	0.12	0.12
Cyclohexane	–	0.003	—

*The "+" and "–" signs correspond to the presence and absence of oxygen respectively.

The appreciable increase of the quantum yield of the reaction in the presence of oxygen is due to the fact that the latter appreciably accelerates the elimination of hydrogen from (E) with formation of HO_2 or H_2O_2.

The lifetimes of the T_1 state of *N*-methyldiphenylamine and triphenylamine in cyclohexane at 20 °C have been determined as respectively 1.36×10^{-8} and 8.16×10^{-8} s.[139] It has been demonstrated directly by flash photolysis[141] that *N*-methyl-4*a*,4*b*-dihydrocarbazole (D) is formed directly from *N*-methyldiphenylamine in the T_1 state and that its spectrum has an absorption maximum at 610 nm. Compound (E) is then

converted into the carbazole (P) via the elimination of a hydrogen atom.



(D) (E) (P)

The quantum yields of 4*a*,4*b*-hydrocarbazole formed from *N*-methyldiphenylamine in the T_1 state have been estimated from the dependence of the yield of carbazole and *N*-methyl-4*a*,4*b*-hydrocarbazole on the oxygen concentration on irradiation by a flash or continuously; the yields are 0.89, i.e. the T_1 state is deactivated almost exclusively via conversion into compound (E).[142]

The unusual influence of oxygen on the yield of carbazole (the dependence of the yield on the oxygen concentration passes through a maximum at O_2 concentrations of 6×10^{-4} M for *N*-methyldiphenylamine and 2×10^{-5} M for diphenylamine in hexane) is associated with the dual role of oxygen: on the one hand, it deactivates the T_1 state of diphenylamines and, on the other, it accelerates the conversion of 4*a*,4*b*-dihydrocarbazoles into carbazoles.[142]

Complete quantitative information concerning the pathways leading to the dissipation of the electronic excitation energy has been obtained for a solution of *N*-methyldiphenylamine in cyclohexane at 20 °C,[141,142] fully confirming the proposed mechanism of the conversion of diphenylamines into carbazoles via the intermediate (E).

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The photonics of amine solutions possess in broad outline features characteristic of both aromatic and aliphatic amines, which makes it possible (despite the wide variety of structures and photochemical properties) to consider them within the framework of a single class of compounds. For all the amines in the lowest electronically excited states, the molecular geometry rearranges and undergoes a change in its electronic configuration, the two processes being associated with the intramolecular charge transfer on excitation and (or) the inclusion of the Rydberg states of the RN< fragment. This leads to an appreciable Stokes band shift in the fluorescence spectra in polar solvents, which is characteristic to a greater or lesser extent of all amines, starting from the simplest aliphatic amines and extending to indole. The main photochemical process for amines is electron transfer and the photodissociation of the N–H bond. The homolytic photodissociation of the N–H bond is the dominant process for all the primary and secondary amines in the absence of special conditions for electron transfer (polar solvents and electron acceptors).

It is essential to note that, whereas the luminescence spectroscopic properties of amines in the condensed phase have been investigated in fair detail and a fairly elegant theory, relating the electronic structure of amines to their luminescence spectroscopic properties has been constructed, the mechanism of the photochemical reactions of the same amines has been studied quite inadequately. The lack of quantitative data concerning the efficiency of N–H bond dissociation process makes it impossible to characterise the influence of the structure of the molecule on the mechanism of its photochemical reactions. This is why most difficulties are observed in the study of the many processes occurring when amine molecules absorb light in those cases where photodissociation processes are possible.

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