

THE REACTIVITY OF ACRIDINIUM SALTS AND RELATED COMPOUNDS

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Abstract—Reactions of quaternary acridinium salts and of *N*-substituted acridan systems are presented, along with derivatives and acridinium salts applied as chemiluminescent agents or DNA intercalators.

I. INTRODUCTION

The present paper dealing with acridinium salts and related compounds^{1,2} is a continuation of our study concerning *N*-substituted salts of azaaromatics.³⁻⁷

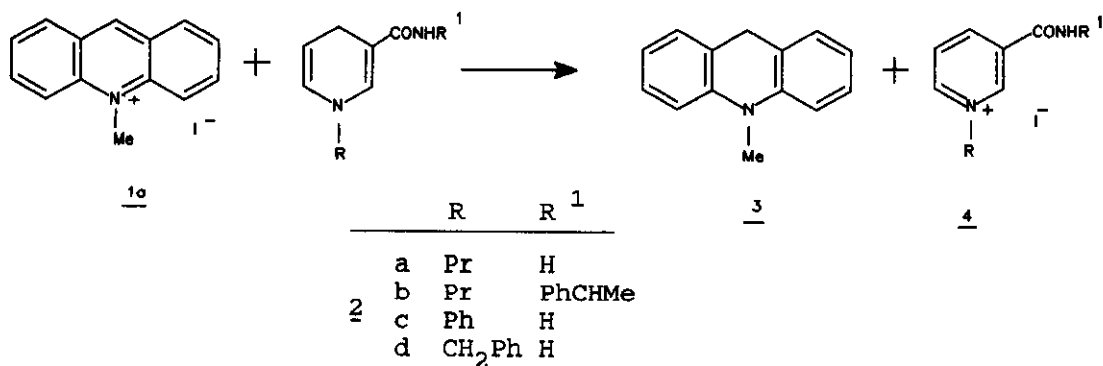
The chemistry of *N*-substituted salts of azaaromatics is interesting in view of their reactivity,^{8,9} biological activities^{10,11} and applications, for example as dyes^{12,13} or surfactants;^{14,15} also it should be pointed out their usefulness in modification of polymers^{16,17} and in the construction of electronic devices.¹⁸⁻²⁰

There will be described:

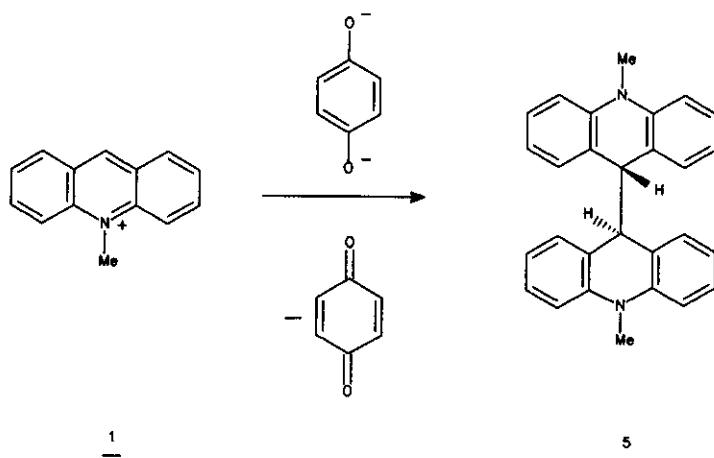
- reactions of *N*-substituted acridinium salts
- reactions of 10-substituted acridan systems leading to acridinium salts
- acridine orange derivatives
- *N*-substituted acridinium salts as chemiluminescent agents and as DNA intercalators.

II. REACTIONS OF *N*-SUBSTITUTED ACRIDINIUM SALTS

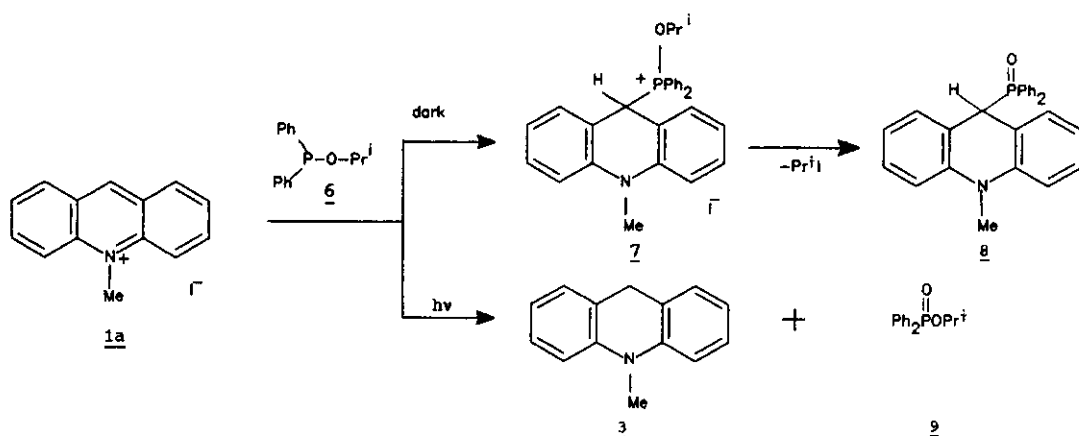
Among reactions of acridinium salts large group are their reductions processes, and they will be presented at first. An example may be reduction of *N*-methylacridinium iodide (1a) by *N*-substituted 1,4-dihyronicotinamides serving as NADH models, e.g. 2, leading to 10-methylacridan (3) and the salt (4).²¹



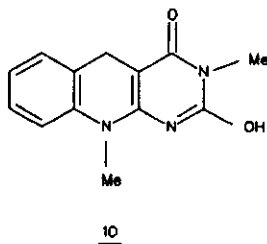
In the study of electron transfer processes it was established that the reaction of the cation (1) with hydroquinone dianion gives rise to the dimer (5) and *p*-benzoquinone.²²



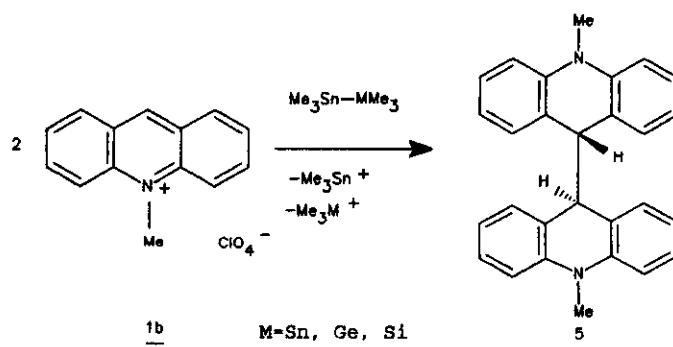
The thermal and photochemical reactions of 1a with diphenylphosphinite (6) were investigated. In the dark, in acetonitrile the nucleophilic attack of 6 to the position 9 of 1a leads to the intermediate phosphonium ion (7); its gradual decomposition affords phosphine oxide (8). However under irradiation, the formation of 10-methylacridan (3) and isopropyl diphenylphosphinate (9) takes place. This photoreaction proceeds via single electron transfer from 6 to 1a; yields may be increased by the addition of iodine even in the catalytic amount.²³



The hydride transfer from an anionic reduced deazaflavin (10) to NAD analogue (1a) gives 9,10-dihydroacridan system; it was found that no high energy intermediates such as radicals or radical ions intervene in this reaction.²⁴

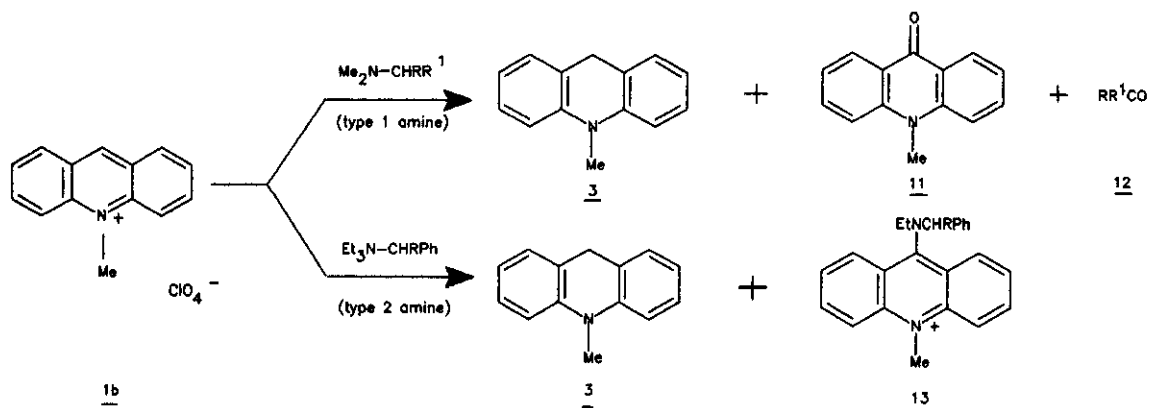


10-Methylacridinium perchlorate (**1b**) can be reduced by group 4B dimetals, i.e. two-electron d donors in deaerated acetonitrile to afford selectively the dimer which is the one-electron reduced product. The reduction proceeds via electron-transfer radical chain processes, this fact being confirmed by the strong inhibitory effect of oxygen.²⁵



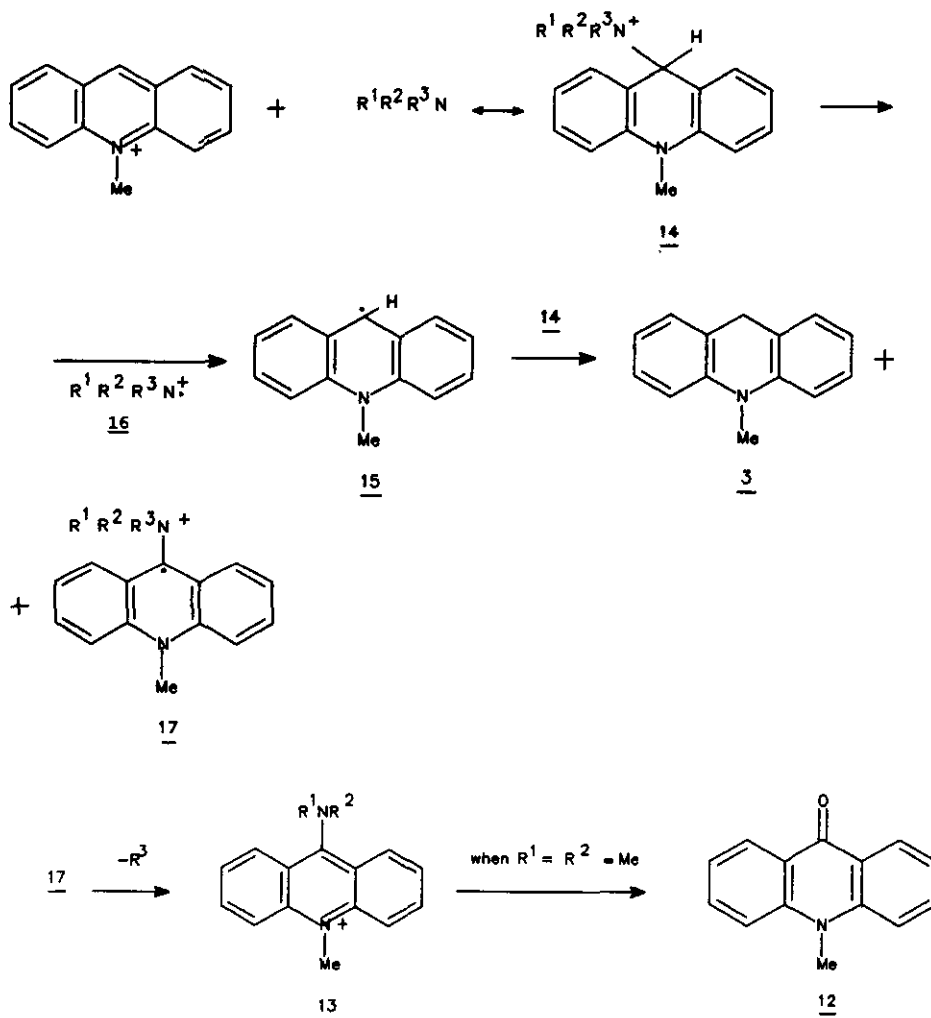
Next the processes other than reduction will be described.

In the study of the reaction of **1b** with tertiary amines carried out in acetonitrile at 50°C it was observed that its result depends on the nature of amines. In the case of amines $\text{Me}_2\text{N-CHR}^1$ (1 type amines) the products are 10-methylacridan (**3**) and acridinone (**11**), along with the ketone (**12**) while the reaction with more bulky amines as $\text{Et}_3\text{N-CHRPh}$ (2 type amines) affords **3** and **13**.



The first step is the formation of the adduct (14) which undergoes the dissociation into the acridinyl radical (15) and an aminium cation radical (16). The next hydrogen atom transfer from 14 to 15 leads to 3 and the cation radical (17) releasing one of the substituents as a free radical to give 13.

In the case of the 2 type amines (13) is the end product, while in the case of less bulky amines it hydrolyzes to the acridinone (12).²⁶



The interaction of *N*-methylacridinium salts (1a,b) used as electron acceptors with amines: aniline, *p*-toluidine, diphenylamine and *N,N*-dimethylaniline serving as electron donating species in dichloroethane affords EDA complexes. The process was followed by conductivity measurement; it was observed that the higher ratio of amine results in the decrease of conductivity.²⁷

In the study of photoreduced electron transfer (PET) reactions in low polarity solvents methylacridinium iodide (1a) and hexafluorophosphate (1c), as well as decylacridinium hexafluorophosphate (18) were used as sensitizers.^{28,29}



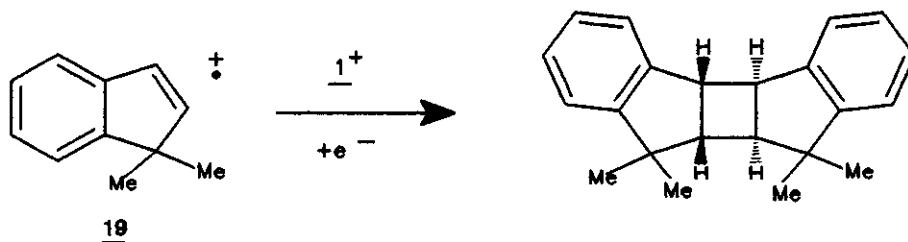
Usually, PET reactions are performed in polar solvents, e.g. acetonitrile, in which the Coulombic barrier to separation is considerably lower as compared to less polar solvents, and the diffusive separation predominates over return electron transfer within the radical ion pairs.

The PET reactions would be more useful if initially formed radical ions could be photochemically generated in nonpolar solvents. When 1a,c or 18 are applied as sensitizers in PET reactions in nonpolar solvents, the electron transfer from a neutral donor to the excited state of cationic acceptor results in the formation of a neutral radical / radical cation pair in which no Coulombic barrier to separation exists.

In the experiments, as the electron donor was chosen biphenyl, a frequently used "cosensitizer" in electron transfer reactions.^{30,31} To measure the quantum yields of formation of separated radical ions produced upon quenching of the first excited states of the above sensitizers by biphenyl, the transient absorption and photoacoustic techniques were applied.³⁰

It was obtained the increased yield of separated radical cations; these results show that separation within radical / radical cation pairs competes more effectively with return electron transfer in solvents of the polarities lower than that of acetonitrile.

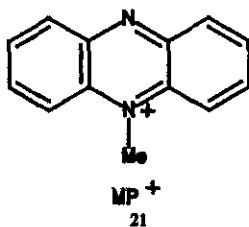
As an example of steady state product formation the I^+ sensitized dimerization of 1,1-dimethylindene (19) was examined. The head-to-head dimer (20) can be obtained in 80% yield by irradiation of 19 and I^+ in methylene dichloride.



The extent of ion-pairing was investigated by comparing the fluorescence efficiencies of 1a and 1c. In less polar solvents, the fluorescence of 1a is lower than that of 1c, this fact being due to the quenching of the excited state of the acridinium cation by iodide when these species are paired.

The use of *N*-alkylacridinium salts as photosensitizers for producing radical cations in solvents of a low polarity may enlarge the scope of PET reactions.²⁹

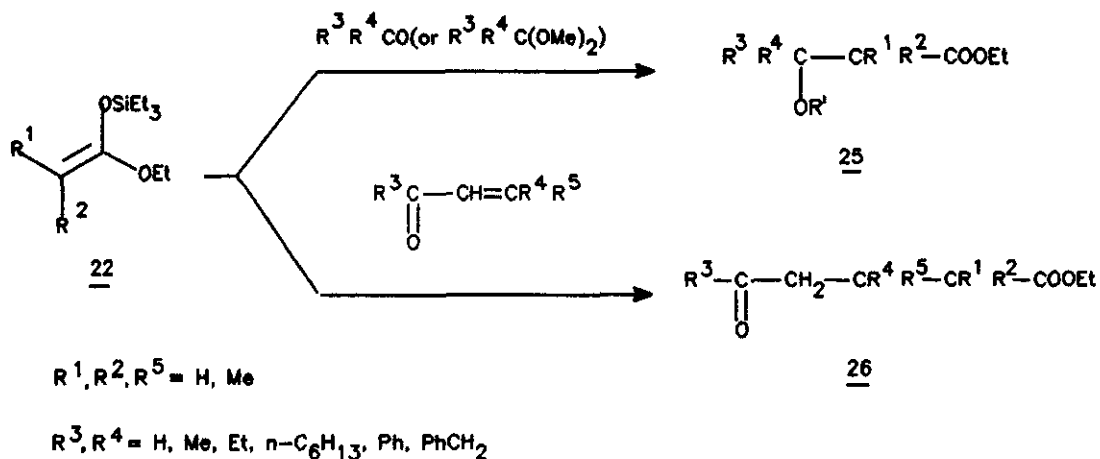
Investigations of a great variety of TCNQ salts of azaaromatics have shown that the substitution of cations by neutral molecules of similar shape and polarizability is possible; in the salt [MP] [TCNQ], having properties an organic metal the cation [MP]⁺ (21) may be replaced by phenazine or 9-methylacridine.^{32,33}



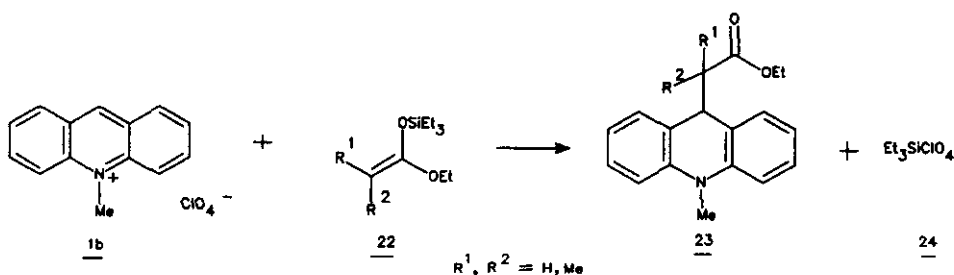
The following example of the reaction of 1b finding synthetic application has been reported. It was found that 1b promotes the reaction of ketene silyl acetals with carbonyls, acetals or α -enones.^{34,35}

An interesting observation is that the catalytic amount of 1b leads to high yields of products while in the case of stoichiometric amount of 1b they are lower.

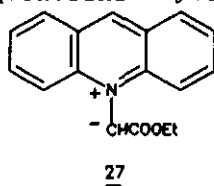
The following reactions were examined.



In the investigation of these processes it was established that 1b serves as an efficient activator of ketene silyl acetals. In the reaction of 1b with 22 the alkylation product (23) is formed; however a promoter of the reaction is not 23 but the not isolated triethylsilyl perchlorate (24) which is produced simultaneously. The first step of the reaction is the formation of 24, the second one leads to products (25) or (26). There should be pointed out that in the case of stoichiometric amount of 1b one of the reactants i.e. 22 would be completely consumed, and the subsequent reaction with carbonyls or α -enones would be impossible. This process is an example of a novel catalysis, in which one of the reactants is precursor of a catalyst (in a contrary to autocatalysis, where one of products catalyzes the reaction generating a catalyst). As 1b is air stable and neutral, it can find various synthetic applications.

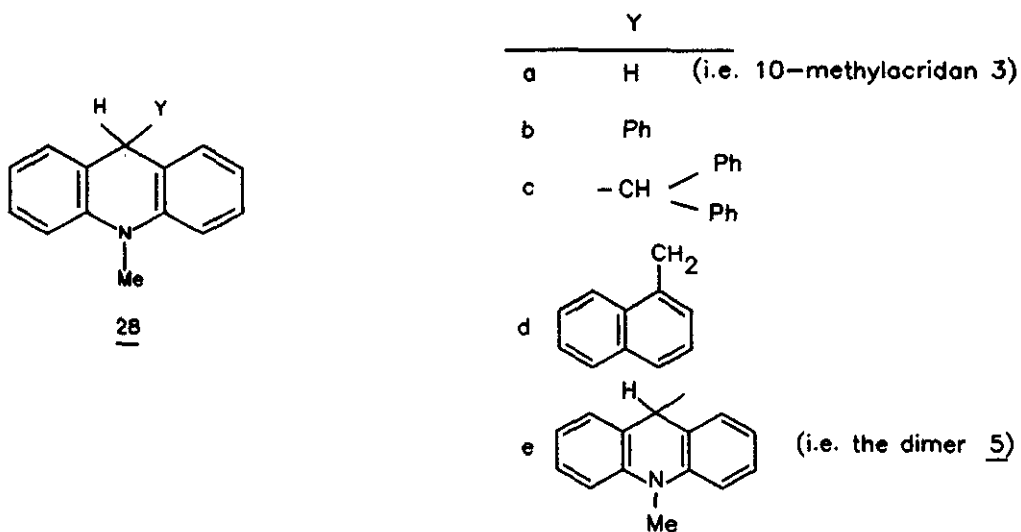


It will be mentioned here also the synthesis of the stable ylide (27) obtained by treatment of acridine with ethoxycarbonylcarbene, generated by thermal or photochemical decomposition of ethyl diazoacetate. Reaction was carried out in hexafluorobenzene; the stability of 27 is higher than that of analogous pyridinium and quinolinium ylides.³⁶

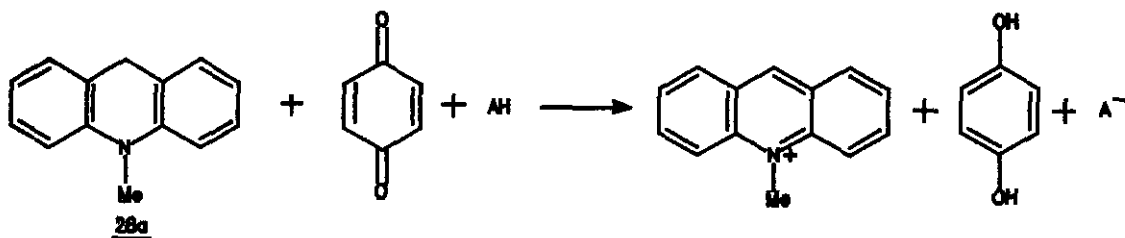


III. REACTIONS OF 10-SUBSTITUTED ACRIDAN SYSTEMS LEADING TO ACRIDIUM SALTS

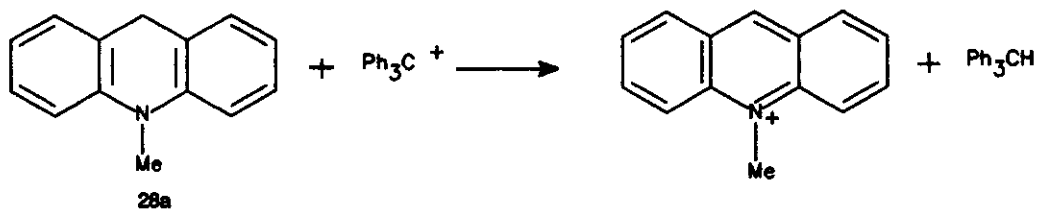
Reactions resulting in acridinium salts include oxidation processes of acridans of the type (28); some examples will be given.



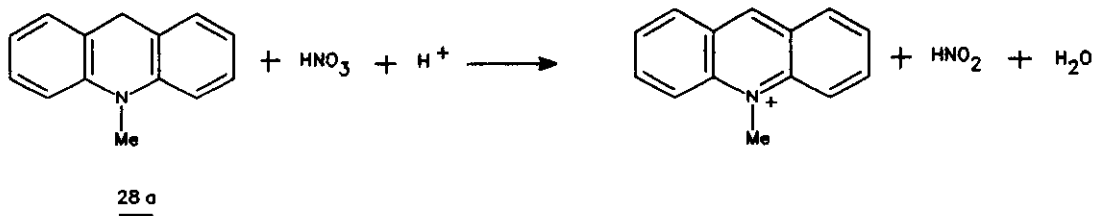
In the study of the reduction of *p*-benzoquinone with an acid stable NADH analogue (28a) in aqueous solvents the analysis of isotope effects of both substrate and solvent has shown that the process is an one-step hydride transfer^{37,40}; however the mechanism involving electron transfer, followed by proton and electron transfer was also proposed^{41,42}



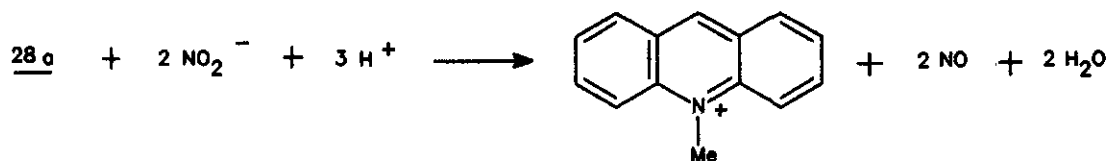
A next example, where 28a acts as a hydride donor is the following two - electron reduction of trityl cation.⁴³



In the search for methods of nonenzymatic reduction of nitrate ion⁴⁴⁻⁴⁶ it was found that the acid stable NADH analogue (28a) can reduce efficiently NO_3^- to NO_2^- in the presence of perchloric acid in acetonitrile *via* novel autocatalytic chain reactions, where HNO_2 plays an important role.⁴⁷



The mechanism of this process may be elucidated in the following way. It is known that NO_2^- is reduced by 28a in the presence of perchloric acid to give NO and I^+ .⁴⁸



The subsequent reaction of NO with NO_3^- in the acidic medium leads to NO_2 and HNO_2 . Having these facts in mind the autocatalytic reduction of HNO_3 by 28a begins presumably by the acid-catalyzed reduction of HNO_3 to HNO_2 , which is the slow, rate determining step of the overall process.

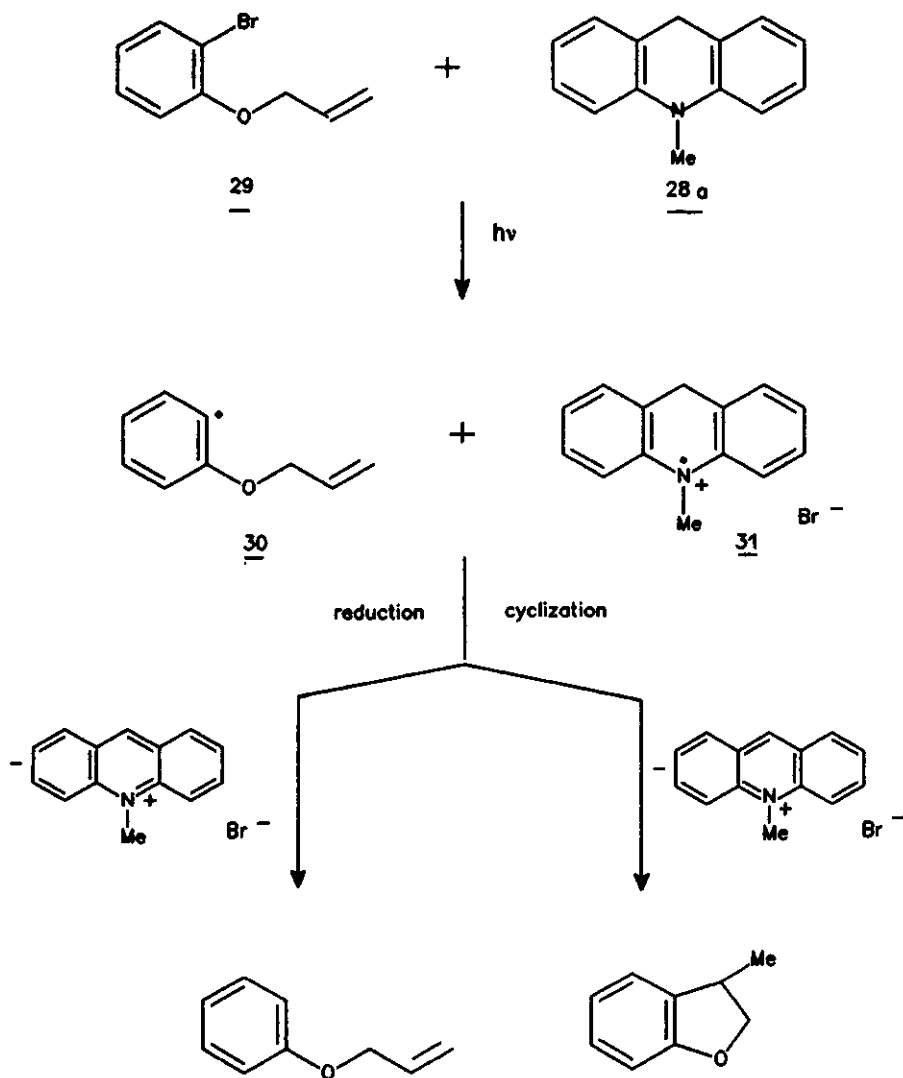
The following rapid autocatalytic buildup of HNO_2 occurs via the facile one-electron reduction of HNO_2 to NO by 28a. The subsequent fast reaction of NO with HNO_3 produces NO_2 and HNO_2 .

For radical intramolecular cyclizations tin hydride method is often used, however, in view of the toxicity of organotin compounds, the following alternative route applying 28a is preferable.

It is known the photocatalytic dehalogenation of aliphatic and aromatic halides, performed by irradiating a solution of the halide in the presence of catalytic amount of 28a and an excess of NaBH_4 in aqueous acetonitrile; the reaction proceeds via the aryl radical intermediate.⁴⁹

This photocatalytic system may be used in the radical cyclization of 1-allyloxy-2-halobenzenes (29).

It was found that two competing reactions i.e. the reduction of the aryl radical (30) and the desired cyclization take place; the reduction predominates over the cyclization in the case of a high concentration of hydrogen donor (31).

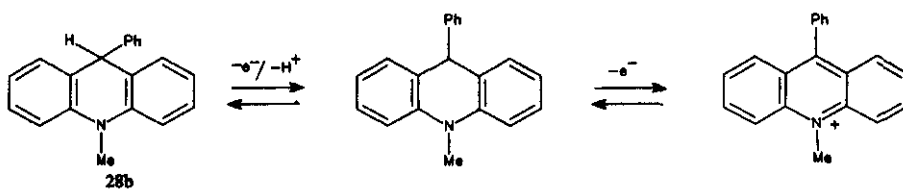


In the presence of an excess of sodium borohydride however, **28a** is regenerated, therefore only its small amount is used, and in this case the reduction product decreases.

As during prolonged irradiation the degradation of NaBH_4 by water occurs, DMF was used as the solvent. The above photocatalytic cyclization is useful for preparative purposes.⁵⁰

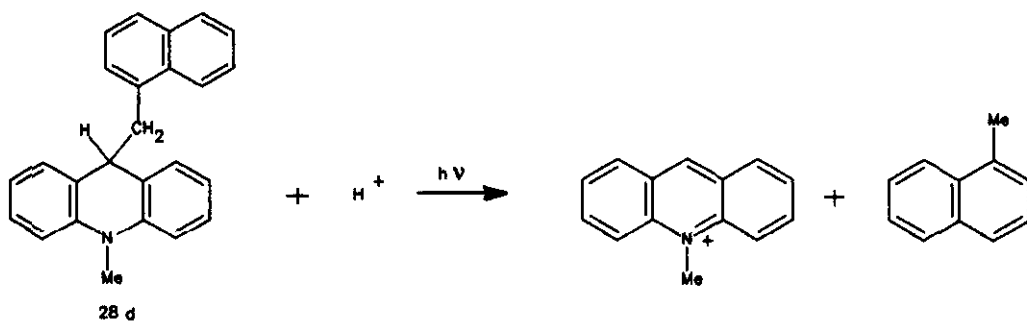
The photoreduction of methyleneblue by *N*-methyl-9-phenylacridan (28b) was studied by means of flash photolysis. In the first step the fast proton shift affords protonated semimethyleneblue (MBH^+) and *N*-methyl-9-phenylacridanyl radical. Then a second electron is transferred from this radical to MBH^+ to give leuco-methyleneblue and *N*-methyl-9-phenylacridinium salts.⁵²

The starting 28b undergoes the following redox reactions:



The system methyleneblue / 28b sensitizes the dediazonation of *p*-*N,N*-dimethylaminobenzenediazonium tetrafluoroborate.

It was established that the C(9)-C single bond of 28cde is readily cleaved by perchloric acid in deaerated acetonitrile under irradiation in the following way.

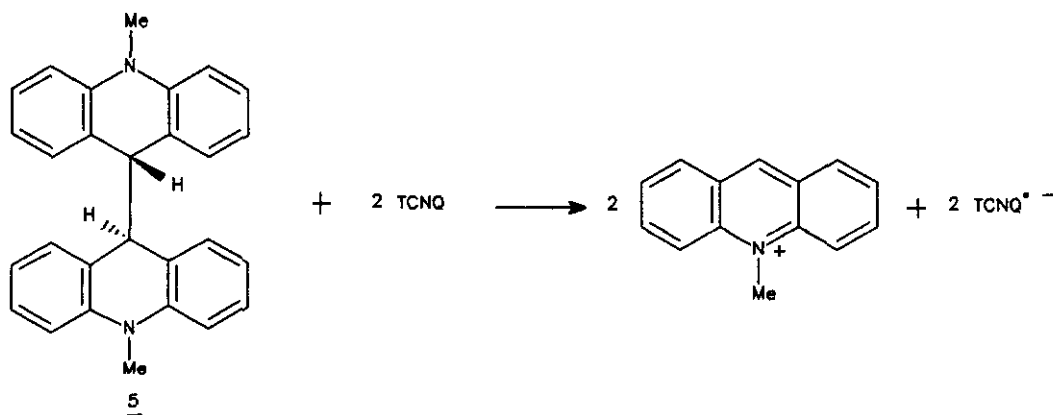


In the dark such reaction does not occur.⁵³⁻⁵⁸

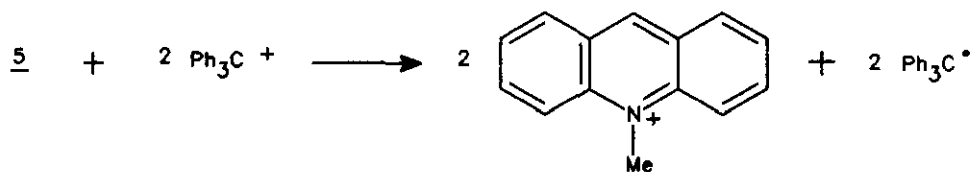
It was found that the dimer (5) acts as a novel two-electron donor in the electron - transfer oxidation with various organic oxidants.^{43,59-63} At first the electron transfer from 5 to oxidant occurs; this is the rate determining step which is followed by the cleavage of the C(9)-C bond.

Rates of electron-transfer reactions from 5 to various inorganic and organic one-electron oxidants depend solely on the one-electron potentials of the oxidants irrespective of the size of the oxidant's indicating that 5 acts as a novel two-electron outer-sphere electron-transfer reagent.

As an example of the two-electron oxidation of 5 may serve its reaction with TCNQ:



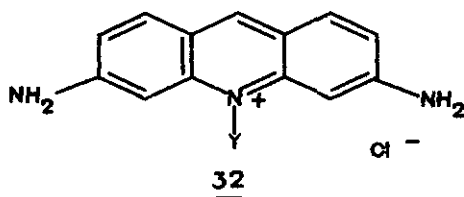
The dimer (5) acts also as a two-electron donor in the reaction with trityl cation:



The course of this reaction is quite different than in the case of the described above reaction of 28a with Ph_3C^+ in which 28a is a hydride donor.

IV. ACRIDINE ORANGE DERIVATIVES

An attention should be paid to acridine orange (32a) and its alkyl derivatives (32b-k). The amphiphilic nature of acridine orange allows its use for probing interfaces; the behaviour of molecules at interfaces is of a great importance in the area of chromatography, molecular electronics and biological systems.⁶⁴⁻⁶⁶ The kinetics of dimerization of 32a-d,f,i was examined in NaCl solution with the use of uv and ^1H nmr spectroscopies, as well as fluorescence measurements.⁶⁷



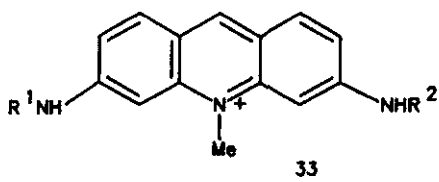
	Y
a	H
b	Me
c	Et
d	Pr ⁿ
e	Bu ⁿ
f	n-C ₅ H ₁₁
g	n-C ₆ H ₁₃
h	n-C ₇ H ₁₅
i	n-C ₈ H ₁₇
j	n-C ₉ H ₁₉
k	n-C ₁₀ H ₂₁

In the study of the adsorption of *N*-alkylated acridine orange derivatives (32b-i) by colloiddally dispersed zirconium phosphate it was found that the dye cations form an aggregate on the polymer. The electronic spectra and the reduced linear dichroism were measured in order to characterize the

adsorption states of molecules. The nature of the binding of dye molecules changes with the length of the alkyl chain. The 32bc cations in which n is 1 or 2 orient their transition moments in the same direction on a zirconium phosphate particle while in the case of $n = 3-9$ the random orientation is observed.⁶⁸

The kinetics of the solubilization of 32a,b,d,f,k into the micelles of sodium dodecyl sulfate was investigated by stopped-flow method with absorption and fluorescence detection. It was found that the rate constants decrease with the length of the alkyl chain.⁶⁹

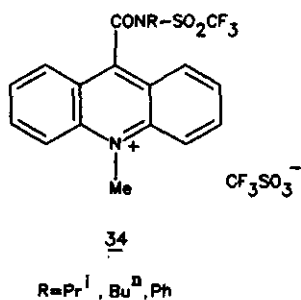
To derivatives of acridine orange belong compounds (33a-c) which are chiral due to the presence of sugar moieties in molecules; their DC spectra were studied in order to detect stacking.⁷⁰



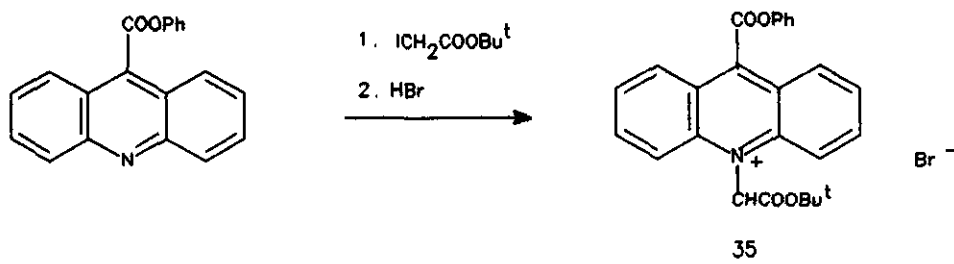
	R ¹	R ²
a	β -D-glucose	β -D-glucose
b	H	β -D-glucose
c	β -D-ribose	β -D-ribose

V. *N*-SUBSTITUTED ACRIDINIUM SALTS AS CHEMILUMINESCENT AGENTS AND AS DNA INTERCALATORS

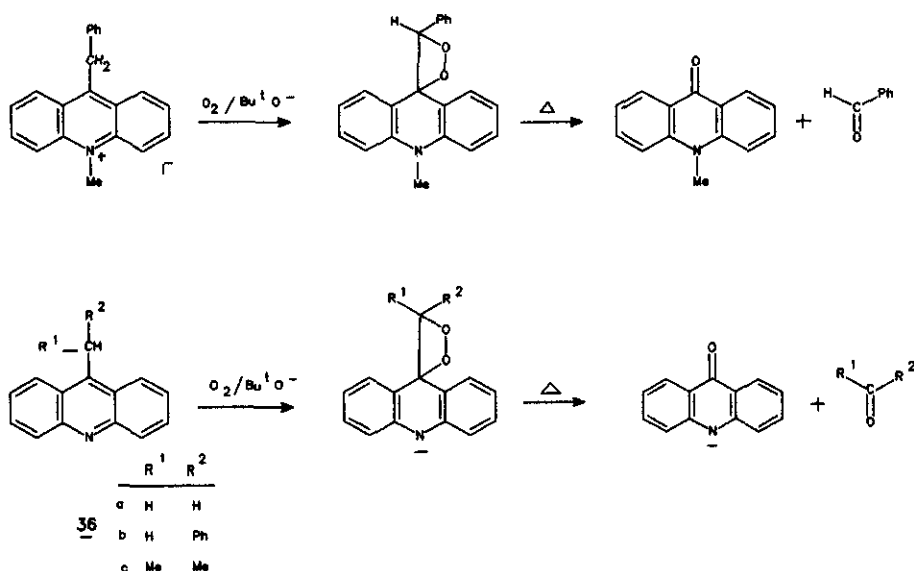
Many *N*-substituted acridinium salts have chemiluminescent properties; an example is 34; the kinetics of its light emission was studied.⁷¹



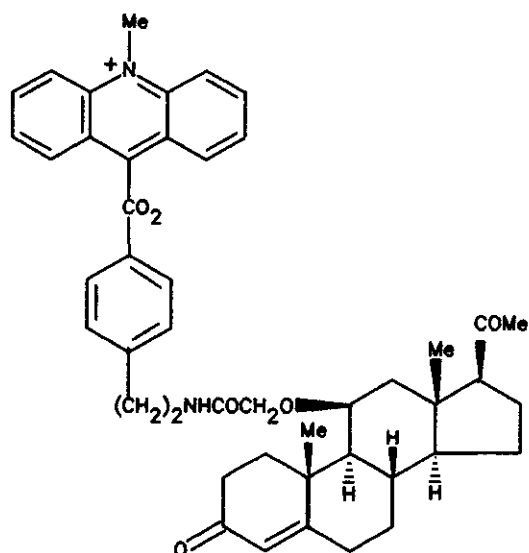
The salt (35), obtained in the quaternization of 9-phenoxyacetylacridine with *t*-butyl iodoacetate followed by the treatment with HBr shows also chemiluminescence; acridinium compounds of this type are chemiluminescent labels - the addition of basic H_2O_2 to a solution of 35 results in chemiluminescence. Such species may be linked to biological compounds by the 10-substituent.⁷²



It was established that the air oxidation of 9-benzyl-10-methylacridinium iodide leads to a visible chemiluminescence while in the case of substituted acridine (36) only a feeble chemiluminescence is observed.⁷³



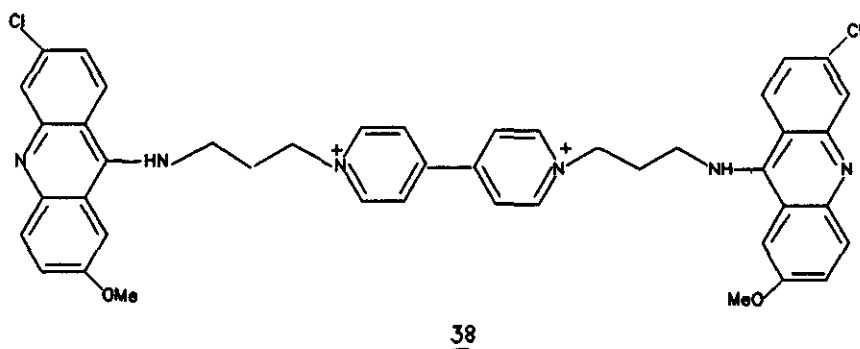
Acridinium salt (37) may be used as the chemiluminescent label in the sensitive, solid-phase chemiluminescence immunoassay for progesterone in plasma.⁷⁴



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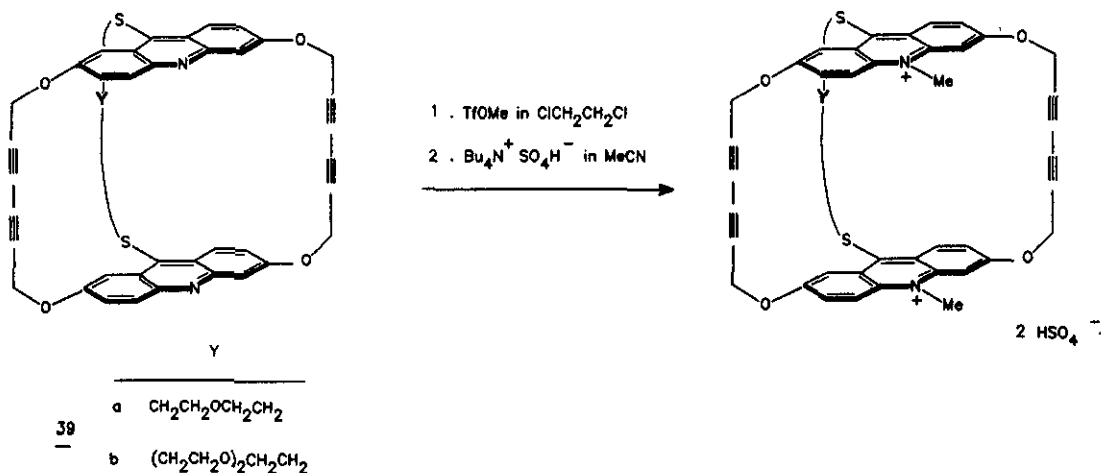
Acridine dyes are intercalators of DNA; there occur stacking interactions between adjacent base pairs of duplex DNA and the positively charged acridinium systems;⁷⁵⁻⁸³ also acridine-modified oligonucleotides are known.^{84,85}

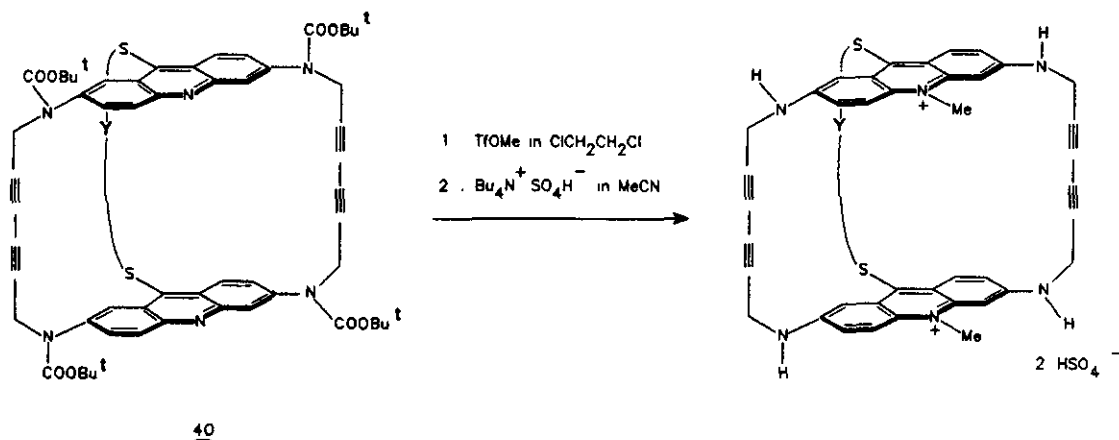
In the search for DNA photocleaving agents⁸⁶ and designing drugs of special physiological activity, 38 consisting of a photosensitizing, intercalating dye, i.e. acridine derivative and an electron mediator i.e. viologen was investigated.^{87,88}



38 forms an intercalation complex with DNA and cleaves the double chain DNA strand under irradiation by visible light. The cleavage involves superoxide species formed by the reaction of dioxygen with the one-electron reduced viologen structure of 38 and proceeds under mild conditions.

To DNA intercalators belong also 39a,b and 40 containing two triple bridged acridine systems; in order to achieve their solubility in water, the following quaternization reactions have been performed.^{81,82}





In the case of 40, along with the *N*-methylation the protecting *t*-butoxycarbonyl groups are removed.

VI. DISCUSSION

Interest in *N*-substituted acridinium salts has grown rapidly in recent years owing to their numerous applications, for example as catalysts, chemiluminescent agents or photosensitizers.

Among these compounds DNA intercalators, potential antineoplastic agents have been the object of increased attention; the elucidation of their interaction with nucleic acids is of a great biological importance.

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