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Nitrenium ions: structure and reactivity

G I Borodkin, V G Shubin

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Abstract. Data on the structure and reactivity of different nitrenium ions are generalised and described systematically. Various reaction pathways of these reactive intermediates resulted from their electronic structure are analysed. The attention is focused on the results of the 'direct' observation of the nitrenium ions and the role of the singlet – triplet conversion of these ions in chemical reactions. The bibliography includes 307 references.

I. Introduction

Over the last decade, nitrenium ion chemistry has actively been developed and attracted the attention of many researchers. Nitrenium ions are $R^1R^2N^+$ species containing a positively charged divalent nitrogen atom.[1–14] Constant interest in nitrenium ions stems from their intermediacy in various important organic reactions, including electrophilic amination of aromatic and heterocyclic compounds,[1,10,14–57] intramolecular cyclisations into N-heterocyclic compounds,[1,3,9,10,58–80] various rearrangements,[6,10,81–87] and photolysis and thermolysis of aminopyridinium and aminosulfonium salts and their analogs.[7,12,27,29,32,88–97] Nitrenium ions are also involved in solvolysis of nitrogen-centred systems, reactions of nitrogen-containing compounds with nucleophiles,[3,9,10,98–118] and polymerisation.[2,119–121] Recently, there has been further growth of interest in these ions because they were found to play an important role in carcinogenesis and mutagenesis processes and in the mechanism of the activity of antitumour drugs.[3,7,12,99,102,103,109–111,122–147] It is believed that reactions involving the formation of nitrenium ions can be realised in outer space, and investigation into their mechanism is vital for the understanding of the C–N bond formation in biorelated molecules.[148]

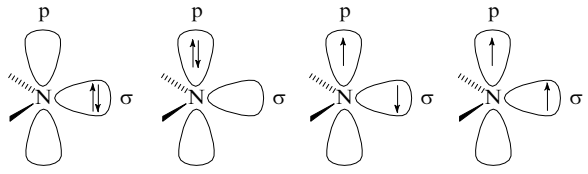
This review analyses data on the structure and reactivity of nitrenium ions published over the last 10 to 15 years. Earlier works are mentioned if required for clarifying the problem under discussion and revealing new tendencies in the field of nitrenium ion chemistry.

II. Electronic structure of nitrenium ions

The nitrenium ions are isoelectronic with carbenes and characterised by the presence of a sextet of electrons and a vacant p-orbital on the nitrogen atom. Like carbenes, they exist in the singlet (S) or triplet (T) state.[1–3,7,10,12,14] In the singlet state, the electrons have antiparallel spins and can occupy both the σ- and p-orbitals filling them completely or partially [the $S(\sigma^2)$, $S(p^2)$, and $S(\sigma p)$ states, respectively].[2,149] Because the σ-orbital is more s-like, it generally lies lower in energy, the $S(\sigma^2)$ state being energetically preferable. In the triplet state, the electron spins are parallel and distributed between the partially filled σ- and p-orbitals [$T(\sigma p)$].

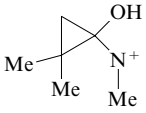
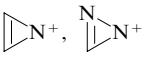
G I Borodkin, V G Shubin N N Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, prosp. Acad. Lavrentieva 9, 630090 Novosibirsk, Russian Federation. Fax (7-383) 330 97 52, tel. (7-383) 330 93 86,
e-mail: gibor@nioch.nsc.ru (G I Borodkin), tel. (7-383) 330 76 51,
e-mail: vshubin@nioch.nsc.ru (V G Shubin)

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In the first approximation, the energy difference between the singlet and triplet states (ΔE_{ST}) depends on the energy difference between two nonbonding orbitals (p and σ). The electron repulsion and exchange interaction (the Hund rule) favour the σ,p-configuration. It is important to reveal whether the singlet or triplet state is preferable in order to determine the reaction routes with various organic molecules. The nitrenium ions in the singlet state are ambident; their vacant p-orbital can be involved in interactions with the occupied orbitals of Lewis bases; the lone electron pair, in interactions with the vacant AOs of acids. In the triplet state, the ions have odd electrons and participate in radical processes. Direct measurements of ΔE_{ST} are generally performed using photoionisation spectroscopy; however, the use of this technique for nitrenium ions with bulky n or π type substituents is hampered because of a large number of vibrational bands that mask the electronic states.[7] Therefore, data about ΔE_{ST} were mainly obtained by quantum chemical methods.

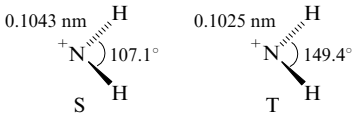
Quantum chemical calculations were carried out for different types of nitrenium ions:

Ions	Ref.
H_2N^+	150–171
$MeHN^+$	150, 153, 154, 160, 169, 172
Me_2N^+	150, 153, 154, 160, 172
	173
$HNCN^+$, 	174
cyclo-$(CH_2)_2N^+$	175
cyclo-$(CH_2)_nN^+$ (n = 4, 5)	150, 153, 154
$(CHX{=}CH)MeN^+$ (X = H, Cl)	154
cyclo-$C_6H_6N^+$, 2-MeO-R-$C_6H_4N^+$ (R = H, 5-Bu^t)	176–179
$ArHN^+$: Ar = 4-RC_6H_4 (R = H, Me, Ph, OMe, NMe_2, NH_2, OH, F, Cl, Ac, CHO, CO_2H, CN, CF_3, CO_2Me, AcNH, PhCH=CH, 3′-MeC_6H_4, 4′-MeC_6H_4, 3′-$MeOC_6H_4$, 4′-$MeOC_6H_4$), 2-MeC_6H_4, 2,6-$Me_2C_6H_3$, 4-Biph, 2-Biph, 1-Naph, 2-Naph, 2-Flu, 4-RC_6F_4 (R = C_6F_5, C(O)NHPr^n), 2-Py, 3-Py, 4-Py, 2-Pyr, 4-Pyr, 5-Pyr, Triaz, *etc*.	97, 106, 150, 152, 154, 172, 180–200
$ArMeN^+$: Ar = 4-RC_6H_4 (R = H, Me, Ph, Cl, OMe), 1-Naph, 2-Naph, 4-Biph, 2-Flu	93, 106, 172, 180, 201, 202
$ArBu^tN^+$: Ar = RC_6H_4 (R = H, 4-Br, 2-Ac), 2-Ac-4-BrC_6H_3	154
Ar_2N^+: Ar = 4-RC_6H_4 (R = H, Cl, Br), Mes, 2,6-$Bu^t_2C_6H_3$	95, 97, 183
$(CHO)XN^+$ (X = H, NH_2, PH_2, OMe, SH, Ph)	152, 203
$MeAcN^+$	150, 172
$ArAcN^+$: Ar = 4-RC_6H_4 (R = H, Me, OMe, OEt, Ph, PhCH=CH), 1-Naph, 2-Naph, 4-Biph, 2-Phen, 2-Flu, 3-Py, 4-Pyr	97, 106, 150, 172, 180, 187, 201
HXN^+ (X = NH_2, PH_2, OH, OMe, SH, F, Cl, Br, I, CN, NC_2)	152, 156, 157, 159, 163, 169, 171, 204, 205
F_2N^+	156, 157, 171, 206–215
X_2N^+ (X = Cl, Br, I)	156, 157, 159, 171
X_2N^+ (X = NH_2, PH_2)	216
$(N_2)_2N^+$	217–223
$(N_3)_2N^+$	224, 225
$(N_4)_2N^+$	226
$(CO)_2N^+$	219
$(OH)FN^+$	208, 227
$FClN^+$	171
N_3X^+ (X = O, S, Se, Te)	228

Note. Hereinafter, the notations are as follows: Naph is naphthyl, Biph is biphenylyl, Flu is fluorenyl, Phen is phenanthrenyl, Py is pyridyl, Pyr is pyrimidinyl, Triaz is triazinyl.

III. Unsubstituted nitrenium cation

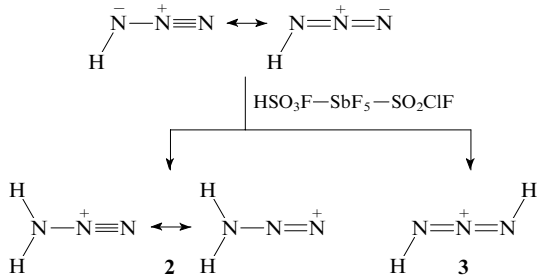
For the unsubstituted nitrenium ion, H_2N^+ (**1**), triplet state $^3B_1$ is the ground state.[2] Quantum chemical calculations give a wide scatter of the values of ΔE_{ST} and $\Delta\Delta H_f$ (S−T) (89–152 kJ mol^{-1}), which depends on the approximation chosen (see Appendix, Tables 1 and 2). The best agreement with the experimental value (ΔE_{ST} = 125.9 kJ mol^{-1})[229] is given by *ab initio* calculations CASSCF-MRCI + ZPE[151,161] and MRCISD(Q)/TZP[158] (Table 2). The MP4(SDTQ)/6-311 + G(3d2f,2p)//MP2/6-311 + G(3d,2p) *ab initio* calculations showed that both the singlet and triplet forms of the cation H_2N^+ were angular, and the angle HNH was much larger in the triplet state.[153]



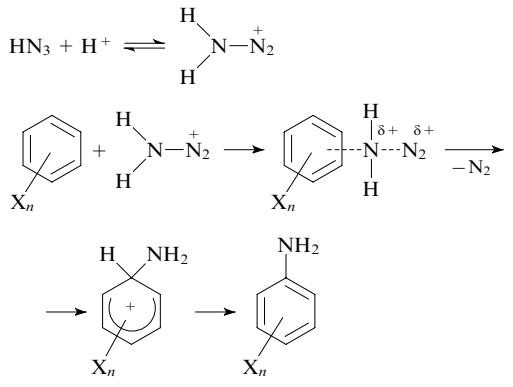
According to quantum chemical calculations for the $X\,^3B_1$ and $b\,^1B_1$ states of the H_2N^+ cation, the activation energy of the transition of the angular structure to the linear one is very small [1.9 (Ref. 167) and 0.7 kJ mol^{-1} (Ref. 170), respectively]. Because these barriers are lower than the zero level energy of the deformation vibrations, the cation H_2N^+ can be regarded as quasilinear.[162,230] In a pulse field ionisation photoelectron spectroscopy study, the dissociation energy of the N−H bond in the cation H_3N^+ was determined, and an exact value of the heat of formation of the nitrenium cation was obtained (ΔH_f = 1266.1 ± 0.3 kJ mol^{-1}),[231] which was close to the value found by the *ab initio* method for the triplet state of the H_2N^+ cation, ΔH_f = 1269.4 [MP4SDTQ(fc)/6-311 + + G(2df,p)//MP2(full)/6-311 + + G(d,p)],[159] 1267.8 kJ mol^{-1} [R/UCCSD(T)].[168] The adiabatic and vertical ionisation potentials were determined by the *ab initio* [CCSD(T)/TZ3P(2f,2d) + 2diff] method for the $X\,^3B_1$ ground state of the NH_2 molecule (11.09 and 12.01 eV) and proved very close to the experimental values (11.14 and 12.00 eV, respectively).[166] Similarly, for the $\tilde{a}\,^1A_1$ state of this molecule, the adiabatic and vertical ionisation potentials (12.39 and 12.46 eV, respectively)

also agree well with the experimental values (12.445 and 12.45 eV).[166] The relatively large values of these potentials are evidently determined by the high electronegativity of the nitrogen atom. An infrared photodissociative spectroscopy study showed that the nitrenium cation formed intermolecular hydrogen bonds with inert gases such as Ar (Ref. 162) and He (Ref. 165) (E_{bnd} = 21.2 and 3.3 kJ mol^{-1}) and that the barrier to the transition of the angular to linear form during complexation decreased (0.8 and 1.3 kJ mol^{-1}, respectively) compared with that for the free nitrenium ion. The B3LYP/6-31G(d) calculations predict that the $^1(H_2N^+)$ cation has a high Lewis acidity relative to that of Hal-, O-, S-, N- , and P-bases, ΔH_f (298.15 K) = 175.3 (HF), 335.6 (HCl), 352.7 (H_2O), 540.6 (H_2S), 567.4 (NH_3), and 699.6 kJ mol^{-1} (PH_3).[171] These values are close to the experimental values of the enthalpies of formation of the complexes NH_2-L^+ [L = H_2O (365.7 kJ mol^{-1}), NH_3 (573.6 kJ mol^{-1})].[171]

Under the 'long life' conditions, the cation H_2N^+ was not generated in solution. It was shown[31] by ^1H and ^{15}N NMR spectroscopy that protonation of hydrazoic acid in superacidic media (HSO_3F-SbF_5, $HF-SbF_5$, $HF-BF_3$) formed the aminodiazonium ion (**2**) rather than the iminodiazonium ion (**3**).



It may be assumed that elimination of the nitrogen molecule from the aminodiazonium ion leads to the formation of the nitrenium ion. However, this is a very unstable species the lifetime of which is very small. Therefore, the formation of the nitrenium ion as a discrete species is often not considered as part of the reaction mechanism. Thus for amination of arenes with hydrazoic acid in a $CF_3SO_3H-CF_3CO_2H$ mixture a concerted mechanism was suggested, which included an attack of the protonated form of hydrazoic acid, $H_2N_3^+$, on the arene with simultaneous elimination of the nitrogen molecule.[44]

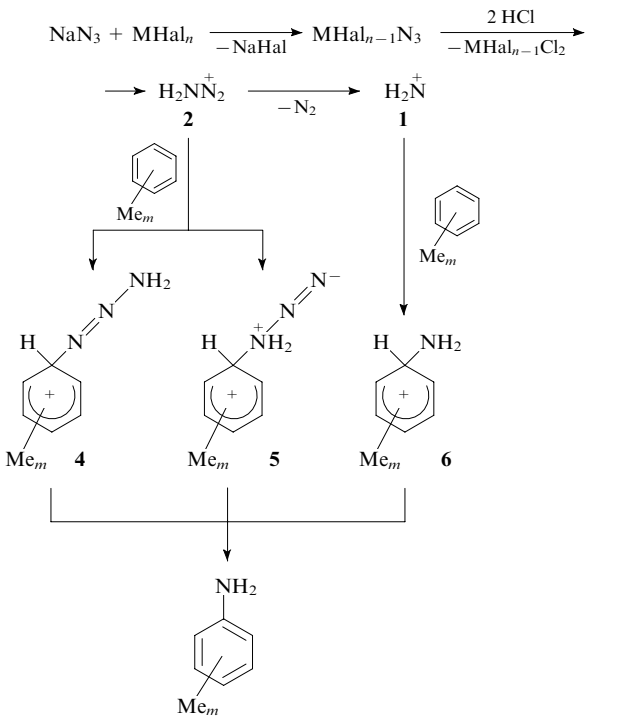


The yield of arylamines depends on the structure of the starting arene and decreases upon introduction of acceptor substituents in the benzene ring. In the absence of CF_3SO_3H, the reaction did not occur, indicating that the generation of the nitrenium ion required a highly acidic medium.

In several cases, indirect evidence was obtained on participation of the nitrenium ion in electrophilic amination of aromatic compounds. Thus in amination with NaN_3-AlCl_3-HCl,[1,31] the highest yields of amines were obtained for arenes with electron-donating substituents; in these reactions, the *ortho*- and *para*-isomers were dominant products, which pointed to the electrophilic character of the active intermediate species.

In the case of amination of mesitylene with the NaN_3-AlCl_3-HCl system, it was shown[19,20] that a very low yield of mesidine was obtained in solvents with a high (> 2) Gutman's donor number (THF, sulfolane, $MeNO_2$ and $PhNO_2$); the most suitable solvents were CH_2Cl_2, $Cl(CH_2)_2Cl$ and a mixture of the ionic liquid 1-butyl-3-methylimidazolium (bmim) chloride with $AlCl_3$ in a molar ratio of 3 : 4.[24] In the presence of HCl, the latter system behaves as a superacid.[232] It was found that the activity sequence of Lewis acids in mesitylene amination in $Cl(CH_2)_2Cl$ ($GaCl_3 \approx ZrCl_4 \approx AlCl_3 > AlBr_3 > FeCl_3 > SbCl_5 \gg SnCl_4$, $TiCl_4 > SbCl_3$, $GeCl_4$) was slightly different from the same series for the Friedel–Crafts catalysts ($Al_2Br_6 > Al_2Cl_6 > Ga_2Cl_6 > Fe_2Cl_6 > SbCl_5 > ZrCl_4$, $SnCl_4 > SbCl_3$).[23] Strong Lewis acids are most active in amination ($GaCl_3$, $ZrCl_4$, $AlCl_3$, $AlBr_3$) because the latter demands highly acidic media. The most probable mechanisms of arene amination with NaN_3-MHal_n-HCl are presented in Scheme 1.[19,20,23,31]

Scheme 1



M = Ga, Zr, Al, Fe, Sb, Sn, Ti; n = 3, 4; m = 2–5.

In the second stage, the protonation of azide $MHal_{n-1}N_3$ affordss the aminodiazonium ion **2**, which gives the nitrenium cation **1** after elimination of the nitrogen molecule. Interaction of arenes with the cation $H_2NN_2^+$ can lead to σ-complexes such as **4** or **5**. According to AM1 quantum chemical calculations of these σ-complexes, in the case of methyl-substituted benzenes (*o*-xylene, mesitylene, durene and pentamethylbenzene), σ-complexes **4** are less stable than the corresponding complexes **5** and hence a mechanism that involves these complexes is very unlikely.[20] A very long H_2N-N bond (~3 Å) is characteristic of σ-complexes **5**, therefore, they are similar to σ-complexes **6**. The latter can be formed by direct interaction

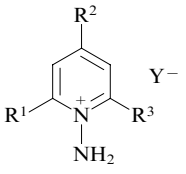
of the nitrenium ion arising from the decomposition of **2** with elimination of the nitrogen molecule.[20] As mentioned above, the ground state of the cation H_2N^+ is the triplet state $^3(H_2N^+)$. Since the formation of **6** demands that the nitrenium ion should be in the singlet state, the conversion of arene should depend on the probability of a singlet – triplet transition for this cation. As is known, this probability increases with the number of heavy atoms and their atomic numbers in the solvent molecule. Indeed, in the amination with NaN_3-AlCl_3-HCl, the conversion of mesitylene and *o*-xylene in different solvents decreases in the series $CH_2Cl_2 > CHCl_3 > CCl_4$, $Cl(CH_2)_2Cl > ClCH_2CCl_3$, and $CH_2Cl_2 > CH_2Br_2$, which is consistent with the participation of the cation H_2N^+ as an active intermediate in the reaction.[20] The limiting stage of the amination is obviously the formation of σ-complex **6**. If we take into account the above considerations, the degree of conversion (η) of methylbenzenes should depend not only on the number of heavy atoms (N) in the solvent molecule, but also on the dielectric constant (ε) of the latter. This is confirmed by the two-parameter correlations[19,20] for reactions of mesitylene (MsH) and *o*-xylene (*o*-XyH),

η (MsH) = $(0.29 \pm 0.08) + (0.067 \pm 0.010)\varepsilon - (0.107 \pm 0.023)N_{Cl}$, $r = 0.97$, $s = 0.08$, $n = 9$;

η (*o*-XyH) = $(0.40 \pm 0.10) + (0.059 \pm 0.012)\varepsilon - (0.143 \pm 0.027)N_{Cl}$, $r = 0.96$, $s = 0.1$, $n = 7$.

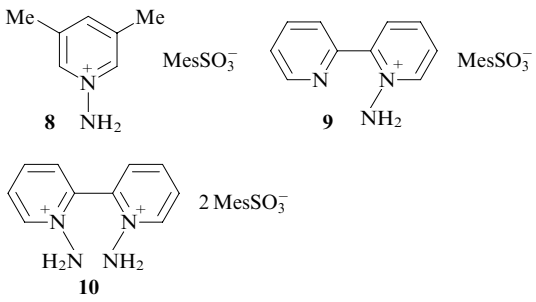
The cation H_2N^+ is a rather reactive intermediate species in arene amination, which results in its low selectivity.[1,20] This follows from the calculated values of the logarithm of the partial rate factor of hydrogen substitution into the *para*-position of toluene ($\log f_p$) and the selectivity factor [$S_f = \log(f_p/f_m)$, where f_m is the rate factor for the substitution into the *meta*-position] for toluene amination with NaN_3-AlCl_3-HCl (0.97 and 0.75, respectively).[20]

The nitrenium ion can be generated by photolysis of *N*-aminopyridinium and *S*-aminosulfonium salts and their analogues. A wide range of these salts (**7**–**14**) were examined to investigate the effects of the structure of the cation and the nature of the counterion on the activity of the corresponding salts in the reaction with arenes.[1,40,42,43,45]

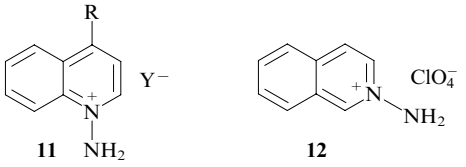


7a–**s**

Compound **7**	R^1	R^2	R^3	Y	Compound **7**	R^1	R^2	R^3	Y
a	H	H	H	Br	**k**	H	COMe	H	$MesSO_3$
b	H	H	H	I	**l**	H	CO_2Me	H	$MesSO_3$
c	H	H	H	ClO_4	**m**	H	CN	H	Br
d	H	H	H	$MesSO_3$	**n**	H	CN	H	ClO_4
e	Me	H	H	I	**o**	H	CN	H	$MesSO_3$
f	MeO	H	H	$MesSO_3$	**p**	H	NO_2	H	$MesSO_3$
g	MeO	H	H	ClO_4	**q**	Me	Me	H	$MesSO_3$
h	H	MeO	H	$MesSO_3$	**r**	Me	Ph	Ph	BF_4
i	H	Me	H	$MesSO_3$	**s**	Ph	Ph	Ph	ClO_4
j	H	Ph	H	$MesSO_3$					

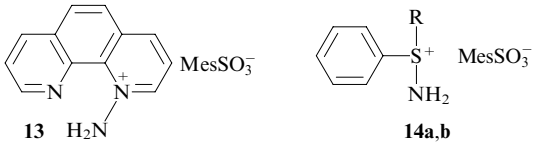


8 **9** **10**



11 **12**

R = H, Me, Cl;
Y = Cl, Br, ClO_4, $MesSO_3$.

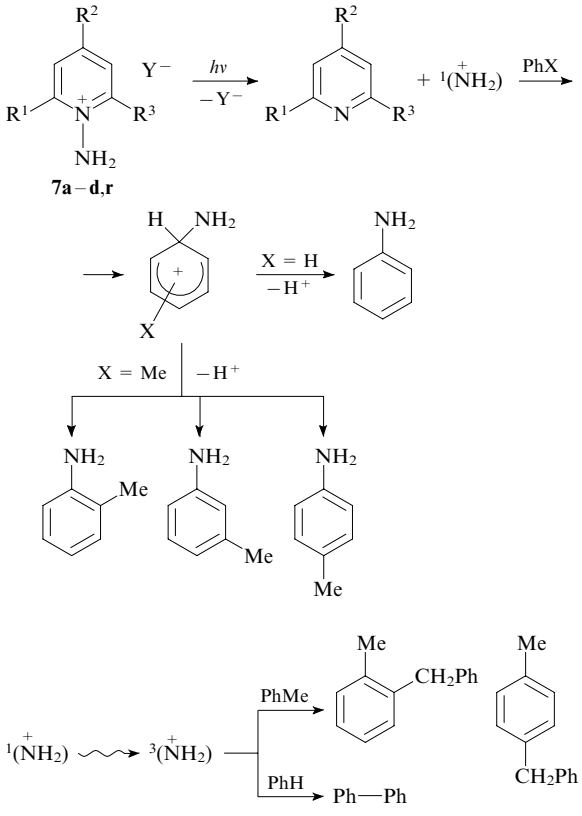


13 **14a**,**b**

R = Me (**a**), Ph (**b**).

Photolysis of 1-aminopyridinium salts **7a**–**d**,**r** in benzene or toluene in the presence of CF_3CO_2H gives aniline and toluidines, respectively. This can be regarded as evidence for the involvement of the nitrenium ion in the singlet state (Scheme 2).[42]

Scheme 2



In addition to the electrophilic substitution products (methylanilines), the reaction affords biphenyl and phenyltolylmethanes, obviously formed *via* the nitrenium cation in the triplet state. The low regioselectivity of the reactions of toluene and naphthalene with the nitrenium cation formed upon photolysis of **7** and **8** in the presence of CF_3CO_2H is consistent with the above data on the high activity of the cation H_2N^+. This also follows from the low absolute value of the sensitivity constant (ρ^+) in the Hammett equation for reactions of alkylbenzenes with the nitrenium cation generated upon photolysis of 1-aminoquinolinium perchlorate ($\rho^+ = -1.9$).[42]

The activity of *N*-aminopyridinium salts **7** and **8** in reactions with arenes in the presence of CF_3CO_2H is considerably affected by the substituents in the pyridine ring and the nature of the counterion.[43,45] The selectivity factor (S_f) increases with the electron-withdrawing character of the substituents in the ring in the amination of toluene. The relative fraction of 1- and 2-aminonaphthalenes formed in the photolysis of **7** and **8** in the naphthalene–CF_3CO_2H system also depends on the structure of the pyridinium fragment and the nature of the counterion.[45] A similar tendency can be traced for photolysis of quinolinium salts **11** in toluene– CF_3CO_2H.[43] The selectivity factor decreases in the series of the anions $Cl^- > Br^- > MsSO_3^- > ClO_4^-$, which was attributed[43] to the degree of delocalisation of the negative charge on the anion. The same order $Br^- > MsSO_3^- > ClO_4^- > I^-$ is observed in the photolysis of 1-aminopyridinium salts **7a**–**d** (Ref. 43).

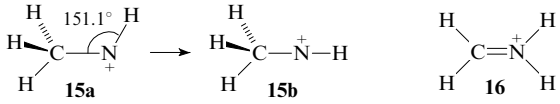
In the photolysis of 1-aminopyridinium and 1-aminoquinolinium mesitylenesulfonates, the addition of small amounts of 18-crown-6 to the benzene–CF_3CO_2H mixture leads to a monotonic increase in the yield of aniline; this is explained by stabilisation of the cation H_2N^+ in the singlet state by its interaction with the crown ether.[43] In the case of perchlorates of these cations, the yield of aniline initially increases and then decreases abruptly, which is attributed to the formation of a sandwich-type complex between the cation H_2N^+ and two crown-ether molecules. This complex is believed to have a decreased reactivity because of steric hindrances as regards the approach of the benzene molecule to the complexed cation H_2N^+.

As a result of photolysis of **7d** and **9** in the benzene–CF_3CO_2H or PhMe–CF_3CO_2H system, the yields of aniline and toluidines decrease if photolysis is carried out in solvents containing heavy atoms (CH_2Cl_2, CH_2Br_2, CH_3I) and in the presence of atmospheric oxygen; this is evidently caused by an increase in the S–T conversion rate of the nitrenium cation.[45] Because of the lower nucleophilicity of sulfides, the nitrenium cation interacts more weakly with the lone electron pair of the sulfur atom in sulfides than with the pair of the nitrogen atom in pyridines. Therefore, for sulfonium salts, S–T conversion must occur at a higher rate. This accounts for the low yield of the amination products in the photolysis of **14a**,**b** in the benzene–CF_3CO_2H and toluene–CF_3CO_2H systems.[45]

Note that heating of a DMSO solution of **13** at 150 °C in the presence of active arenes (mesitylene, anthracene) does not lead to amination products,[233] which is obviously caused by the difficulty of heterolysis of the N–NH_2 bond because of the low stability of the cation H_2N^+. Similarly, reactions of **7b** with strong bases such as Et_3N do not result in a transfer of the cation H_2N^+ to the amine, but afford the corresponding ylide.[234]

IV. Alkyl- and cycloalkylnitrenium ions

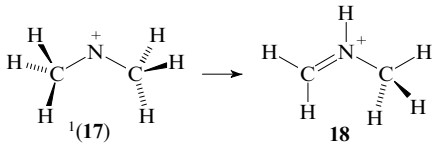
According to quantum chemical calculations (see Appendix, Tables 1 and 2), the ground state of the cation $MeHN^+$ is the triplet state (**15a**) with the angle CNH of 151.1° [HF/6-31G(d) *ab initio* calculations]. As in the case of H_2N^+, structure **15a**, characterised by low activation energy, is transformed into the linear form **15b** (E_a = 4.1 kJ mol^{-1}).[153] The energy difference ΔE_{ST} decreases from H_2N^+ to $MeHN^+$, which is attributed to the stabilising effect of hyperconjugation between the methyl group and the vacant p-orbital of the cation $MeHN^+$ in the singlet state.



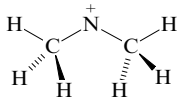
15a **15b** **16**

None of the configurations of the singlet form of $MeHN^+$ corresponds to a minimum on the potential energy surface; the minimum is due to the immonium ion **16**.[153] The methylnitrenium ion **15** was generated from the anion $MeHN^-$ in the gas phase and investigated by mass spectrometry.[235]

As in the case of $MeHN^+$, the singlet state of dimethylnitrenium ion ^{1}(**17**) is not a minimum on the potential energy surface [MP2(full)/6-31G(d) calculation] and is readily transformed into the immonium ion **18** [E_a = 18.8 kJ mol^{-1}, HF/6-31G(d)].[153]



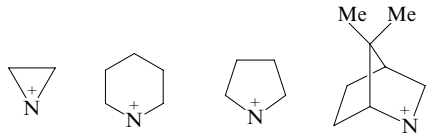
^{1}(**17**) **18**



^{3}(**17**)

Ab initio and MNDO calculations of the cation Me_2N^+ predicted higher stability of the triplet state ^{3}(**17**) relative to the singlet state ^{1}(**17**), while the AM1 method showed that the singlet state was preferable (see Appendix, Tables 1 and 2). Photoelectron spectroscopy studies of ionisation of the radical $Me_2N^{\bullet}$ revealed that the ground state of Me_2N^+ was the singlet state.[236] The first band (9.01 eV) in the spectrum was assigned to the formation of the cation Me_2N^+ in the $^1A_1$ state, while the transition at 9.65 eV, to the formation of the cation in the $^3B_1$ triplet state, which agreed with DFT calculations. The dimethylnitrenium ion **17** was also generated from the anion Me_2N^- in the gas phase.[235] Using the known formation heat of cation **18** and the calculated values of $\Delta\Delta H_f$ of this ion and Me_2N^+, Ford and Herman [153] obtained the heats of formation of the latter cation in the singlet and triplet states (1021 and 1013 kJ mol^{-1}, respectively).

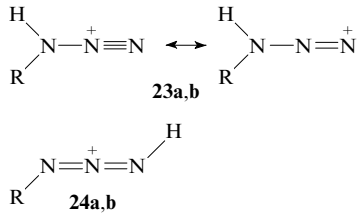
According to *ab initio* quantum chemical calculations for the cyclic nitrenium ions cyclo-$(CH_2)_2N^+$ (**19**) and cyclo-$(CH_2)_5N^+$ (**20**), the triplet state is energetically preferable to the singlet state, whereas for the cation cyclo-$(CH_2)_4N^+$ (**21**), the situation is equivocal (see Appendix, Table 2). For the bicyclic ion **22**, the singlet state is more stable according to the MNDO data.[153]



19 **20** **21** **22**

For **20** and **21**, the MNDO and AM1 semiempirical methods predicted higher stability of the singlet state.

Alkyl- and cycloalkylnitrenium ions were not generated in solution under the 'long-life' conditions. ^{1}H, ^{13}C, and ^{15}N NMR studies[31] showed that protonation of azides RN_3 (R = Me, Et) in superacidic systems (HSO_3F-SbF_5, $HF-SbF_5$, $HF-BF_3$) afforded aminodiazonium ions **23** rather than iminodiazonium ions **24**.

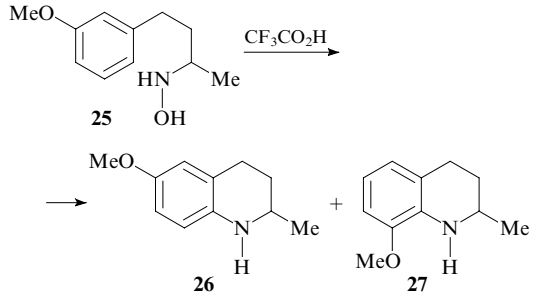


23a,**b**

24a,**b**

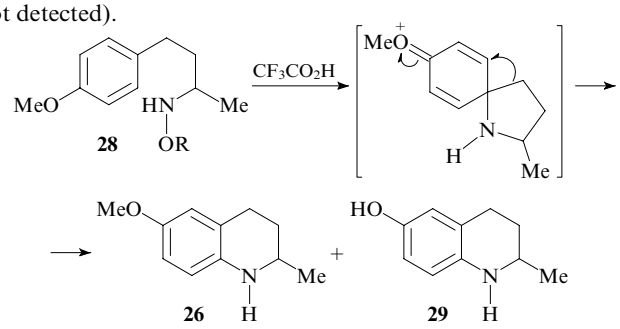
R = Me (**a**), Et (**b**).

It is believed that alkylnitrenium ions are involved in a number of arene amination reactions, both inter- and intramolecular. For example, the reaction of n-butyl azide with benzene or mesitylene in a $CF_3SO_3H-CF_3CO_2H$ mixture affords the corresponding arylbutyl amines.[44] The action of CF_3CO_2H on the *meta*-methoxy derivative **25** results in cyclisation and formation of tetrahydroquinolines **26** and **27**.[237]



25 **26** **27**

The direction of the reaction depends on the position of the MeO substituent in the ring and changes substantially for the *para*-methoxy derivative **28**.[237] In this case, the products are 6-methoxy-2-methyl-1,2,3,4-tetrahydroquinoline (**26**) and the demethylation product, 6-hydroxy-2-methyl-1,2,3,4-tetrahydroquinoline (**29**); this was explained by the participation of the σ-complex in the reaction (the 7-methoxy derivative was not detected).



28 **26** **29**

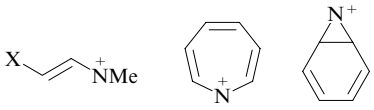
R = H, Ac.

Photolysis of *N*-methylamino- and *N*,*N*-dimethylamino-2-methyl-4,6-diphenylpyridinium tetrafluoroborates in the $PhMe-CF_3CO_2H$ system occurs in the same way as photolysis of **7a**–**d**,**r** in this system, but the yield of the corresponding amines is markedly lower, while the fraction of the radical reaction products is higher.[42] The authors explained this by the higher rate of S–T conversion of the methyl-substituted nitrenium ions $MeHN^+$ and Me_2N^+ compared with the rate of the same process for H_2N^+.

It was shown that arylepoxyalkyl azides treated with Lewis acids can undergo a number of transformations probably with the formation of dialkyl-substituted nitrenium ions (Scheme 3).[64]

V. Enylnitrenium ions

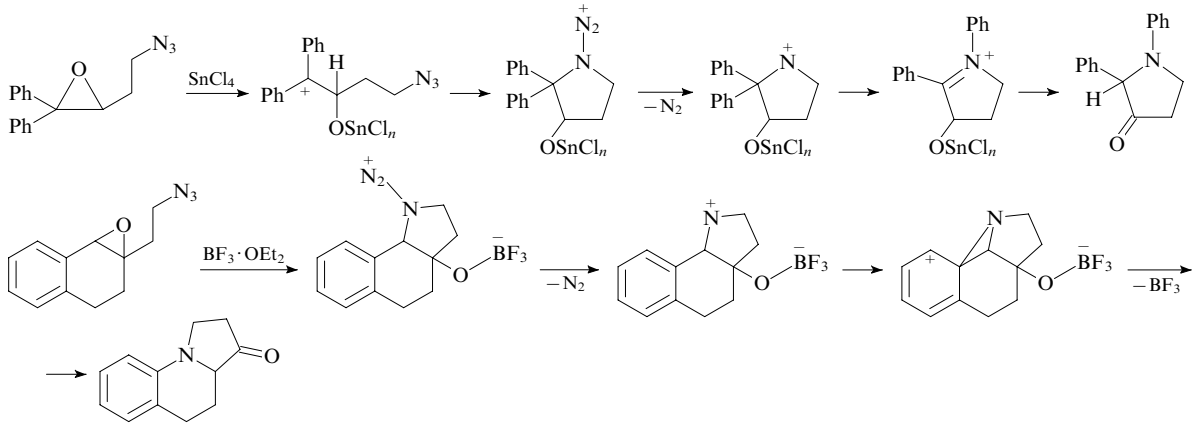
According to MNDO and AM1 quantum chemical calculations for enylnitrenium ions **30a**,**b**, the singlet state is energetically more favourable (see Appendix, Table 1), while the *ab initio* method predicts that the ground state for cation **30a** will be triplet (see Appendix, Table 2). For the tropylium cation analogue, *viz*, azepinenitrenium ion **31**, the *ab initio* method predicts that the singlet state will be energetically preferable (see Appendix, Table 2).



30a,**b** **31** **32**

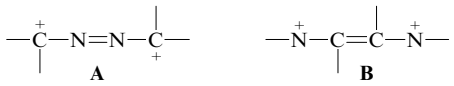
X = H (**a**), Cl (**b**).

Scheme 3



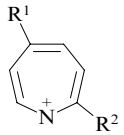
The interaction of the cation $N^+(^3P)$ with benzene was studied [148] by the B3LYP/6-31G* method. The cation N^+ initially attacks the carbon–carbon bond of the benzene ring to form the nitrenium ion bridge **32** in the triplet state, which rearranges into the triplet azepinenitrenium ion **31**. These (and also CAS//RHF/3-21G) calculations showed that the ground state of **31** was the singlet state and the angle CNC in the singlet state was smaller than in the triplet state (127° and 144°, respectively).

The first 'direct' observation of enylnitrenium ions in the solid state by ^{15}N and ^{13}C NMR spectroscopy has shown [238] that polyazine $-(N{=}C(R){-}C(R){=}N)_n-$ doped with iodine was transformed into a polycation in which the positive charge was localised on the nitrogen (structure **B**) rather than on the carbon (structure **A**) atoms. However, later this treatment was criticised [239] based on the data of AM1, RHF/6-31G*, and MP2/6-31G* calculations.



A **B**

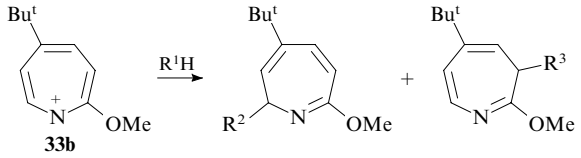
The action of $TiCl_4$ on 2-methoxy-4-R^1-7-R^2-2*H*-azepines ($R^1 = R^2 = Bu^t$; $R^1 = Bu^t$, R^2 = MeO) and 2-isopropoxy-7-methoxy-2*H*-azepine afforded azepinium ions **33a–c** (Refs 177–179). Their structures were confirmed by ^1H and ^{13}C NMR.



33a–c

$R^1 = Bu^t$: $R^2 = Bu^t$ (**a**), MeO (**b**);
R^1 = H, R^2 = MeO (**c**).

In the reactions of cation **33b** with water, propylamine, arenes PhX (X = H, OH, MeO), furan, thiophene or pyrrole, the corresponding substituent occupies the position 3 or 7 in the azepine ring.[177, 178]

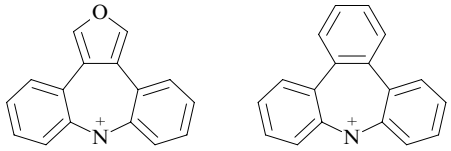


33b

R^1H = PhH, MeOPh, PhOH, furan, thiophene, pyrrole, H_2O, $PrNH_2$;
R^2 = Ph, 2-$MeOC_6H_4$, 4-$MeOC_6H_4$, 2-HOC_6H_4, 4-HOC_6H_4, 2-C_4H_3O, 2-C_4H_3S, 2-C_4H_3NH, OH, NHPr;
R^3 = Ph, 4-$MeOC_6H_4$, 4-HOC_6H_4, 2-C_4H_3O, 2-C_4H_3S, 2-C_4H_3NH.

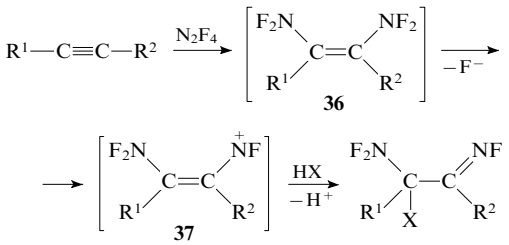
According to B3LYP/6-31G(d) calculations, the azepinium ion is 69.9 kJ mol^{-1} less stable than the tropylium cation.[177]

Attempts to generate di- and tribenzoazepinium ions **34** and **35** by treatment of 8*H*-furo[3,4-*d*]dibenzo[*b*,*f*]azepine and 9*H*-tribenzo[*b*,*d*,*f*]azepine with CF_3CO_2Ag failed.[240]



34 **35**

Solvolysis of 1,2-bis(difluoroamino)ethylenes **36** in MeOH, EtOH or AcOH is assumed to occur *via* nitrenium ions **37**.[241]

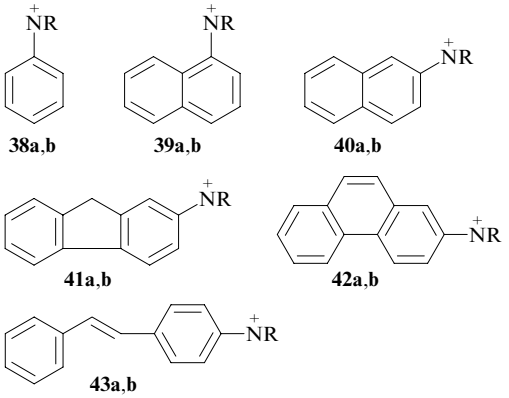


36 **37**

$R^1 = R^2$ = Et, Ph; R^1 = Ph, R^2 = Me;
X = MeO, EtO, AcO.

VI. Aryl-substituted nitrenium ions

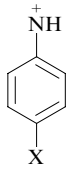
Arylnitrenium ions are currently investigated most intensely because they are considered as active intermediates in electrophilic amination reactions,[1] carcinogenesis,[3, 7, 102, 122, 126–128, 134, 140–143, 147] action of several drugs,[146, 242] synthesis of electroconducting polymers [119, 120] and as the potential precursors of organic magnetic materials.[149] For arylnitrenium ions **38–43**, the ground state is singlet (see Appendix, Tables 1 and 2) because of the stabilising interaction of the occupied π-orbitals of the aromatic ring with the vacant p-AO of the ion in the singlet state.



38a,b **39a,b** **40a,b** **41a,b** **42a,b** **43a,b**

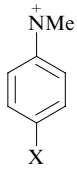
R = H (**a**), Ac (**b**).

According to the data of quantum chemical calculations of cations **44–46**, the singlet state is destabilised relative to the triplet state when the withdrawing character of the substituent X in the aromatic ring increases (see Appendix, Tables 1 and 2).



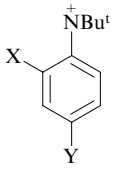
44a–p

X = NMe_2 (**a**), NH_2 (**b**), OH (**c**), MeO (**d**), Me (**e**), CHO (**f**), CO_2H (**g**), CO_2Me (**h**), Ac (**i**), CF_3 (**j**), CN (**k**), Cl (**l**), F (**m**), NO_2 (**n**), NHAc (**o**), NMeAc (**p**).



45a–d

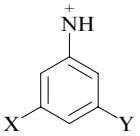
X = Me (**a**), Cl (**b**), Ph (**c**), MeO (**d**).



46a–d

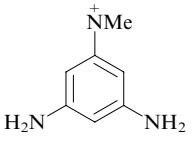
X = H: Y = H (**a**), Br (**b**);
X = Ac: Y = H (**c**), Br (**d**).

For arylnitrenium ions **47**–**49** with substituents in the *meta*-position, the situation is equivocal.[149] Surprisingly, the introduction of strong donating (NH_2, NMe_2, PMe_2) and withdrawing (CN, NO) substituents in the aromatic ring stabilises the triplet state relative to the singlet state (see Appendix, Table 2). In the case of **38a** and **44a**–**n**, a linear correlation was found between the ΔE_{ST} and the σ^+ constants (or σ_R^+) of the substituents, which points to the similarity of the arylnitrenium ions to the benzyl cations with considerable resonance interactions between the ring substituents and the carbocation centre.[185]

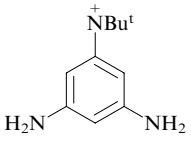


47a–**p**

X = H: Y = Me (**a**), $SiMe_3$ (**b**), F (**c**), CN (**d**), OH (**e**), $CH{=}CH_2$ (**f**), PH_2 (**g**), PMe_2 (**h**), C_4H_3 (**i**), MeO (**j**), NH_2 (**k**), NO (**l**), SH (**m**), 1-NC_2H_2 (**n**);
X = Y = NH_2 (**o**), NMe_2 (**p**).

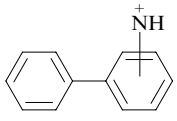


48

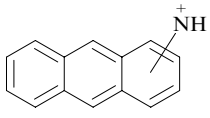


49

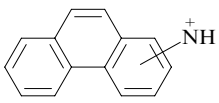
Ab initio and AM1 calculations of nitrenium ions **38a** and **50**–**54** showed that the stability of $ArHN^+$ type cations increases with the length of the aromatic π-system, and that the relative stability series of these ions is parallel to that for the isoconjugated arylmethyl cations.[181, 186] According to the data from HF-6-31G(d) *ab initio* calculations, the barriers to the interconversion of the *syn*- and *anti*-isomers for **50**–**54** are rather high and depend slightly on the nature of the aryl group ($\Delta E^{\neq} = 116 \pm 8$ kJ mol^{-1}).[186]



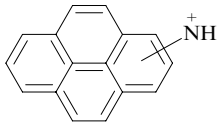
50



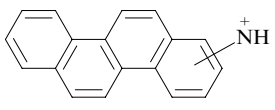
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52

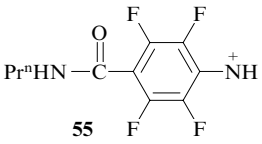


53



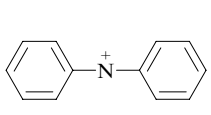
54

B3LYP/6-31G* calculations of the energies of the singlet and triplet states of the fluorinated arylnitrenium ion **55** indicate that the ground state is singlet, and the value of S–T splitting is rather high (~84 kJ mol^{-1}).[192] In contrast, HF/6-31G* calculations predict that the ground state will be triplet and the energy difference will be smaller (ΔE_{ST} = 20.9 kJ mol^{-1}).[192]

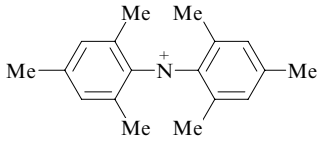


55

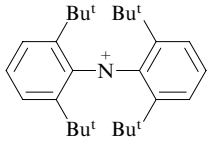
According to AM1 data, the singlet state of the arylnitrenium ions $PhRN^+$ is destabilised relative to the triplet state when the steric effect of the substituent R increases (Bu^t > H) (see Appendix, Table 1).[154] Similarly, the loss of conjugation in Ar_2N^+ (**56**–**58**) as a result of the introduction of bulky substituents in the *ortho*-positions of the benzene rings also leads to destabilisation of the singlet state; according to AM1 calculations, the ground state of **58** is triplet, but singlet for **56** and **57** (see Appendix, Table 1).[183]



56

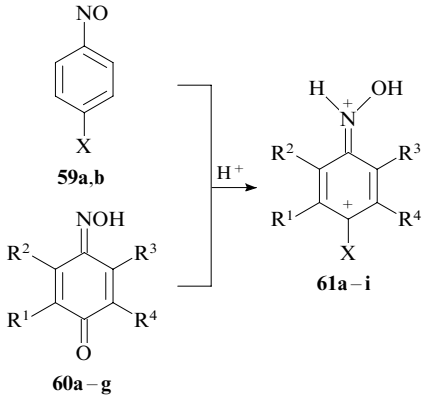


57



58

Spectral data for arylnitrenium ions are rather scarce compared with the data for their isoelectron analogues, carbocations ArC^+RH.[2, 3, 12, 90, 92, 130] An attempt to generate arylhydroxynitrenium ions by protonation of nitrosoarenes **59a**,**b** or benzoquinone monoximes **60a**–**g** in superacidic media ($HSO_3F-SbF_5-SO_2$) failed.[243] Protonation led to benzimininium dications **61a**–**i**.



59a,**b**

60a–**g**

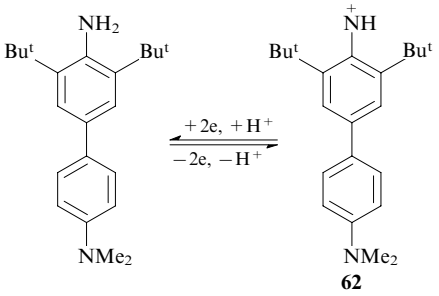
61a–**i**

X = MeO (**59a**), NMe_2 (**59b**), OH (**61a**–**g**);
$R^1 = R^2 = R^3 = R^4$ = H: X = MeO (**61h**), NMe_2 (**61i**).

Compounds **60**, **61a**–**g**	R^1	R^2	R^3	R^4
a	H	H	H	H
b	Me	H	H	H
c	H	Me	H	H
d	Me	Me	H	H
e	Me	H	H	Me
f	H	Me	Me	H
g	Me	H	Me	H

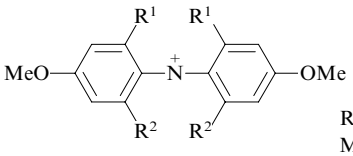
The reason for the failure evidently lies in the ambident character of the nitrenium cations; along with the electrophilic properties they can exhibit nucleophilic properties by adding a proton at the lone electron pair.

Previously, it has been shown[244, 245] that electrochemical oxidation of 4-amino-3,5-di(*tert*-butyl)-4′-dimethylaminobiphenyl in MeCN gave arylnitrenium ion **62**. The structure of the ion was confirmed by the ^{1}H NMR and electronic absorption spectra (EAS).[244]



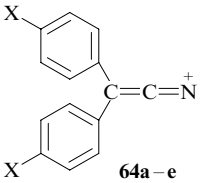
62

ortho- and *para*-Methoxy-substituted arylnitrenium ions **63a–c** [246,247] were generated electrochemically. The ^1H, ^{13}C and ^{15}N NMR spectroscopic data were analysed, and strong arguments were given in favour of the fact that cyanodiphenylmethyl cations **64a–e**, which are analogues of diarylnitrenium ions according to the principle of vinilogy, are essentially nitrenium ions in character.[248–250]



63a–c

R^1 = H: R^2 = H (**a**), MeO (**b**); R^1 = R^2 = MeO (**c**).



64a–e

X = H (**a**), Me (**b**), MeO (**c**), Cl (**d**), F (**e**).

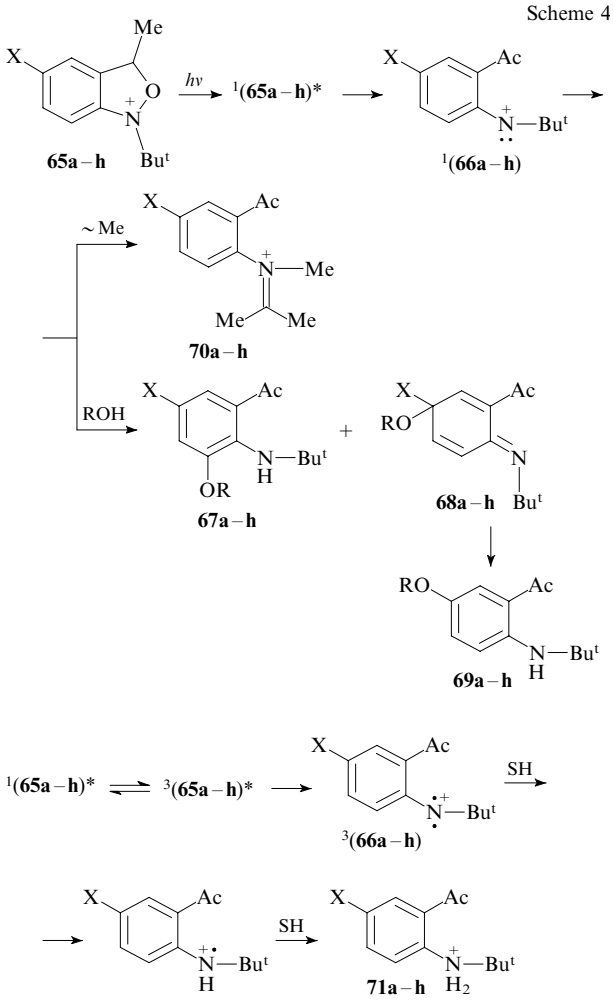
One of the methods for the direct generation of arylnitrenium ions in a condensed phase is nuclear chemical synthesis based on β-decay of tritium atoms.[14,194,251–253]



When generated by this procedure, arylnitrenium ions appear without a counterion, due to which they can be studied as species in the 'free state'. Investigation of the electrophilic substitution of the hydrogen atom in benzene and its monosubstituted derivatives (toluene and nitrobenzene) under the action of the phenylnitrenium ion $PhTN^+$ showed that the reaction occurred both at the N and C atoms and formed diphenylamines and aminobiphenyls, respectively; in the case of toluene, 4-methyldiphenylamine was the sole product, while for nitrobenzene, *o*-, *m*-, and *p*-aminobiphenyls were obtained along with nitrodiphenylamines.[251–253] An analysis of the experimental data and the results of AM1 calculations showed that in the reaction of benzene with the phenylnitrenium ion, the reaction products depended on the comparable contributions of the equilibrium constants of the formation of the σ-complexes and their deprotonation rate constants.[194]

Data on 'direct' observation and reactivity of arylnitrenium ions were mostly obtained by photolysis (Refs 2, 3, 7, 12, 29, 32, 80, 88–97, 129–131, 135–137, 139, 141, 147, 200, 254–270). Salts of *N*-(*tert*-butyl)-3-methylanthranilium ions **65a–h** were used [147,254–258] for generating the nitrenium cations, which were identified by electron spectroscopy (Scheme 4). The higher stability of the singlet state of the nitrenium ions ^{1}(**66a–f**) followed from the absence of the effect of O_2 on their lifetimes.[147,255,256] The interaction of ^{1}(**66b–d**) with water and alcohols obeys the pseudofirst order kinetic equation (k is 10^6–10^9 litre mol^{-1} s^{-1}) and forms the *ortho*-(**67b–d**) and *ipso*-substitution products (**68d**, **69b**,**c**). For the nucleophiles ROH, the reactivity decreases in the series MeOH > EtOH > $Pr^iOH \approx H_2O$ > Bu^tOH, which is similar to the series for diarylmethyl cations.[256]

Scheme 4



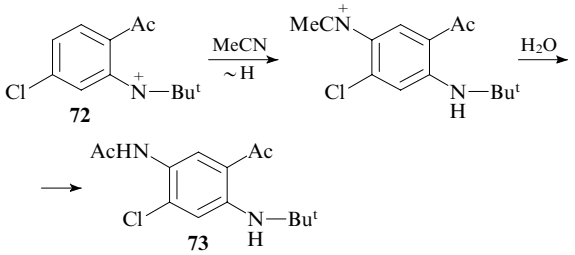
X = H (**a**), Br (**b**), Cl (**c**), Me (**d**), MeO (**e**), Ph (**f**), CN (**g**), NO_2 (**h**);
SH = ROH, H_2O, MeCN–H_2O, MeCN–ROH (R = Me, Et, Pr^i, Bu^t).

It was assumed that the nucleophiles ROH attack the *para*-position relative to the nitrenium centre of ^{1}(**66a**) and that **69a** is formed as a result of 1,5-migration of the hydrogen atom.[256] In the absence of nucleophiles, the ^{1}(**66b–d**) ions in MeCN have lifetimes from 119 to 440 ns, while for ^{1}(**66e**,**f**) the lifetimes are higher (30 and 600 μs, respectively).[147] The lifetime of ^{1}(**66a**), formed upon photolysis of **65a** in CH_2Cl_2, is quite sufficient for this ion to be almost entirely rearranged into iminium ion **70a** by 1,2-migration of the methyl group.[254] A similar rearrangement was used to explain the formation of aniline upon the photochemical transformation of *N*-(methylphenylamino)-2,4,6-trimethylpyridinium tetrafluoroborate.[91]

The yield of protonated amines **71b**,**c**, evidently formed upon reaction of the triplet nitrenium ions ^{3}(**66b**,**c**) with SH, decreases when tetramethyldiazetine dioxide is added to quench the triplet state.[255] Photolysis of **65h** in MeCN–H_2O or MeCN–MeOH mixtures affords cations **70h** and **71h**, while the nucleophilic substitution products are absent, which points to the formation of cation ^{3}(**66h**) in the triplet state.[257] In the presence of O_2, the relative fraction of cation **71h** decreases, and the addition of Ph_3CH leads to an increase in the **71h** : **70h** ratio and to isolation of the 4-Ph_3C-4-H-C_6H_4=CPh_2 dimeric product, which confirms the formation of the radical $Ph_3C^{\bullet}$.[257]

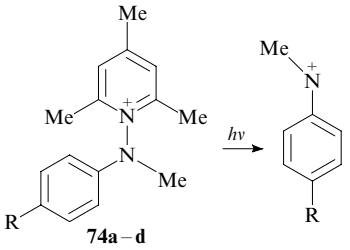
An analysis of the kinetic data showed that the lifetime of the triplet *N*-*tert*-butyl(2-acetyl-4-nitrophenyl)nitrenium cation was ~2 μs.[257]

Acetonitrile is a weak nucleophile that reacts only with sufficiently reactive arylnitrenium ions such as **72** to form the substitution product **73**.[258]



Time-resolved IR studies showed that the diphenylnitrenium ion has an iminocyclodienyl structure.[92] This structure is characteristic of 4-acetamido-, 4-methoxy-, 4-ethoxy-, 4-(*N*-methylacetamido)phenylnitrenium, 4-biphenylylnitrenium, and 2-fluorenylnitrenium ions, which is confirmed by the Raman spectra.[188, 189, 191, 196] The contribution of the iminohexadienyl structure depends on the nature of substituents in the benzene ring (increasing with their donating character), on the orientation of the phenyl rings relative to the nitrenium centre, and on the nature of the substituents directly bound to this centre.[196] Picosecond Raman spectroscopy was used to study the nitrenium cations generated by photolysis of 2-fluorenyl- and 4-methoxyphenyl azides in an MeCN–H_2O mixture.[262] In the first stage, azides are transformed into nitrenes, which react with water to give 2-fluorenyl- and 4-methoxyphenylnitrenium ions in the singlet state, respectively. The reaction of 4-methoxyphenylnitrene with H_2O is a considerably faster process than of 2-fluorenylnitrene, which follows from the appearance of bands at 1632 and 1630 cm^{-1} in the Raman spectrum of the 4-methoxyphenyl- and 2-fluorenylnitrenium ions.[262]

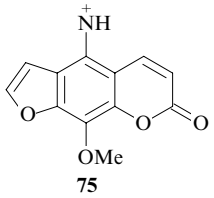
Laser flash photolysis of *N*-aminopyridinium tetrafluoroborates **74a–d** in MeCN afforded 4-R-phenylmethylnitrenium ions.[94] It appeared that the position of the longwave absorption band in the electronic spectrum depended on the nature of the substituent R (λ_{max} = 480, 450, and ~470 nm for R = Ph, MeO, and Me, respectively).



R = Ph (**a**), Me (**b**), MeO (**c**), Cl (**d**).

It was assumed that the phenylsulfopropylnitrenium ion with an absorption maximum at 453 nm, was an intermediate in electrochemical polymerisation of *N*-(3-sulfopropyl)aniline.[120] Irradiation of 4-EtO- and 4-$MeOC_6H_4N_3$ in water yielded the corresponding nitrenium ions, for which the EAS showed absorption at 300 nm. This was explained by a significant contribution of an iminium type limiting structure to the resonance hybrid.[136] For the 1,3,5-tribromophenylnitrenium ion generated by protonation of the corresponding nitrene in the MeCN–H_2O system, there is a considerable bathochromic shift of the absorption bands in the EAS (λ_{max} = 420 and 600 nm).[261]

In more extended aromatic systems, substituents also produce a substantial effect on the position of the longwave absorption band. Thus in the flash photolysis of 4-azidobiphenyl[264] and 2-azidofluorene[129] in MeCN–H_2O or of 4′-amino-4-biphenylyl azide[138] in H_2O, the EAS exhibited the bands at 460, ~450, and 470 nm, which were assigned to the 4-biphenylylnitrenium, 2-fluorenylnitrenium and 4-aminobiphenylylnitrenium cations, respectively. The situation is similar for the $(4\text{-}XC_6H_4)_2N^+$ cations (X = H: 420, 640 nm; X = Cl: 440, 680 nm; X = Br: 450, 690 nm).[95] The RB3LYP/6-31G calculations of the transitions corresponding to the longwave absorption band for these cations agree with the experiment (λ_{calc} = 645, 637, and 647 nm, respectively).[95] Likewise, good agreement between the calculated (CASPT2) and experimental EAS was obtained for biphenyl-4-yl-, biphenyl-2-yl-, and 1-naphthylnitrenium ions generated by irradiation of the corresponding azides in the presence of HCl using the matrix isolation method.[200] If the nitrenium centre (Ph_2N^+)[32, 90] or the extended π-system [4-(4-X-styryl)phenylnitrenium ions (X = H, 4-Br, 3-Me, 4-Me, 4-NAcMe, 4-MeO),[267] 1-naphthyl-*N*-methylnitrenium ion,[96] and cation **75** (Ref. 268)] has two phenyl substituents, the EAS shows a longwave absorption maximum (λ_{max} = 660, 500–600, 500, and 500–520 nm, respectively).



For polyfluorinated arylnitrenium ions $4\text{-}XC_6F_4HN^+$ generated by flash photolysis of the appropriate azides in MeCN or MeOH in the presence of H_2SO_4, the band position in the EAS is almost independent of the nature of the substituent (the highest value of λ was observed in MeCN, and the lowest, in MeOH):[260]

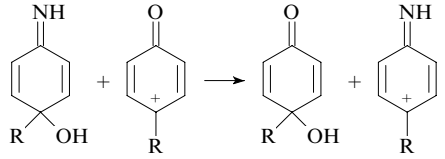
X	F	CO_2Me	CH_2Br	CN	CH_2OH	CH_2NMe_2
λ/nm	375	375	380	365	380	370
	365	370	365	365	375	370

The lifetimes of these cations are extraordinarily large ($> 10^{-3}$ s) as compared with the lifetimes of their nonfluorinated analogues, which was attributed to the stabilising interaction of the p-AOs of the F atoms with the vacant p-orbital of the nitrenium centre.[260] For the cations $4\text{-}XC_6F_4N^+H$ (X = C_6F_5, CONHPr) in MeCN–HCl, two absorption bands were observed, their positions being almost independent of the substituent X (330 and 530 nm).[192]

The iminohexadienyl character of the arylnitrenium ions leads to a considerable difference between their properties and the properties of the corresponding benzyl carbocations. Thus the lifetime of the 4-(*N*-methylacetamido)phenylnitrenium ion in water is 5000 times larger than of the 4-methoxy-substituted cation, although the MeO group is a stronger electron-donating substituent than the NAcMe group [σ^+(MeO) = −0.78, σ^+(AcMeN) = −0.60].[139] The difference between the properties of the nitrenium ions and carbocations also lies in the absence of linear correlation between the logarithms of the rate constants of the reactions of the cations $4\text{-}XC_6H_4N^+H$ (X = H, Me, Ph, MeO, PhO, NH_2, NAcMe, Cl) with water

and the σ^+-constants of the substituents X.[139] A similar pattern is observed for the reactions of the cations 4-$XC_6H_4N^+Ac$ (X = H, Me, Ph, EtO)[106] and X-biphenyl-4-ylnitrenium ions (X = 4′-MeO, 3′-MeO, 4′-Me, 3′-Me, H, 4′-F, 4′-Cl, 3′-Cl, 4′-CF_3) with water.[138,265] A satisfactory correlation was obtained[265] by processing the data in terms of the Yukawa–Tsuno equation; the high value of the parameter r^+ (2.8) reflects the increased effect of the π-donating substituents lying in the resonance position relative to the nitrenium centre on the reaction rate. A linear correlation is observed between the values of log *k* of the reaction of the 4-(4-X-styryl)phenylnitrenium cations (X = H, Br, Me, MeO) with water in $MeCN-H_2O$ and of the corresponding phenethyl cations in ROH-type media; this suggests a relationship between the strongly delocalised nitrenium ions and the carbocations.[267]

The pBP/DN*//HF/6-31G* calculations (including the zero-point vibration energy) of isodesmic reaction (1) showed that the cations 4-$RC_6H_4N^+H$ (R = H, Me, Ph) were 82.8, 80.3, and 51.5 kJ mol^{-1} more stable than the corresponding oxenium-type cations,[190,193] probably because of the higher electronegativity of the oxygen atom.



(1)

R = H, Me, Ph.

This agrees with the experimental data, according to which the lifetime of biphenyl-4-nitrenium ion in aqueous solutions at 30 °C is much larger than that of biphenyl-4-yloxenium ion (300 and 12 ns, respectively).[193] Note that the lifetimes of the carbocations formed from 4-ethyl- and 4-isopropylbiphenyl are still smaller (0.1 and 0.5 ns, respectively).[190] It is also interesting to note that the lifetimes of the biphenyl-4-ylnitrenium and 4-phenyl-1,1-dimethylbenzenium ions in aqueous solutions at 20–25 °C are comparable (300 and ~150 ns), which confirms the iminocyclohexadienyl character of arylnitrenium ions.[271] The introduction of the donating substituents X in the cations of the type 4-(4-XC_6H_4)$C_6H_4Y^+$ (X = MeO, Me; Y = NH, O) decreases the reaction rates with water of the nitrenium (X = MeO, Me; Y = NH) and, to an approximately equal extent, oxenium (X = MeO, Me; Y = O) cations relative to the reaction rates of the corresponding unsubstituted ions (X = H) (~1500-fold for X = MeO and ~10-fold for X = Me).[272] The lifetime (τ) of the cation 4-$XC_6H_4N^+H$ in aqueous solutions depends significantly on the substituent X,

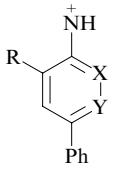
X	τ /ns	X	τ /μs
PhO	50	Pr^iO	1.25
4-$MeOC_6H_4O$	70	Bu^tO	1.56
MeO	370	4-MeO-1-Naph	1.35
EtO	550		

Note that for the cation 4-$MeOC_6H_4N^+H$, it is approximately the same as for the biphenyl-4-ylnitrenium ion, although it must be substantially larger based on the comparison of the σ^+-constants of MeO and Ph groups.[266] This is probably explained by localisation of the positive charge on the MeO oxygen atom adjacent to the reaction site at which the water molecule attacks.[266]

The nitrenium ions react at high rates even with very weak bases. Thus the cation Ph_2N^+, generated upon photolysis of 1-(*N*,*N*-diphenylamino)-2,4,6-trimethylpyridinium tetrafluoroborate in MeCN reacts with compounds RH [1-methylcyclohexa-1,4-diene, tri(n-butyl)stannane, cyclopenta-1,3-diene, cyclohexa-1,4-diene, cycloheptatriene, tris(trimethylsilyl)silane and toluene] with hydride transfer; the reaction rate depends significantly on the structure of the source of the hydride ion (rate constants are 10^8, 1.6×10^7, $<1.7\times10^6$, 6.5×10^6, 1.4×10^7, $<10^6$ and $<10^6$ litre mol^{-1} s^{-1}, respectively).[88]

Many reactions of arylnitrenium ions with N- and O-bases are known. The reactions of the biphenyl-4-yl- and fluoren-2-ylnitrenium ions with N_3^- in an $MeCN-H_2O$ mixture at 20 °C are similar to diffusion-controlled reactions ($k_{az} > 10^9$ litre mol^{-1} s^{-1}), while the rate constants for reactions with water are much lower (k_w is 1.8×10^6 and 3.4×10^4 s^{-1}, respectively).[264] This explains the decreased k_{az}/k_w ratio on passing from cation **76a** to more reactive nitrenium ions **76b–d**,[112]

Ion	**76a**	**76b**	**76c**	**76d**
k_{az}/k_w	2900	10	300	79



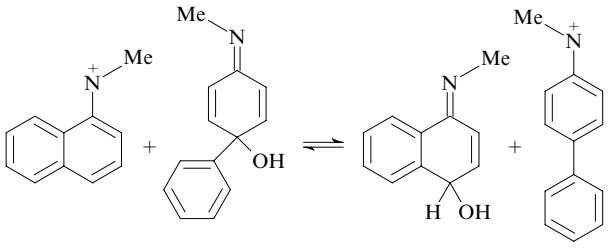
76a–d

X = Y = CH, R = H (**a**);
X = N, Y = CH: R = H (**b**), Me (**c**);
X = CH, Y = N, R = H (**d**).

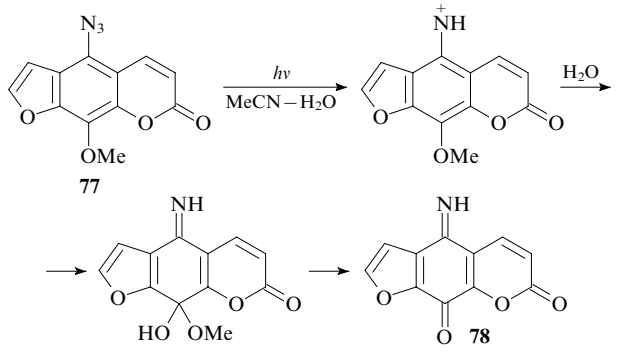
The reactions of the ions 4-$XC_6H_4(Me)N^+$ (X = Me, Ph, Cl) with amines (Bu^nNH_2, Bu^tNH_2, Pr^i_2NH, Et_3N, $PhNH_2$) and pyridine are similar to diffusion-controlled reactions ($k > 10^9$ litre mol^{-1} s^{-1}).[94] In the case of the less reactive ion with X = MeO, the rate of the reactions with sterically hindered amines slightly decreases,[94]

Amine	Bu^tNH_2	Pr^i_2NH	Et_3N
$k\times10^{-8}$ /litre mol^{-1} s^{-1}	6.3	0.47	3.8

The reaction rate constants for the *N*-methyl-*N*-(1-naphthyl)nitrenium ion in MeCN with such nucleophiles as Cl^-, Et_3N, Bu^nNH_2, Bu^tNH_2, MeOH, EtOH, and H_2O, are higher than for the *N*-(biphenyl-4-yl)-*N*-methylnitrenium cation; for O-bases, the difference in the rate constants is over three orders of magnitude.[96] These data qualitatively agree with the results of B3LYP/6-31G(d,p) quantum chemical calculations for the isodesmic transfer of the OH group ($\Delta E = -43.1$ kJ mol^{-1}).[96]

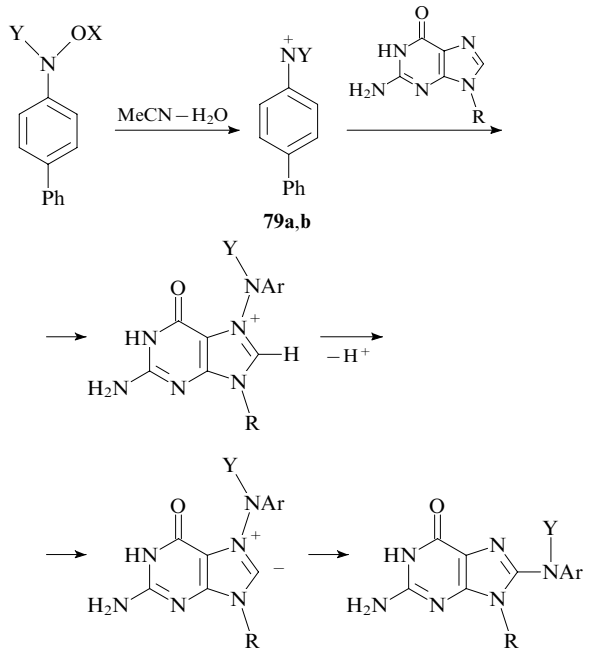


Flash photolysis of 5-azido-8-methoxypsoralene (**77**) in an $MeCN-H_2O$ mixture leads to the formation of 5-imino-5,8-dihydropsoralen-8-one (**78**) in a nearly quantitative yield.[268]



77 **78**

It was assumed that the reactions of arylnitrenium cations **79a**,**b** with purine nucleosides occurred with an initial attack at the N(7) nitrogen atom and further proton elimination and 1,2-migration of the NYAr group; the reaction rate constant of the nitrenium ion with the nucleoside was close to the diffusion limit ($\sim 2 \times 10^9$ litre mol^{-1} s^{-1}).[111]

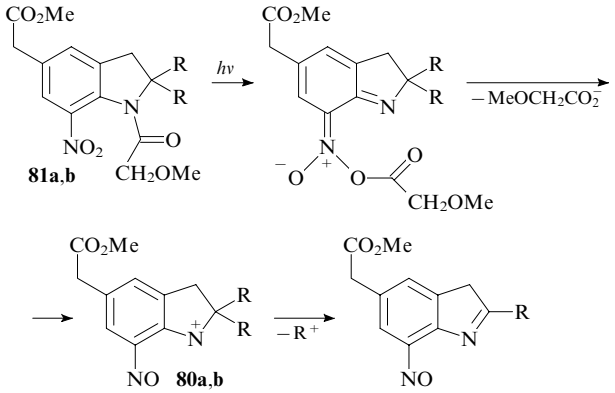


79a,**b**

X = SO_3^-, C(O)Bu^t; Y = H (**a**), Ac (**b**); R is 2-deoxy-β-D-ribofuranosyl; Ar = 4-Biph.

A similar viewpoint concerning the mechanism of reactions of arylnitrenium ions with guanine derivatives was reported.[102, 123] Later, for the reaction of the fluoren-2-ylnitrenium ion generated upon photolysis of 2-azidofluorene with *N*-methyl- and *N*,*N*-dimethylguanosine it was found that the most probable mechanism was the direct attack of the nitrenium ion at the C(8) atom of the base.[125] A similar mechanism was also suggested for the reaction of this cation with 2-deoxyguanosine.[129] Time-resolved Raman spectroscopic studies provided data about the formation of an adduct at the C(8) atom in the reaction of the fluoren-2-ylnitrenium ion with guanosine.[263] However, the mechanism with an initial attack of the nitrenium ion on the N(7) atom of deoxyguanine and further quick transformation of the resulting intermediate into the C(8)-adduct is not ruled out.

Presumably, arylnitrenium cations **80a**,**b** are formed upon photolysis of 1-acyl-7-nitroindolines **81a**,**b** in an $H_2O-MeCN$ mixture as a result of the migration of the $MeOCH_2CO$ group with further elimination of the $MeOCH_2CO_2^-$ anion.[270]



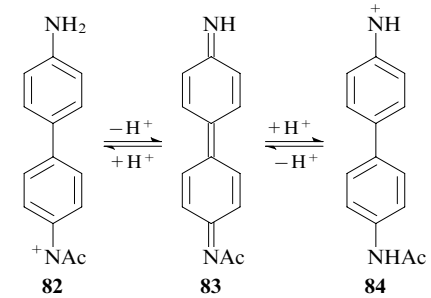
81a,**b** **80a**,**b**

R = H (**a**), D (**b**).

Arylnitrenium ions are regarded as intermediates in electrophilic amination of arenes and intramolecular cyclisation. These reactions are discussed in detail in a recent review.[1]

VII. Formyl- and acetyl-substituted nitrenium ions

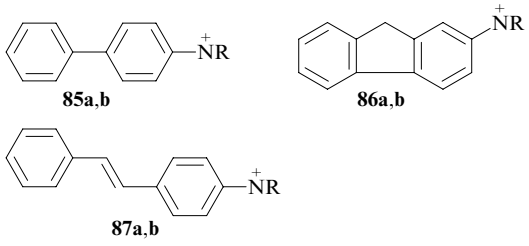
According to the MNDO data, the singlet state is preferable for formyl-substituted nitrenium ions R(HCO)N$^+$ with substituents exhibiting the positive mesomeric effect (+*M*) (R = Ph, OH, SH, NH_2, PH_2), and the triplet state, for R = H, Me (see Appendix, Table 1). This is the case for acetyl-substituted nitrenium ions (see Appendix, Tables 1 and 2). The singlet state is destabilised relative to the triplet state where the withdrawing character of the aryl group in the ions ArAcN$^+$ increases (Ar is biphenyl-4-yl-, 3-pyridyl, and pyrimidin-4-yl) (see Appendix, Table 2).



82 **83** **84**

Flash photolysis has shown that the acetylnitrenium ion **82**, which is believed to be generated during the carcinogenic action of benzidine, is quite stable; at pH ~ 7 it is in equilibrium with the neutral conjugated base **83** and with 4′-(acetylamino)biphenyl-4-ylnitrenium ion **84**, the relative fraction of the latter being small.[137]

Replacement of the acetyl group for the hydrogen atom in the NH fragment of arylnitrenium ions **85a** and **86a** increases the rate of their reactions with water and the azide ion,[264] which is probably determined by the destabilising effect of this group. Similarly, replacement of the hydrogen atom by the



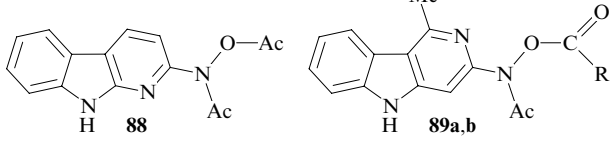
85a,**b** **86a**,**b** **87a**,**b**

R = H (**a**), Ac (**b**).

acetyl group in **87a** decreases the lifetime of the nitrenium ion in $MeCN-H_2O$ (160 and 40 ns, respectively);[267] the water molecule and the azide ion attack predominantly the β-position of the vinyl group.[113] The *N*-acetyl-*N*-(1-naphthyl-) and *N*-acetyl-*N*-(2-naphthyl) nitrenium ions have considerably smaller lifetimes in aqueous solutions ($\sim 10^{-10}$ s).[114]

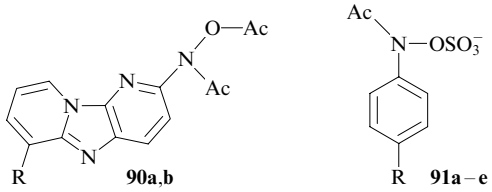
The absence of correlation between $\log(k_{az}/k_w)$ in the competitive reaction of the ions $4\text{-}XC_6H_4(Ac)N^+$ with the azide anion and water and the σ^+ constants of substituents confirms the iminocyclohexadienyl character of these nitrenium ions.[106]

The replacement of the NH fragment by NAc generally results in a decrease in the rate constant for the N–O bond heterolysis by approximately five orders of magnitude.[107] Similar retardation is also observed for hydrolysis of the heteroaromatic compound **88** in an $MeCN-H_2O$ mixture.[107]



88 **89a**,**b**

R = Me (**a**), Bu^t (**b**).



90a,**b**

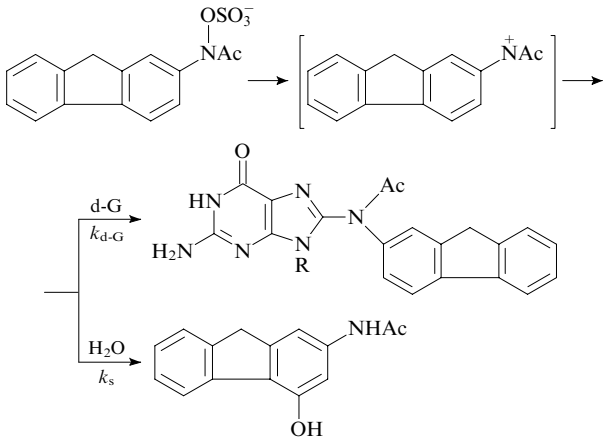
R = H (**a**), Me (**b**).

91a–**e**

R = H (**a**), Me (**b**), OEt (**c**), Ph (**d**), fluoren-2-yl (**e**).

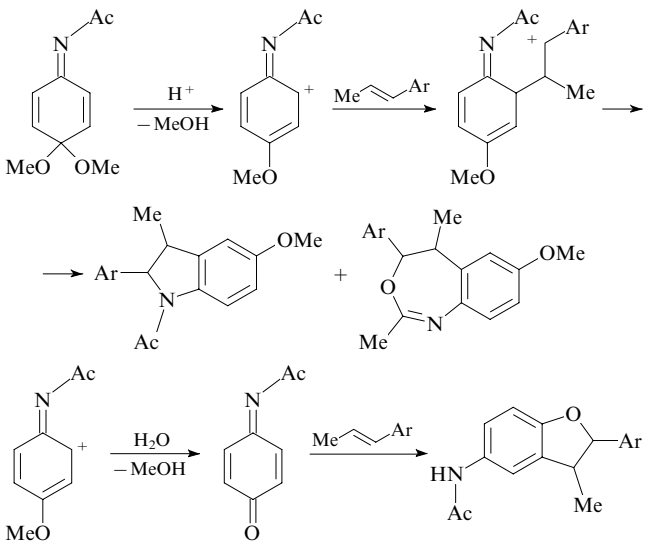
In the $MeCN-H_2O$ system at neutral pH, **89a** undergoes heterolysis at the C–O bond, while **89b** and **90a**,**b** experience heterolysis at the N–O bond.[115, 133] Solvolysis of *N*-acetyl-*N*-sulfonatooxyaminoarenes **91a**–**e** also occurs with the N–O bond cleavage and formation of the corresponding *N*-acetylnitrenium ions.[105, 106, 109, 110, 132]

The *N*-acetyl-*N*-(fluoren-2-yl)nitrenium ion reacts with 2′-deoxyguanosine (dG) in aqueous media predominantly at the N atom, while the reaction with water occurs at the C atom and at a considerably lower rate ($k_{dG}/k_s \approx 10^3$ litre mol^{-1}).[132]



R is 2-deoxy-β-D-ribofuranosyl.

It is believed that the acetylnitrenium ions are intermediates in electrophilic amination of arenes and intramolecular cyclisation [1] and can also be involved in addition reactions to alkenes.[273]



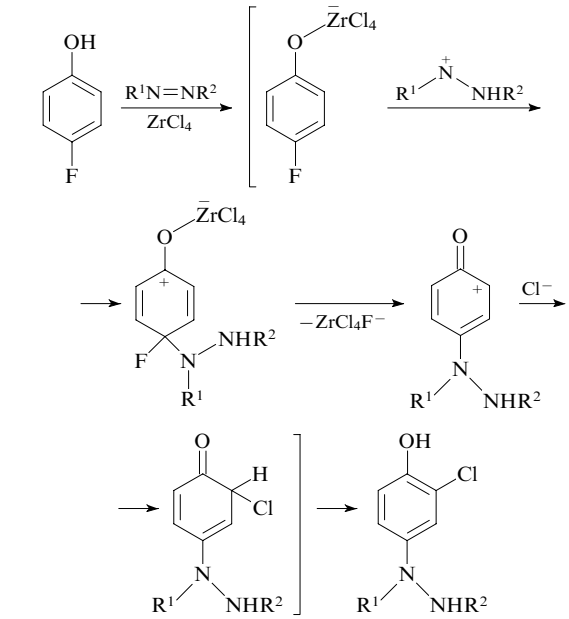
Ar = 3,4-$(MeO)_2C_6H_3$.

VIII. Nitrenium ions with NR^1R^2 and PR^1R^2 substituents

According to the MNDO and *ab initio* data, the singlet state is preferable for the nitrenium ions of the type RN^+NH_2 and RN^+PH_2 (R = H, CHO, NH_2) because of the strong electron-donating effect of the NH_2 and PH_2 groups (see Appendix, Tables 1 and 2). The nitrenium ion $(NH_2)_2N^+$ has an angular configuration with an angle N–N–N of 120°, while $(PH_2)_2N^+$ is linear; distortion of the latter to the angle P–N–P of 150° leads to a very minor change in the energy (3.1 kJ mol^{-1}).[216]

Azaallyl cations of the type $R^1R^2N^+{=}N{-}NR^3R^4$ were isolated as stable salts (tetrafluoroborates, perchlorates or iodides).[274]

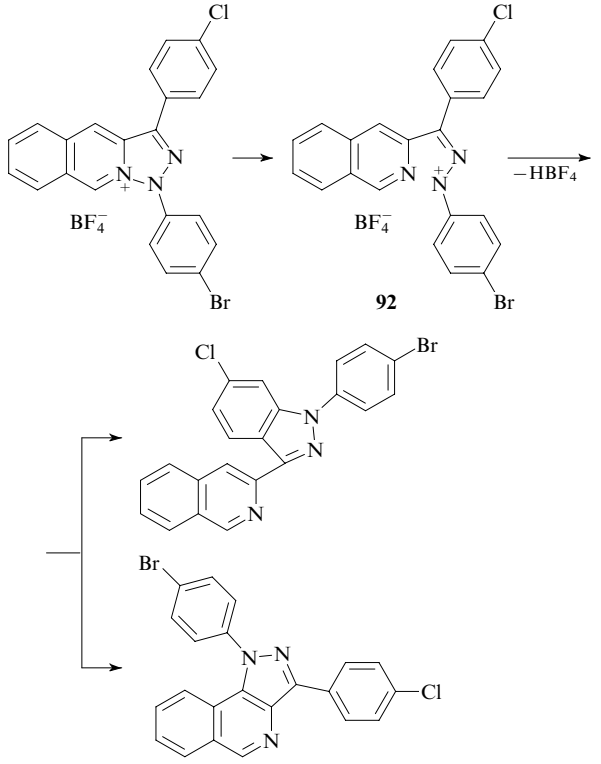
Amine-substituted nitrenium ions are postulated as intermediates of the amination of aromatic compounds with diazenes.[1] Recently, it has been found [275] that in the electrophilic amination of 4-fluorophenol with diazenes in the pres-



$R^1 = R^2 = CO_2Pr^i$, CO_2Et, $CO_2(CH_2CH{=}CH_2)$;
$R^1 = C(O)NH(CH_2)_2Cl$, $R^2 = CO_2Me$.

ence of $ZrCl_4$ the fluorine atom is replaced by the $NR^1(NHR^2)$ groups.

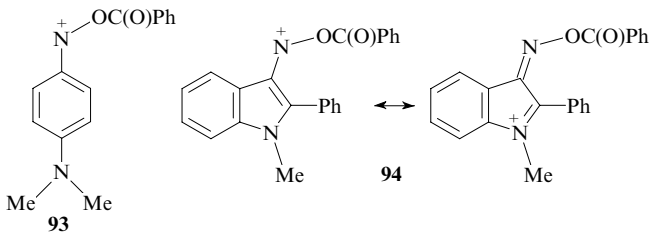
Heating of 1-(4-bromophenyl)-3-(4-chlorophenyl)[1,2,3]-triazolo[1,5-*b*]isoquinolinium tetrafluoroborate results in the cation valence isomerisation into an open nitrenium ion **92**, which subsequently forms new heterocyclic compounds.[86]



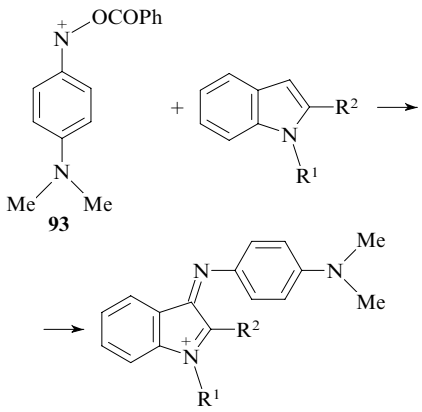
IX. Nitrenium ions with OR and SR substituents

According to MNDO and *ab initio*/6-31G** calculations, the singlet state is more favourable for the nitrenium ions $R(OH)N^+$ and $R(SH)N^+$ (R = H, CHO) because of the strong electron-donating effect of the OH and SH groups (see Appendix, Tables 1 and 2).

N,*N*-Dimethyl-*p*-nitrosoaniline and 1-methyl-3-nitroso-2-phenylindole react with benzoyl chloride to give nitrenium ions **93** and **94**.[276] In contrast to **93**, cation **94** is iminium in character; in particular, according to X-ray diffraction data, it has an N=C double bond (1.298 Å).

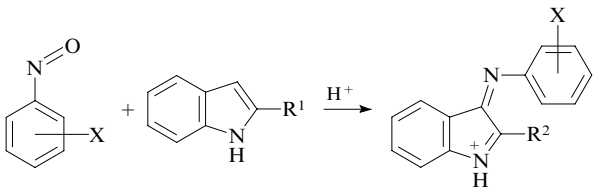


Cation **93** reacts with indoles and indolizines to yield new heterocyclic compounds, in which the C=N bond is formed due to the nitrenium form of the ion.[277]



R^1 = H: R^2 = Ph, Bu^t; R^1 = Me, R^2 = Ph.

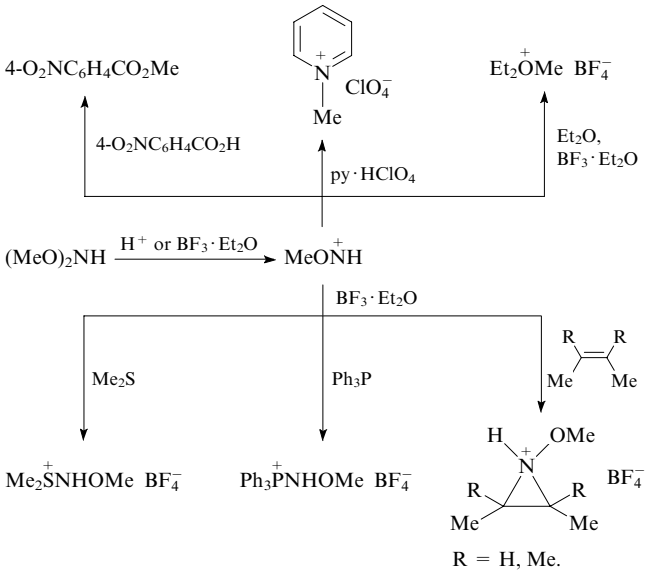
The reactions of substituted nitrosobenzenes with indoles in the presence of $ClCH_2CO_2H$ occur in a similar way.[28, 278, 279]



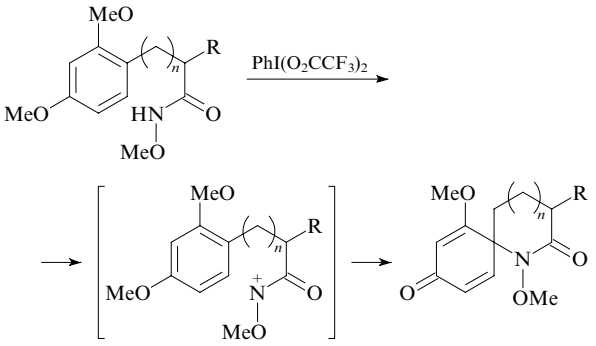
X = H, 2-Me, 4-Me, 4-Cl, 4-Br; R^1 = H, Me, Bu^t, Ph;
R^2 = Me, Bu^t, Ph, NHC_6H_4X, indol-3-yl.

Presumably, the electrophile-catalysed N–O bond cleavage in dimethoxyamine results in the methoxynitrenium ion; the latter is ambident in reactions with nucleophiles; namely, it methylates hard nucleophiles and is involved in the addition reactions with soft bases (Scheme 5).[101, 280]

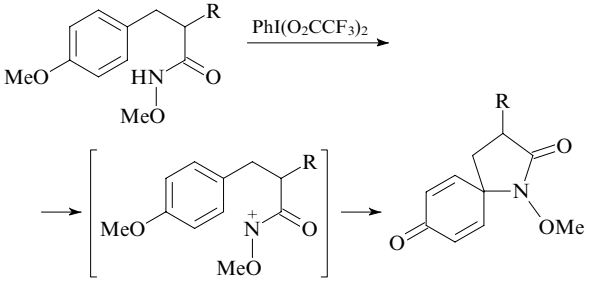
Scheme 5



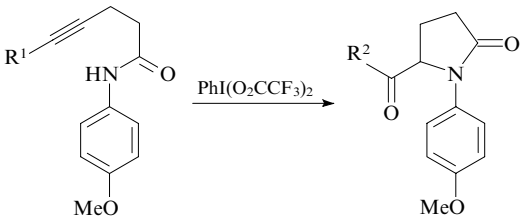
N-Methoxy-substituted nitrenium ions are involved in oxidative cyclisation reactions.[1] The reactions of hypervalent iodine compounds with amides lead to the formation of N-heterocyclic compounds.[1, 70, 71, 75, 77, 78, 281–283]



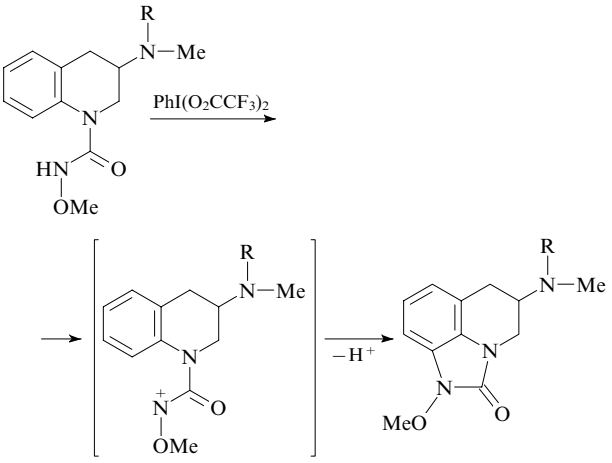
R = H, Alk, Ar, OR, NHR; $n = 0-2$.



R = H, $NHCO_2Me$.



R^1 = Ph, 4-MeC_6H_4, 3-MeC_6H_4, 2-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-$NO_2C_6H_4$, 4-$(NHCO_2Et)C_6H_4$, 1-Naph, $CH_2{=}CH$, PhCH=CH, MeCH=CMe; for R^1 = 4-MeC_6H_4 R^2 = 3-MeC_6H_4, for R^1 = 4-$MeOC_6H_4$ R^2 = 3-$MeOC_6H_4$; $R^1 = R^2$ in all other cases.

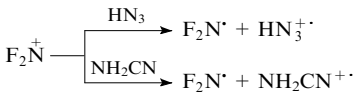


R = $PhCH_2C(O)$.

X. Halogen-substituted nitrenium ions

According to *ab initio* calculations, the singlet state is preferable for nitrenium ions of the type RHN^+ and R_2N^+ with R = F, Cl, Br, and I; the stabilising effect of the replacement of two hydrogen atoms by halogen atoms is much higher than for the replacement of one atom (see Appendix, Table 2). Calculations at a high level of theory showed that the nitrenium ions RHN^+ (R = H, Me, Cl, F, CN) reacted with water almost without the activation energy and formed the complexes $(HNROH_2)^+$ the relative stabilisation energy of which increased in the series Me < Cl < CN < F < H.[169]

The interaction of the cation F_2N^+ with HN_3 and NH_2CN was investigated by mass spectrometry and ion cyclotron resonance.[212, 284]



Thermochemical calculations ($\Delta H^\circ = -82.8$ and -117 kJ mol^{-1}, respectively) indicate that the reactions are highly exothermic probably due to the high oxidative ability of F_2N^+. The reactions of this cation with H_2O, HF and N_2O in the gas phase are also exothermic.[207, 213, 214] The G2MS calculated affinity (A) of F_2N^+ to various ligands correlates with the proton affinity.[207]

Ligand	A /kJ mol^{-1}	Ligand	A /kJ mol^{-1}
HF	42.3	CO	104.6
CO_2	44.8	H_2O	138.5
NF_3	71.1	H_2S	241.0
N_2O	73.2	NH_3	326.4
HCl	86.6	PH_3	354.4

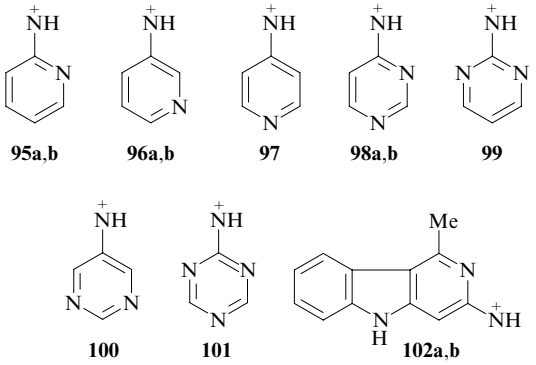
The cation F_2N^+ forms two types of complexes with the NF_3 molecule, $F_2N^+-FNF_2$ and $F_2N^+-NF_3$, the dissociation energies of which are rather small (-35.6 and -74.1 kJ mol^{-1}, respectively). At high temperatures, the complex $F_2N^+-FNF_2$ is readily transformed into $F_2N^+-NF_3$.[211] The mechanism of the spin-forbidden transfer of F^+ from the cation $^1(F_2N^+)$ to the CO molecule was studied by mass spectrometry, and an intermediate complex $NF_2^+\cdots CO$ was obtained.[215] Calculations at the G3 level give good agreement of the enthalpy of formation of F_2N^+ with the experimental value (ΔH_f° = 1160.2 and 1156.9 kJ mol^{-1}, respectively).[209]

Isomerisation of the cation $HONF^+$ was studied by the MP2(FULL)/6-31G* method.[208] Calculations at the G2MS level showed that the chlorine atom decreased the Lewis acidity of nitrenium ions of the type XHN^+ and X_2N^+ more significantly than the fluorine atom; it was found that the acidity decreased in the series $H_2N^+ > FHN^+ > F_2N^+ \approx ClHN^+ > FClN^+ > Cl_2N^+$ (Ref. 171).

Data about halogen-substituted nitrenium ions in the condensed phase are limited to one example. The ion F_2N^+ was generated by the matrix isolation method, which was confirmed by the similarity between the calculated (CASSCF) and the experimental IR spectra.[285]

XI. Heterocyclic nitrenium ions

Replacement of the CH fragment in the aromatic ring of the arylnitrenium ion by the nitrogen atom destabilises the singlet state relative to the triplet one; this effect increases from *ortho*- to *meta*- and *para*-substituted derivatives and with the number of nitrogen atoms introduced in the ring (ions **95**–**101**) (see Appendix, Table 2).[187]



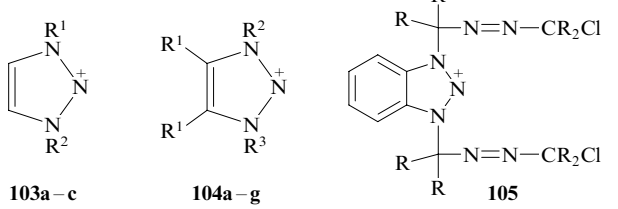
95a,b **96a,b** **97** **98a,b** **99**

100 **101** **102a,b**

Isomers: *syn* (**a**), *anti* (**b**).

The large differences in the relative free energies of the *syn*- and *anti*-isomers of **95a**,**b** and **98a**,**b** (Table 2) in the singlet state are obviously due to the anomeric effect and the favourable electrostatic interaction between the hydrogen atoms of the NH groups and the nitrogen atom in the 2 position of the heterocycle.[187] The same explains the higher stability of *syn*-isomer **102a** relative to *anti*-isomer **102b** ($\Delta\Delta H_f$ = 31.8 kJ mol^{-1}).[186]

For the cyclic nitrenium ions of triazolium (**103**–**106**) and triazolinium (**107**–**109**) types, the ground states are singlets.[259, 286–301] According to (BPW91/cc-pVDZ) *ab initio* calculations for 1,3-dimethylbenzotriazolium ion **106c**, ΔE_{ST} is −270.7 kJ mol^{-1}, which agrees well with the experimental value obtained by laser flash photolysis (−276 ± 13 kJ mol^{-1}).[259]

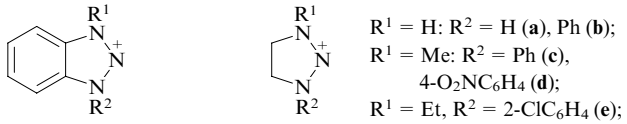


103a–c **104a–g** **105**

$R^1 = R^2$ = H (**a**);
R^1 = Me, R^2 = Bn (**b**);
$R^1 = R^2$ = Bn (**c**).

R = Me (**a**), 2 R = $(CH_2)_5$ (**b**).

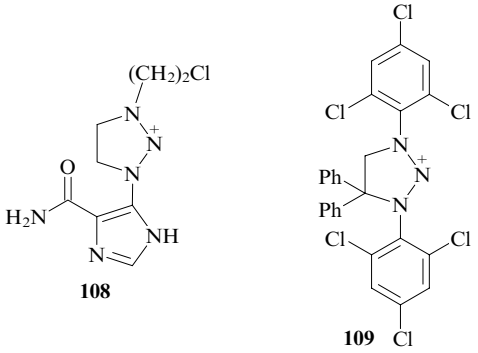
Cation **104**	R^1	R^2	R^3
a	Et	2,4,6-$Cl_3C_6H_2$	2,4,6-$Cl_3C_6H_2$
b	Et	4-ClC_6H_4	4-ClC_6H_4
c	Et	Me	4-MeC_6H_4
d	Ph	Me	4-MeC_6H_4
e	Ph	2,4,6-$Cl_3C_6H_2$	2,4,6-$Cl_3C_6H_2$
f	CH_2Cl	2,4,6-$Cl_3C_6H_2$	2,4,6-$Cl_3C_6H_2$
g	CO_2Me	2,4,6-$Cl_3C_6H_2$	2,4,6-$Cl_3C_6H_2$



106a–c **107a–f**

R^1 = H: R^2 = H (**a**), OH (**b**);
$R^1 = R^2$ = Me (**c**).

R^1 = H: R^2 = H (**a**), Ph (**b**);
R^1 = Me: R^2 = Ph (**c**), 4-$O_2NC_6H_4$ (**d**);
R^1 = Et, R^2 = 2-ClC_6H_4 (**e**);
$R^1 = R^2$ = Bn (**f**).

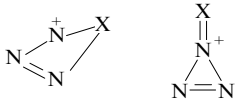


108 **109**

The high absolute value of ΔE_{ST} for **106c** can be explained by the presence of two nitrogen atoms adjacent to the nitrenium centre with the lone electron pairs involved in conjugation, and also by the aromatic character of the triazolium type system. The presence of conjugation is proved by X-ray diffraction data for **103b**, **104a**,**f**, **106b**,**c**, **107c**–**f**, and **109**.[286, 289–293, 295, 297–301] The corresponding bond lengths between the nitrogen atoms in these cations (1.26–1.37 Å) are intermediate between the lengths of the N−N single bond (1.425 Å) and N=N double bond (1.240 Å).[302]

Ab initio calculations showed that the ground state of the 4-(1,2,4-triazolium) cation was the $^1(A_1)$ singlet state, but the $^3B_1$ triplet state was only 4.2 kJ mol^{-1} higher in energy.[303]

According to B3LYP/6-311+G* calculations, the local minima on the potential energy surface correspond only to structures with X = S, Te among quasiplanar rhombic structures **110** (X = O, S, Se, Te); the global minima correspond to structures **111** (X = O, S, Se, Te). However, the latter species are kinetically unstable and readily undergo elimination of the nitrogen molecule [at the CCSD(T)/6-311+G* level of theory, the activation barriers are 55.6, 34.3, 33.1, and 33.5 kJ mol^{-1}, respectively].[228]



110 **111**

An electron absorption spectroscopic study showed that the basicity of X-substituted 1,2,3-triazoles in aqueous H_2SO_4 was substantially affected by the structural factors, pK^+_{BH} = −0.16 (X = H), −6.80 (X = 4-NO_2), −0.11 (X = 1-Ph), −5.21 (X = 2-Ph), −5.36 (X = 4-Ph).[304]

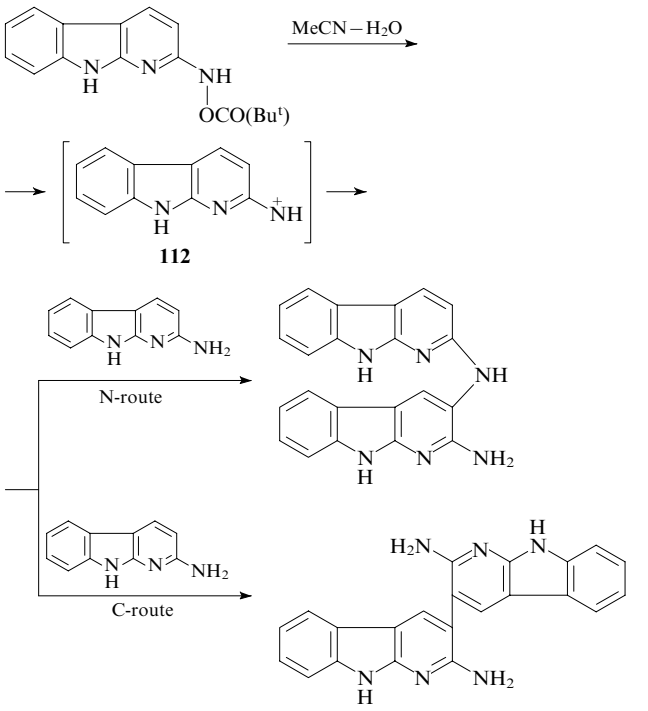
Irradiation of 2-azido-1-methylimidazole in aqueous solutions generated the 2-imidazolyl-1-methylnitrenium ion with the lifetime in water of 100 ms.[305]

Like aryl-substituted nitrenium ions, heteroaromatic nitrenium cations react with nucleophiles to form C−N (N-route) and C−C (C-route) bonds. Thus solvolysis of 2-amino-2-*N*-(pivaloyloxy)-α-carboline in aqueous MeCN forms nitrenium ion **112**, which reacts with the amine produced in the reaction by N- and C-routes (Scheme 6).[35]

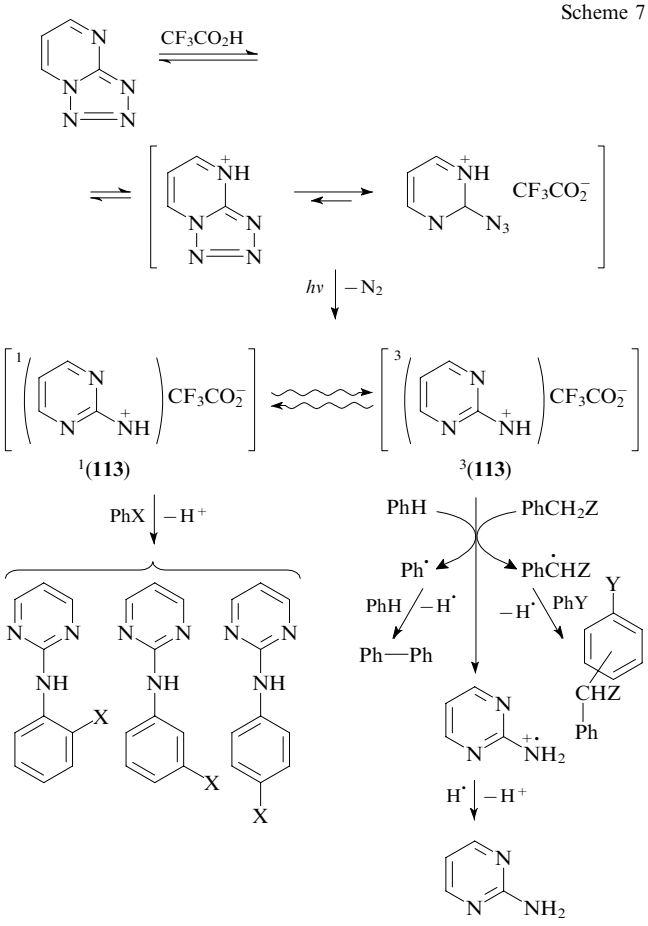
Photochemical amination of benzene and its derivatives with tetrazolo[1,5-*a*]pyrimidine in the presence of CF_3CO_2H affords substituted anilinopyrimidines and 2-aminopyrimidine, biphenyl, and diarylmethanes (Scheme 7).[46]

When analysing the effect of the heavy atom of the solvent, the authors assumed that substituted anilinopyrimidines were formed with participation of nitrenium ion **113** in the singlet

Scheme 6



Scheme 7



X = H, Me, Et, OMe, Cl; Y = Me: PhCHZ = 2-PhCH$_2$, 4-PhCH$_2$; Y = Et, PhCHZ = 4-PhCHMe.

state, while aminopyrimidine and diarylmethanes were formed with participation of this ion in the triplet state. Note that according to quantum chemical calculations for the gas phase, the ground state of this ion is the triplet state, although the energy difference between the triplet and singlet states is small.[187] The formation of nitrenium ion **113** is suggested by the linear correlation between the values of $\log k$ of the formation of substituted anilinopyrimidines and the σ^+-constants of the substituents X; the relatively low absolute value of the reaction sensitivity constant [$\rho^+(25\ ^\circ C) = -2.9$] points to the higher electrophilicity of the singlet pyrimidinylnitrenium ion compared with the phenylnitrenium cation.[46]

XII. Conclusion

An analysis of the publications reviewed in the present paper allows us to draw the following conclusions. The diversity of the reaction routes of nitrenium ions with nucleophilic reagents is primarily determined by the properties of the ions themselves, but not by the reaction conditions or the nature of the nucleophile; the ions can be involved in reactions in the singlet or triplet states and exhibit an electrophilic or radical character, respectively. The $+M$ type substituents in the cations HRN^+ and R_2N^+ (R = Ar, NR_2, OR, SR, Hal) stabilise the singlet state of the nitrenium ions due to the $\pi-p$ and $n-p$ resonance interactions that dominate their electron acceptor inductive effect. The increased acceptor character of the substituent generally stabilises the triplet state, initiating the radical route of transformations. According to the data from quantum chemical calculations, the singlet state of the ions $PhRN^+$ and Ar_2N^+ is destabilised relative to the triplet state when the steric effect of the substituents R and Ar increases. The barriers to the interconversion of the *syn*- and *anti*-isomers of the ions $ArHN^+$ are rather high and almost independent of the nature of the aryl group. The relative stability of arylnitrenium ions is parallel to that of the isoconjugated arylmethyl cations. To control the singlet – triplet conversion of nitrenium ions in electrophilic aminations of arenes, one can effectively use the heavy atom effect of the solvent and complexation with crown ethers.

In discussing prospects for theoretical studies, it is important to note that data on the properties of nitrenium ions were largely obtained from quantum chemical calculations, but the calculated parameters of these species often cannot be compared with experimental data because of the limited number of 'direct' experimental observations. The data on the properties of nitrenium ions were mostly obtained by mass spectrometry and ion cyclotron resonance. However, the possibilities of these methods are restricted by the observation of charged species in a rarefied gas atmosphere. In recent years, flash photolysis has become a popular technique for investigating the properties of nitrenium ions in the condensed phase. Recently, a new method for generating nitrenium ions was suggested; it is based on fragmentation of *N*-nitrosoamines by exposure to X-ray radiation in an argon matrix.[306] These methods, however, use detection of nitrenium ions from the electronic absorption, IR or Raman spectra, often providing limited information about the structure and properties of these species, which often cannot be reliably interpreted. For example, ultrafast photolysis of phenyl azide in HCO_2H forms phenylnitrene, which is probably protonated into the phenylnitrenium cation with a broad absorption band (in the range 400 – 600 nm).[307] However, other species generated in the reaction mixture might also absorb in this range. Therefore, challenges for the nearest future are the development of methods for generating various long-lived nitrenium ions in

the condensed phase and their investigation using more informative physical methods such as multinuclear magnetic resonance.

The high chemical and biochemical activity of the nitrenium ions also stimulates further systematic studies of the kinetics and mechanisms of reactions involving these species, including *in vivo* studies of reactions with biomolecules and model compounds.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 06-03-32 406) and the Division of Chemistry and Materials Science of the Russian Academy of Sciences (Programme No. 5.1.9).

XIII. Appendix

Table 1. Stabilisation energies (ΔE) relative to the ion H_2N^+ and the differences between the heats of formation ($\Delta\Delta H_f$) of the singlet and triplet states of the nitrenium ions obtained by semiempirical methods (in kJ mol^{-1}).

Ion	MNDO			Ref.	AM1	Ref.
	ΔE(S) [a]	ΔE(T) [a]	$\Delta\Delta H_f$(S–T) [b]		$\Delta\Delta H_f$(S–T) [b]	
H_2N^+ (**1**)	0	0	88.7	150	104.2	154
	–	–	69.9	154	–	–
$MeHN^+$ (**15**)	−154.8	−92.0	25.9	150	7.9	154
	–	–	6.7	154	–	–
Me_2N^+ (**17**)	−238.5	−184.1	33.5	150	−19.7	154
	–	–	5.0	154	–	–
cyclo-$(CH_2)_4N^+$ (**20**)	−292.9	−159.0	−43.9	150	−91.2	154
	–	–	−44.4	154	–	–
cyclo-$(CH_2)_5N^+$ (**21**)	−301.2	−192.5	−18.8	150	–	–
	–	–	−19.2	154	−59.4	154
22	–	–	−60.7	153	–	–
$(CH_2{=}CH)MeN^+$ (**30a**)	–	–	−6.7	154	−31.0	154
$(CH_2{=}CCl)MeN^+$ (**30b**)	–	–	−22.2	154	−29.3	154
$PhHN^+$	−443.5	−246.9	−109.2	150	−117.2	154
	–	–	−105.9	152	–	–
	–	–	−140.2	154	−84.9	183
(1-Naph)HN^+ (**39a**)	−502.1	−292.9	−120.9	150	–	–
(1-Naph)AcN^+ (**39b**)	∼−602	∼−393	−121.3	150	–	–
(2-Naph)HN^+ (**40a**)	−493.7	−309.6	−94.6	150	–	–
(2-Naph)AcN^+ (**40b**)	−589.9	∼−410	−91.6	150	–	–
(2-Flu)HN^+ (**41a**)	−510.4	−284.5	−139.3	150	–	–
(2-Flu)AcN^+ (**41b**)	∼−611	∼−343	−178.7	150	–	–
(2-Phen)HN^+ (**42a**)	−502.1	−334.7	−79.1	150	–	–
(2-Phen)AcN^+ (**42b**)	∼−602	∼−439	−75.7	150	–	–
4-$(PhCH{=}CH)C_6H_4HN^+$ (**43a**)	−510.4	−313.8	−109.6	150	–	–
4-$(PhCH{=}CH)C_6H_4AcN^+$ (**43b**)	∼−594	∼−414	−108.8	150	–	–
$(CHO)HN^+$	–	–	82.6	152	–	–
$(CHO)NH_2N^+$	–	–	−162.4	152	–	–
$(CHO)PH_2N^+$	–	–	−118.7	152	–	–
$(CHO)OHN^+$	–	–	−50.3	152	–	–
$(CHO)SHN^+$	–	–	−63.0	152	–	–
$(CHO)PhN^+$	–	–	−93.3	152	–	–
$MeAcN^+$	∼−268	∼−209	29.3	150	–	–
$PhAcN^+$	∼−544	∼−351	−105.9	150	–	–
HNH_2N^+	–	–	−135.4	152	–	–
HPH_2N^+	–	–	−56.9	152	–	–
$HOHN^+$	–	–	−91.2	152	–	–
$HSHN^+$	–	–	−77.7	152	–	–
$Ph(Bu^t)N^+$	–	–	−120.1	154	−86.6	154
$(4\text{-}BrC_6H_4)Bu^tN^+$	–	–	−82.0	154	−91.2	154
$(2\text{-}AcC_6H_4)Bu^tN^+$	–	–	−60.7	154	−64.0	154
$(2\text{-Ac-}4\text{-}BrC_6H_3)Bu^tN^+$	–	–	−57.3	154	−61.5	154
Ph_2N^+ (**56**)	–	–	–	–	−46.9	183
Mes_2N^+ (**57**)	–	–	–	–	−24.3	183
$(2,6\text{-}Bu^t_2C_6H_3)_2N^+$ (**58**)	–	–	–	–	30.5	183

[a] The relative stabilisation energies were calculated using isodesmic reactions. [b] The negative value points to the higher stability of the singlet state as compared with the triplet state.

Table 2. Energy difference (ΔE_{ST}) between the singlet and triplet states of the nitrenium ions as calculated by the *ab initio* and DFT (in kJ mol^{-1}) methods.

Ion	ΔE_{ST} (see [a])	Calculation procedure, basis set	Ref.
H_2N^+ (**1**)	133.1	MP4/6-311G + G(3d,2f,2p)//MP2(full)/6-311 + G(3d,2p)	153
	151.9	UCISD/6-311G*//UHF/6-31G*	154
	140.2	MP4/6-311G(2df) + ZPVE	156, 157
	127.6	MRCISD(Q)	158
	125.9	MRCISD(Q)/TZP	158
	126.4	MP4SDTQ(fc)/6-311 + + G(2df,p)//MP2(full)/6-311 + + G(d,p)	159
	125.6	TZ2P(f,d)CASSCF-SOCI + ZPE	161
	125.8	CASSCF-MRCI + ZPE	161
	140.5	B3LYP/6-311 + + G**	163
	141.6	QCISD/6-311 + + G**	163
	123.0	TZ3P(2f,2d) + 2diffCASSCF-SOCI	164
$MeHN^+$ (**15**)	59.0	MP4/6-311G(d,p)//HF/6-31G(d)	153
	87.0	UCISD/6-311G*//UHF/6-31G*	154
$H(CN)N^+$	92.0	QCISD(T)	163
Me_2N^+ (**17**)	92.9	UCISD/6-311G*//UHF/6-31G*	154
	26.4	MP4/6-31G(d,p)//HF/6-31G(d)	153
cyclo-$(CH_2)_2N^+$	45.2	CCSD(T)/B1//MP2/B1	175
	46.4	BVWN5/B3//MCSCF/B1	175
	45.2	BLYP/B3//MCSCF/B1	175
cyclo-$(CH_2)_4N^+$ (**20**)	−23.8	MP2/6-31G(d)//HF/6-31G(d)	153
	18.0	UCISD/6-31G*//UHF/6-31G*	154
cyclo-$(CH_2)_5N^+$ (**21**)	21.8	MP2/6-31G(d)//HF/6-31G(d)	153
	40.2	UCISD/6-31G*//UHF/6-31G*	154
$(CH_2{=}CH)MeN^+$ (**30a**)	41.8	UCISD/6-311G*//UHF/6-31G*	154
$(CH_2{=}CCl)MeN^+$ (**30b**)	−7.1	UCISD/6-31G*//UHF/6-31G*	154
cyclo-$(CH)_6N^+$ (**31**)	−279.9	MP2//HF/3-21G	176
	−486.6	CAS//RHF/3-21G	176
	−178.5	B3LYP/6-31G*	148
$PhHN^+$	−147.3	MP4/SDTQ/6-31G**//HF/6-31G*	195
	−85.8	UCISD/6-31G*//UHF/6-31G*	154
	−88.7	BVWN5/cc − pVTZ//BVWN5/cc-pVDZ	182
	−78.7	BPW91/cc-pVDZ + ZPVE	185
	−87.0	BPW91/cc-pVDZ	183
	−80.3	UB3LYP/6-31G(d,p)	149
	−79.5	pBP/DN* + ZPE	199
$PhMeN^+$	−59.0	BPW91/cc-pVDZ + ZPVE	202
$(4\text{-}NMe_2C_6H_4)HN^+$	−115.9	BPW91/cc-pVDZ + ZPVE	185
$(4\text{-}NH_2C_6H_4)HN^+$	−116.3	BPW91/cc-pVDZ + ZPVE	185
$(4\text{-}HOC_6H_4)HN^+$	−106.3	BPW91/cc-pVDZ + ZPVE	185
$(4\text{-}MeOC_6H_4)HN^+$	−111.7	BPW91/cc-pVDZ + ZPVE	185
	−117.2	(U)BPW91/cc-PVDZ	196
	−146.9	(U)MP2/cc-PVDZ	196
$(4\text{-}EtOC_6H_4)HN^+$	−117.6	(U)BPW91/cc-PVDZ	196
	−148.5	(U)MP2/cc-PVDZ	196
$(4\text{-}MeC_6H_4)HN^+$	−91.6	BPW91/cc-pVDZ + ZPVE	185
	−94.6	pBP/DN* + ZPE	199
$(4\text{-}CHOC_6H_4)HN^+$	−51.0	BPW91/cc-pVDZ + ZPVE	185
$(4\text{-}ClC_6H_4)HN^+$	−89.1	BPW91/cc-pVDZ + ZPVE	185
	−102.9	pBP/DN* + ZPE	199
$(4\text{-}FC_6H_4)HN^+$	−92.9	BPW91/cc-pVDZ + ZPVE	185
$(4\text{-}HO_2CC_6H_4)HN^+$	−67.8	BPW91/cc-pVDZ + ZPVE	185
$(4\text{-}AcOC_6H_4)HN^+$	−69.0	BPW91/cc-pVDZ + ZPVE	185
$(4\text{-}AcC_6H_4)HN^+$	−56.5	BPW91/cc-pVDZ + ZPVE	185
$(4\text{-}CF_3C_6H_4)HN^+$	−74.9	BPW91/cc-pVDZ + ZPVE	185
$(4\text{-}CNC_6H_4)HN^+$	−73.2	BPW91/cc-pVDZ + ZPVE	185
$(4\text{-}NO_2C_6H_4)HN^+$	−70.3	BPW91/cc-pVDZ + ZPVE	185
$(4\text{-}MeC_6H_4)MeN^+$	−71.1	BPW91/cc-pVDZ + ZPVE	93
$(4\text{-}ClC_6H_4)MeN^+$	−74.1	BPW91/cc-pVDZ + ZPVE	93
$(4\text{-}PhC_6H_4)MeN^+$	−76.1	BPW91/cc-pVDZ + ZPVE	93
	−94.1	pBP/DN*//HF/6-31G	199
$(4\text{-}MeOC_6H_4)MeN^+$	−89.1	BPW91/cc-pVDZ + ZPVE	93

Table 2 (continued).

Ion	ΔE_{ST} (see [a])	Calculation procedure, basi set	Ref.
(3-MeC_6H_4)HN^+ (**47a**)	−79.1	UB3LYP/6-31G(d,p)	149
(3-$Me_3SiC_6H_4$)HN^+ (**47b**)	−80.3	UB3LYP/6-31G(d,p)	149
(3-FC_6H_4)HN^+ (**47c**)	−71.5	UB3LYP/6-31G(d,p)	149
(3-CNC_6H_4)HN^+ (**47d**)	−72.8	UB3LYP/6-31G(d,p)	149
(3-HOC_6H_4)HN^+ (**47e**)	−56.9	UB3LYP/6-31G(d,p)	149
[3-(CH_2═CH)C_6H_4]HN^+ (**47f**)	−44.8	UB3LYP/6-31G(d,p)	149
(3-$PH_2C_6H_4$)HN^+ (**47g**)	−41.0	UB3LYP/6-31G(d,p)	149
(3-HSC_6H_4)HN^+ (**47m**)	−26.8	UB3LYP/6-31G(d,p)	149
(3-$MeOC_6H_4$)HN^+ (**47j**)	−28.9	UB3LYP/6-31G(d,p)	149
(3-$NH_2C_6H_4$)HN^+ (**47k**)	1.7	UB3LYP/6-31G(d,p)	149
(3-NOC_6H_4)HN^+ (**47l**)	9.6	UB3LYP/6-31G(d,p)	149
(3-$PMe_2C_6H_4$)HN^+ (**47h**)	23.8	UB3LYP/6-31G(d,p)	149
(3-$C_4H_3C_6H_4$)HN^+ (**47i**) (see [b])	88.7	UB3LYP/6-31G(d,p)	149
3-(1-NCHCH)C_6H_4(H)N^+ (**47n**) (see [c])	46.0	UB3LYP/6-31G(d,p)	149
3,5-$(NH_2)_2C_6H_4$(H)N^+ (**47o**)	32.2	UB3LYP/6-31G(d,p)	149
3,5-$(NMe_2)_2C_6H_4$(H)N^+ (**47p**)	49.4	UB3LYP/6-31G(d,p)	149
4-(NHAc)C_6H_4(H)N^+	−115.5	(U)BPW91/cc-PVDZ	191
4-(NMeAc)C_6H_4(H)N^+	−116.3	(U)BPW91/cc-PVDZ	191
3,5-$(NH_2)_2C_6H_3$(Me)N^+ (**48**)	12.6	UB3LYP/6-31G(d,p)	149
3,5-$(NH_2)_2C_6H_3$(Bu^t)N^+ (**49**)	−19.7	UB3LYP/6-31G(d,p)	149
4-Pr^nNHC(O)C_6F_4(H)N^+ (**55**)	∼−84	B3LYP/6-31G*	192
	20.9	HF/6-31G*	192
Ph_2N^+ (**56**)	−48.5	BPW91/cc-pVDZ	183
	−94.1	pBP/DN*//HF/6-31G	199
$PhAcN^+$	−28.5(−49.0)	BPW91/cc-pVDZ	187
(4-Biph)AcN^+ (**85b**)	−41.8(−66.5)	BPW91/cc-pVDZ	187
(3-Py)AcN^+	−4.2(−20.5)	BPW91/cc-pVDZ	187
(4-Pyr)AcN^+	25.1(11.7)	BPW91/cc-pVDZ	187
(2-Flu)HN^+ (**86a**)	−42.3(−67.4)	BPW91/cc-pVDZ	187
syn-(2-Py)HN^+ (**95a**)	−60.7(−73.2)	BPW91/cc-pVDZ	187
anti-(2-Py)HN^+ (**95b**)	−23.4(−38.9)	BPW91/cc-pVDZ	187
syn-(3-Py)HN^+ (**96a**)	−25.1(−32.2)	BPW91/cc-pVDZ	187
anti-(3-Py)HN^+ (**96b**)	−38.5(−48.1)	BPW91/cc-pVDZ	187
(4-Py)HN^+ (**97**)	−15.1(−20.5)	BPW91/cc-pVDZ	187
syn-(4-Pyr)HN^+ (**98a**)	22.6(16.7)	BPW91/cc-pVDZ	187
anti-(4-Pyr)HN^+ (**98b**)	37.7(30.1)	BPW91/cc-pVDZ	187
(2-Pyr)HN^+ (**99**)	29.3(23.0)	BPW91/cc-pVDZ	187
(5-Pyr)HN^+ (**100**)	3.3(0)	BPW91/cc-pVDZ	187
(Triaz)HN^+ (**101**)	45.6(43.9)	BPW91/cc-pVDZ	187
HNH_2N^+	−248.1	6-31G**	152
$(NH_2)_2N^+$	−444.9	ACPF	216
HPH_2N^+	−134.2	6-31G**	152
$(PH_2)_2N^+$	−136.6	ACPF	216
$HOHN^+$	−129.5	6-31G**	152
$HSHN^+$	−106.2	6-31G**	152
HFN^+	−33.9	MP4/6-311G(2df) + ZPE	156, 157, 205
	−19.6	QCISD(T)	163
$HClN^+$	−17.2	MP4/6-311G(2df)) + ZPE	156, 157, 205
	−26.4	MP4SDTQ(fc)/6-311 + + G(2df,p)// MP2(full)/6-311 + + G(d,p)	159
	−17.6	QCISD(T)(full)/6-311 + + G(2df,p)// MP2(full)/6-311 + + G(d,p)	159
	−17.2	MP4/6-311G(2df) + ZPE	157
	−5.1	QCISD(T)	163
$HBrN^+$	−26.8	MP4/6-311G(2df) + ZPE	156, 157
HIN^+	−31.4	MP4/6-311G(2df) + ZPE	156, 157
F_2N^+	−231.6	G2	215
	−239.7	MP4/6-311G(2df) + ZPE	156, 157

Table 2 (continued).

Ion	ΔE_{ST} (see [a])	Calculation procedure, basis set	Ref.
Cl_2N^+	−82.8	MP4/6-311G(2df) + ZPE	156, 157
	−188.7	MP4SDTQ(fc)/6-311 + + G(2Df,p)// MP2(full)/6-311 + + G(d,p)	159
	−180.3	QCISD(T)(full)/6-311 + + G(2df,p)// MP2(full)/6-311 + + G(d,p)	159
Br_2N^+	−68.2	MP4/6-311G(2df) + ZPE	156, 157
I_2N^+	−47.3	MP4/6-311G(2df) + ZPE	156, 157
$(N_2)_2N^+$	−37	B3LYP/6-311 + G(3df)	217
	−26	CCSD(T)/6-311 + G(3df)	217

[a] The negative value points to the higher stability of the singlet state compared with the triplet state. The values in parentheses are G°_{S-T} including solvation by water molecules within the framework of the SM5.42R/BPW91/DZVP model;

[b] C_4H_3 =  ; [c] 1-NCHCH =  .

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