

Radical Cations of Phenyl-Substituted Aziridines: What Are the Conditions for Ring Opening?

Carsten Gaebert,^[a, d] Jochen Mattay,^{*[a]} Marion Toubartz,^[b] Steen Steenken,^[b] Beat Müller,^[c, e] and Thomas Bally^{*[c]}

Abstract: Radical cations were generated from different phenyl-substituted aziridines by pulse radiolysis in aqueous solution containing TlOH⁺, N₃[•] or SO₄^{•-} as oxidants or in *n*-butyl chloride, by ⁶⁰Co γ radiolysis in Freon matrices at 77 K, and in some cases by flash photolysis in aqueous solution. Depending on the substitution pattern of the aziridines, two different types of radical cations are formed: if the N atom carries a phenyl ring, the aziridine appears to retain its structure after oxidation and the resulting radical cation shows an intense band at 440–480 nm, similar to that of the radical

cation of dimethylaniline. Conversely, if the N atom carries an alkyl substituent while a phenyl ring is attached to a C-atom of the aziridine, oxidation results in spontaneous ring opening to yield azomethine ylide radical cations which have broad absorptions in the 500–800 nm range. In aqueous solution the two types of radical cations are quenched by O₂ with different rates,

Keywords: azomethine ylides • density functional calculations • matrix isolation • radical ions • reaction mechanisms

whereas in *n*-butyl chloride, the ring-closed aziridine radical cations are not quenchable by O₂. The results of quantum chemical calculations confirm the assignment of these species and allow to rationalize the different effects that phenyl rings have if they are attached in different positions of aziridines. In the pulse radiolysis experiments in aqueous solution, the primary oxidants can also be observed, whereas in *n*-butyl chloride a transient at 325 nm remains unidentified. In the laser flash experiments, both types of radical cations were also observed.

Introduction

Aziridines and their reactions are of great interest due to their synthetic and pharmacological importance.^[1,2] Upon ir-

radiation or on thermal activation aziridines undergo ring opening to the corresponding azomethine ylides which can be trapped in [3+2] cycloadditions with various dipolarophiles, to form nitrogen containing five-membered heterocycles.^[3–5] Under photoinduced electron transfer (PET) conditions aziridines are oxidized to the corresponding radical cations, which can react in a similar manner.^[6–10] In the course of our investigations aimed at the applications of aziridines in organic synthesis^[10,11] we became interested in the reactive intermediates of the [3+2] cycloadditions, that is, azomethine ylides and radical cations of aziridines, to elucidate the mechanisms of the reactions. A few years ago we published the results of studies in which azomethine ylides were generated by laser flash photolysis.^[12,13] In the present study we investigate the *radical cations* that are obtained on pulse radiolysis or ⁶⁰Co γ radiolysis of different phenylaziridines.

Reports on radical cations of aziridines are scarce. In 1976 Holmes and Terlouw^[14] reported that the metastable peaks and kinetic energy release of C₂H₅N^{•+} obtained from dimethylamine, piperidine, or pyrrolidine were indistinguishable from those obtained from aziridine. This led them to pro-

[a] Dr. C. Gaebert, Prof. J. Mattay
Fakultät für Chemie, Universität Bielefeld
33501 Bielefeld (Germany)
E-mail: mattay@uni-bielefeld.de

[b] M. Toubartz, Prof. S. Steenken
Max-Planck-Institut für Bioorganische Chemie
45470 Mülheim/Ruhr (Germany)

[c] Dr. B. Müller, Prof. T. Bally
Departement de Chimie, Université de Fribourg
1700 Fribourg (Switzerland)
Fax: (+41)26-300-9737
E-mail: thomas.bally@unifr.ch

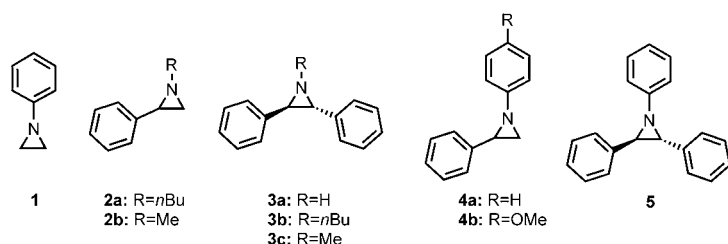
[d] Dr. C. Gaebert
Present address:
Consortium für elektrochemische Industrie GmbH
Zielstattstrasse 20, 81379 München (Germany)

[e] Dr. B. Müller
Present address: Bundesamt für Umwelt, Wald und Landschaft
3003 Bern (Switzerland)

pose for the first time that aziridine undergoes ring opening to azomethine ylide radical cation on ionization. Conversely, three years later Maquestiau et al. reported that $C_2H_5N^+$ generated from aziridine and pyrrolidine have distinct collision induced dissociation (CID) spectra, which led them to claim that the aziridine radical cation retains its ring-closed structure.^[15] In 1984 Lien and Hopkinson carried out UHF/4-31G calculations which predicted that the ring opening of the aziridine radical cation is exothermic by over 26.5 kcal mol⁻¹.^[16]

Around the same time Schaap et al. investigated the photooxygenation of various substituted aziridines.^[17–19] They explained the observed reaction products in terms of ring-opened intermediates. Finally, in 1986 Qin and Williams measured the ESR spectra of parent aziridine subjected to γ radiolysis in Freon glasses at 77 K. The spectra showed the unmistakable signature of an allylic radical which led these authors to propose that the aziridine radical cation undergoes ring opening, even under cryogenic conditions.^[20]

The substrates examined experimentally in the present study are 1-phenylaziridine **1**, 1-butyl-phenylaziridine **2a**, the *trans*-2,3-diphenylaziridines **3a** and **3b**, the 1,2-diphenylaziridines **4a** and **4b**, and 1,2,3-triphenylaziridine **5**. Computational model studies were done on compounds **2b** and **3c**, instead of the *n*-butyl derivatives, **2a** and **3b** (see Scheme 1).



Scheme 1.

Results and Discussion

Pulse radiolysis and ⁶⁰Co γ irradiation

N-Phenylaziridine (1): The UV spectrum recorded 0.9 μ s after irradiating an N_2O saturated solution of 0.1 mM 1-phenylaziridine (**1**) containing 1 mM Tl_2SO_4 at pH 6.6 with an electron pulse (Figure 1) shows the 360 nm band of the oxidant, $TlOH^+$.^[21] This absorption decreases with a rate constant of $k = 1.4 \times 10^9 M^{-1} s^{-1}$, while a new band arises with the same rate constant at 440 nm (its maximum intensity is reached after 15.3 μ s). The presence of an isosbestic point at 420 nm suggests that the observed transformation occurs in a single step. The 440 nm transient is quenchable with oxygen ($k = 5.5 \times 10^7 M^{-1} s^{-1}$).

Another transient was formed which has an absorption peak near 335 nm the maximum of which is reached 5.3 μ s after the electron pulse (i.e., about three times more rapidly than that of the 440 nm transient). Unfortunately, the ab-

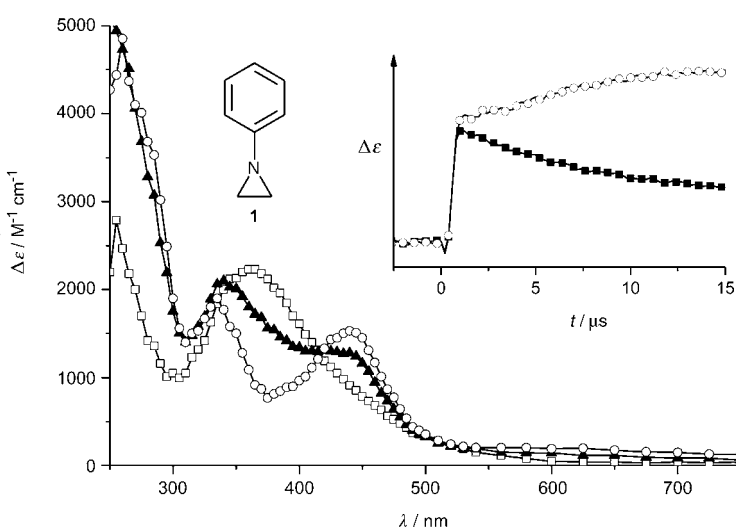


Figure 1. Transient absorption spectrum obtained after pulse radiolysis of a 0.1 mM aqueous solution of **1**, saturated with N_2O and containing 1 mM Tl_2SO_4 at pH 6.6; \square 0.9 μ s, \blacktriangle 5.3 μ s, \circ 15.3 μ s after the electron pulse. The insets shows the kinetics at 360 (\blacksquare , $k = 1.4 \times 10^9 s^{-1}$) and 440 nm (\circ , $k = 1.2 \times 10^5 s^{-1}$).

sorptions of $TlOH^+$ prevented a quantitative assessment of the kinetics for the formation and decay of this species which might be an adduct radical of **1** and OH^\cdot (see below).

When oxidation was effected by $SO_4^{\cdot-}$ (Figure 2) the 440 nm transient arose with a rate constant of $9.2 \times 10^9 M^{-1} s^{-1}$. Its quenching with oxygen occurred with a rate constant ($k = 6.0 \times 10^7 M^{-1} s^{-1}$) in good agreement with the one found after oxidation of **1** with $TlOH^+$. Pulse radiolysis of 4 mM of aziridine **1** in *n*-butyl chloride, and ⁶⁰Co γ radiolysis in a Freon matrix at 77 K (lower part of Figure 2) generated the same species with $\lambda_{max} = 440$ nm but in *n*-butyl chloride this transient is not quenchable with oxygen.

In the spectrum recorded after oxidation with N_3^\cdot the band at 440 nm occurred only as a minor constituent that arose with a rate constant of $8.0 \times 10^8 M^{-1} s^{-1}$. The major transient, which was formed with a rate constant of $3.3 \times 10^8 M^{-1} s^{-1}$ showed the same 335 nm band that was observed also after pulse radiolysis of aziridine **1** with Tl_2SO_4 . Under an atmosphere of $N_2O:O_2$ 4:1, this 335 nm absorption was completely quenched, so this transient is very sensitive to oxygen. We propose that this species is an adduct radical formed by attack of OH^\cdot onto a phenyl group of **1**. In the spectrum obtained with $SO_4^{\cdot-}$ as oxidant there is no absorption at 335 nm because the *tert*-butanol that was added in this experiment immediately traps all OH radicals. This, and the fact that adducts of aromatic systems with OH radicals generally show absorptions in this region,^[22–24] supports the assignment of the 335 nm transient to an adduct radical. In order to confirm this assignment we subjected a 0.1 mM solution of **1** in N_2O -saturated water at pH 8 to pulse radiolysis. Thereby we detected also a major transient at 335 nm (Figure 3) while the 440 nm absorption appeared as a minor secondary transient by OH^- elimination from the adduct radical. The same OH adduct radical may also be formed in the experiments with Tl_2SO_4 described above.

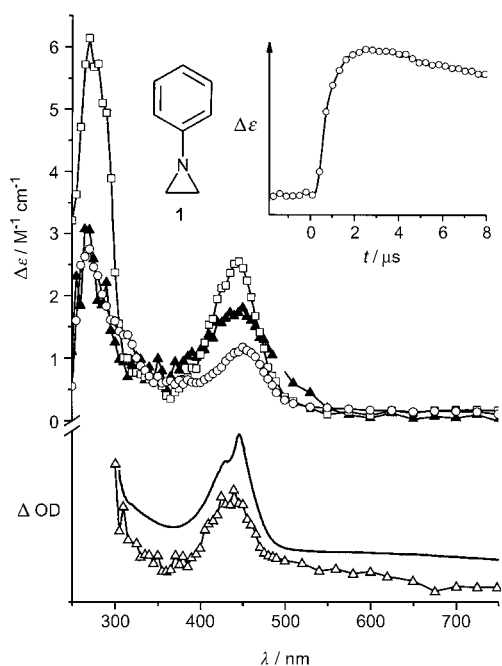


Figure 2. Top: Transient absorption spectrum obtained after pulse radiolysis of a 0.2 mM aqueous solution of **1** containing 1 mM $K_2S_2O_8$ and 0.1 M *tert*-butanol at pH 6.6; \blacktriangle 0.7 μ s, \square 7.1 μ s, \circ 765 μ s after the electron pulse. Inset shows the kinetics at 440 nm ($k = 1.8 \times 10^5 \text{ s}^{-1}$); bottom: Transient absorption spectrum recorded after pulse radiolysis of 4 mM of **1** in *n*-butyl chloride (Δ) and after ^{60}Co γ radiolysis in a Freon matrix at

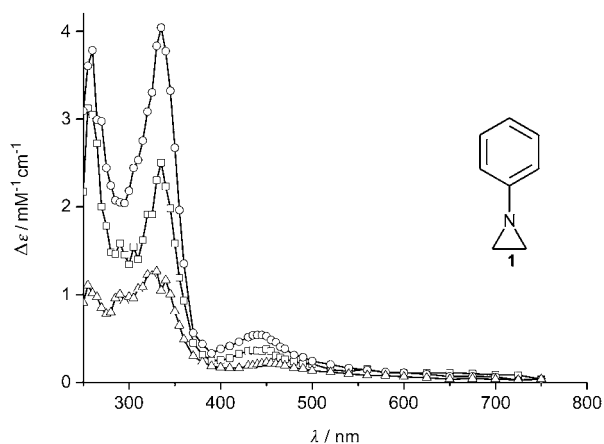


Figure 3. Transient absorption spectrum of 0.1 mM **1** observed on pulse radiolysis of an N_2O -saturated aqueous solution at pH 8; Δ 0.8 μ s, \square 7.3 μ s, \circ 785 μ s after the electron pulse.

77 K (—).

By comparison with the absorption spectrum of the radical cation of *N,N*-dimethyl aniline ($\text{DMA}^{\bullet+}$) which shows an intense band at 465 nm,^[22,25] we assigned the 440 nm band of ionized **1** to the (ring closed) radical cation of *N*-phenylaziridine (a discussion of the electronic structure of $\mathbf{1}^{\bullet+}$ will be provided in Section on Calculations).

1-Butyl-2-phenylaziridine (2a): In the spectrum of 0.2 mM aziridine **2a** in an aqueous solution containing 2 mM potassi-

um peroxodisulfate a new strong absorption occurred at 380 nm and a flat, weak one at 550 nm (Figure 4). These bands rise concurrently, with a similar rate as that observed for the decay of the sulfate radical anion at 450 nm^[26,27] ($k = 9.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$), and they are also quenchable by oxygen ($k = 1.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). A similar pair of bands ($\lambda_{\text{max}} = 575$ and 390 nm) was also observed on γ radiolysis of aziridine **2a** in a Freon matrix at 77 K (Figure 4, solid line). On pulse irradiation of 9 mM **2a** in *n*-butyl chloride, a different transient with a band at 325 nm was formed, which can also be quenched by oxygen but we have been unable to assess the identity of this species.

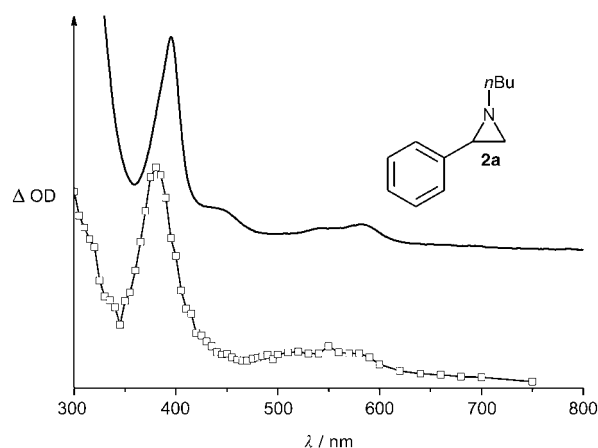


Figure 4. Transient absorption spectrum observed 15 μ s after pulse radiolysis of a 0.2 mM aqueous solution of **2a** containing 2 mM $K_2S_2O_8$ and 0.1 M *tert*-butanol at pH 6 (\square), and on ^{60}Co γ radiolysis in a Freon matrix at 77 K (—).

Evidently, these spectra are quite different from those found for the radical cations of *N*-phenylaziridines, which should come as no surprise because **2a** lacks the *N,N*-dialkylanilino chromophore which was found to be responsible for the 440–490 nm bands that are characteristic for the corresponding radical cations. However, calculations predict that *C*-phenylaziridines undergo facile ring opening to azomethine ylide radical cations on ionization (see below), so the chromophore that is responsible for the spectra in Figure 4 is of an altogether different nature in this case. Very similar spectra were obtained also for the corresponding *N*-methyl as well as for the *N*-H derivative on γ radiolysis in Freon glasses.^[28]

trans-2,3-Diphenylaziridines 3a and 3b: ^{60}Co γ radiolysis of **3a** and **3b** in a Freon matrix at 77 K yields nearly indistinguishable spectra (shown in Figure 5), so we can assume that similar cations are formed. As will be shown below, 2,3-diphenylaziridines undergo spontaneous ring opening upon ionization to yield azomethine ylide radical cations of the same type as **2a**, cations which are characterized by their broad bands in the 500–800 nm range.

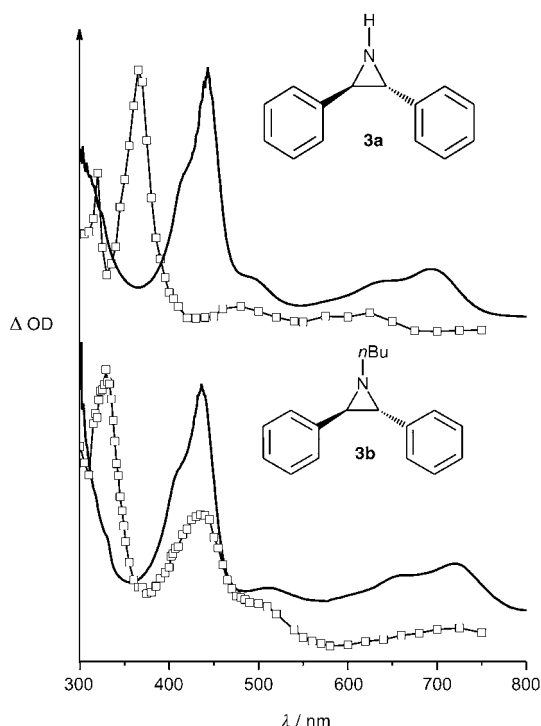


Figure 5. Transient absorption spectra recorded after pulse radiolysis of 8 mM of **3a** (□, 2.5 μs) and 9 mM of **3b** (□, 2 μs after the electron pulse) in *n*-butyl chloride and after ^{60}Co γ radiolysis of the same two 2,3-diphenylaziridines in a Freon matrix at 77 K (—).

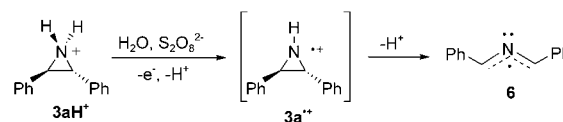
Conversely, the spectra obtained on pulse radiolysis of 8 mM **3a** and 9 mM **3b** in *n*-butyl chloride are quite different in appearance (Figure 5). That obtained from **3b** shows bands with peaks at 430 and about 700 nm which arise and decay with the same rate. The same bands are also observed if $\text{SO}_4^{\cdot-}$ is used as an oxidant whereby they also build up with the same rate ($k=9.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and are both quenched by oxygen ($k=7.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$). Since the two bands coincide with those in the spectra obtained after γ radiolysis in Freon, we conclude that the same radical cation is formed in the two sets of experiments. In contrast to the radical cations of the *N*-arylaziridines **1**, **4a**, and **4b** (see below), this one is, however, also quenched with oxygen in *n*-butyl chloride. Similar to the case of **2a** we cannot explain the oxygen quenched transient absorbing at 330 nm after pulse radiolysis in butyl chloride.

In addition, there are pronounced shoulders at 480 (**3a**) and 500 nm (**3b**), respectively, the kinetics of which differ from that for the formation and decay of the 430 and 700 nm bands. Previous flash photolysis experiments in acetonitrile and methanol had given rise to bands at 480 (**3a**) or 500 nm (**3b**)^[12] which were assigned to the neutral azomethine ylides that are formed by ring opening of aziridines.^[29] Perhaps the same species are formed as minor products on pulse radiolysis in BuCl or γ radiolysis in Freon.^[30]

In contrast, the spectrum obtained on pulse radiolysis of **3a**, either in *n*-butyl chloride or in aqueous peroxodisulfate solution, differs strongly from that found after γ radiolysis in

Freon. It shows four absorptions at 280, 320, 380 and 630 nm that appear with the same rate constant ($k=6.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and are quenched with oxygen ($k=5.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, the highest such rate constant observed in this study!) in the peroxodisulfate experiments. We also note that the major absorption at 380 nm is very intense ($\epsilon=21100 \text{ M}^{-1} \text{ cm}^{-1}$) compared with those of the oxidation products of the other aziridines ($\epsilon=2000\text{--}4000 \text{ M}^{-1} \text{ cm}^{-1}$) that were identified in this study.

In order to identify the transient observed upon pulse radiolysis of **3a** we measured the conductivity of an aqueous peroxodisulfate solution of this compound and compared it with a similar solution containing aziridine **3b** (note that these solutions have a pH of 4.9 so the aziridines are present mostly in their protonated forms, **3H**⁺). After the pulse the conductivity was found to be much higher in the case of **3a** than if the solution contained **3b**. This finding leads us to postulate that **3a**⁺ undergoes spontaneous deprotonation to yield radical **6** (Scheme 2), a decay pathway that is not available to **3b**⁺.



Scheme 2.

We propose a ring-opened structure for the **6** because a) calculations predict that **3a**⁺ undergoes spontaneous ring opening (see below) and b) because the allylic radical **6** enjoys considerably more stabilization by the two terminal phenyl rings than an aziridinyl radical. Of course in *n*-butyl chloride, spontaneous deprotonation of **3a**⁺ is not expected to occur because the proton cannot be solvated. We can see two possibilities for the formation of **6** under these conditions: either **3a**⁺ is deprotonated by neutral **3a**, or **3a** undergoes hydrogen atom loss on radiolysis in *n*-butyl chloride. A similar process was observed by Qin and Williams to occur on γ irradiation of parent aziridine in a $\text{CF}_2\text{ClCCl}_2\text{F}$ matrix at 114 K which led, next to the ring-opened azomethine ylide radical cation, to the aziridinyl radical.^[20]

In aqueous solution **2a**⁺ and **3b**⁺ are trapped faster by oxygen than the radical cations of the 1-arylaziridines and, in contrast to the latter, **3b**⁺ is quenched with oxygen even in *n*-butyl chloride. The fact that **3b** was found to undergo [3+2] cycloadditions with various dipolarophiles under PET conditions^[6,7,10–13] also speaks for a ring-opened structure of the radical cation.

1-Aryl-2-phenylaziridines 4a and 4b: Upon pulse radiolysis of an aqueous solution of 0.2 mM 1,2-diphenylaziridine (**4a**) containing peroxodisulfate a transient absorbing at 440 nm builds up with a rate constant of $6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. This transient is quenched with oxygen ($k=5.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$). Pulse radiolysis of a 9 mM solution of **4a** in *n*-butyl chloride also af-

forded a broad absorption with a maximum at 440 nm which is, however, not quenchable by oxygen. Additional evidence for the identification of this species is obtained by the results of γ radiolysis in a Freon matrix at 77 K which leads to a spectrum with an intense band peaking at 445 nm (solid line in Figure 6). In addition, a broad band with $\lambda_{\text{max}} \approx 650$ nm, similar to that observed after ionization of 1-butyl-2-phenyldiaziridine **2a**, was observed. However, this latter band can be bleached separately by irradiation through a 590 nm cutoff filter, so it does not belong to the same species as the intense UV band. Apparently this second, unidentified species was not formed on pulse radiolysis in solution.

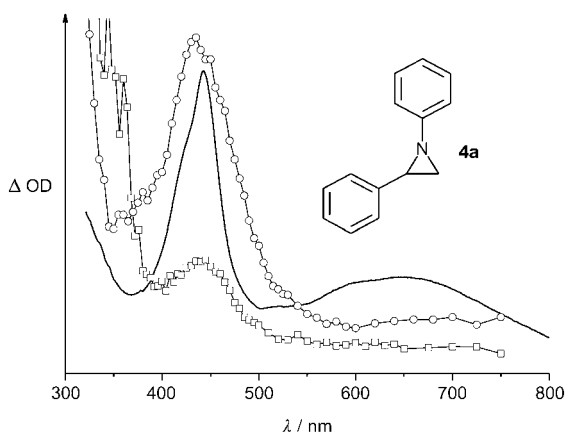


Figure 6. Transient absorption spectra recorded after pulse radiolysis of a 0.2 mM aqueous solution of **4a** containing 1 mM $\text{K}_2\text{S}_2\text{O}_8$ and 0.1 M *tert*-butanol at pH 6, 62 μs after the electron pulse (\circ), on pulse radiolysis of a 9 mM solution of **4a** in *n*-butyl chloride, 2.5 μs after the electron pulse (\square), and on ^{60}Co γ radiolysis in a Freon matrix at 77 K (—).

Aqueous peroxodisulfate *spontaneously* oxidized 1-(*p*-methoxyphenyl)-2-phenylaziridine (**4b**), even at room temperature, to yield a purple solution with a concomitant decrease of the pH. Therefore **4b** cannot be subjected to pulse radiolysis to generate its radical cation under controlled conditions. However, if N_3^- is used as oxidant we observed a transient absorption at 470 nm which arose with a rate constant of $2.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and was quenched by oxygen ($k = 1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$). Once again, pulse radiolysis of a 9 mM solution of aziridine **4b** in *n*-butyl chloride resulted in a similar absorption which was, however, not quenchable with oxygen. A 480 nm band with a tail that extended to over 700 nm was observed after γ radiolysis of **4b** in a Freon matrix at 77 K (Figure 7).

The similarity in the kinetic and spectroscopic data of the oxidized 1-phenyl and the 1-aryl-2-phenylaziridines indicated that the resulting radical cations retain a ring-closed structure in all cases. This conclusion was confirmed by preparative studies which yielded no products from reactions with dipolarophiles, products that would have indicated that ring opening to azomethine ylide radical cations had occurred, under PET conditions.^[11]

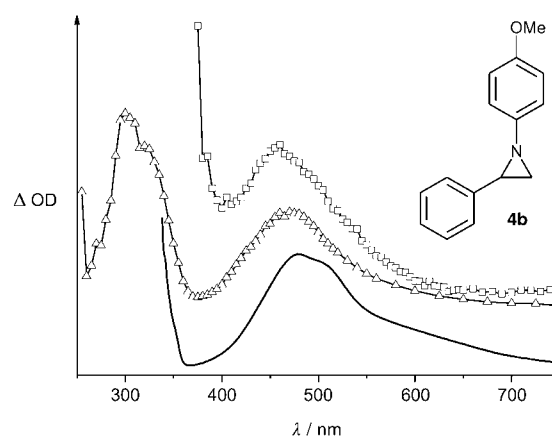


Figure 7. Transient absorption spectra observed after pulse radiolysis of a 0.1 mM aqueous solution of **4b** containing 10 mM NaN_3 at pH 8, 7.1 μs (\triangle), a 9 mM solution of **4b** in *n*-butyl chloride, 2.3 μs (\square), and on ^{60}Co γ radiolysis of **4b** in a Freon matrix at 77 K (—).

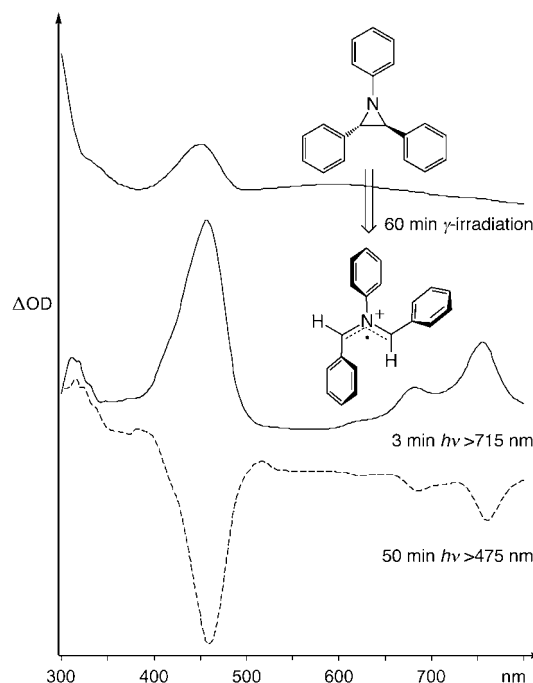


Figure 8. Top: difference spectrum observed after γ radiolysis of 1,2,3-triphenylaziridine (**5**) in Freon at 77 K; center: difference spectrum for the subsequent photolysis at >715 nm; bottom: difference spectrum for the bleaching of the azomethine ylide radical cation at 475 nm.

1,2,3-Triphenylaziridine (5): This compound was only investigated by γ radiolysis, but the results proved to be quite interesting: After radiolysis, a spectrum with a band peaking at 451 nm, that is, in the region where N-phenylaziridine radical cations absorb, was observed in addition to a broad, weak absorption between 500 and 700 nm (Figure 8a). After only three minutes of photolysis through a 715 nm cutoff filter, a much more intense spectrum arose (Figure 8b) which could in turn be bleached completely by irradiation at >475 nm (Figure 8c). This latter spectrum was similar to

those observed after radiolysis of the 2,3-diphenylaziridines **3a** and **3b** which underwent spontaneous ring opening upon oxidation.

Thus, **5** appeared to retain its ring-closed structure after ionization at 77 K but can be converted to its ring-opened azomethine ylide radical cation by subsequent photolysis, a unique behaviour in the series of phenyl substituted aziridines investigated in this study.

Calculations

In an effort to substantiate the conclusions we had reached from the experiments described above, and to understand the reasons for the different fate of the ionized aziridines and the electronic structure of the resulting transients, we carried out a comprehensive set of quantum chemical calculations the results of which are presented and discussed in this Section.

N-Phenylaziridine (1): On ionization of **1** an electron is removed from the HOMO depicted on the right-hand side of Figure 9. Contrary to that of the iso- π -electronic benzyl anion, this MO is antibonding between the phenyl ring and the N atom, hence we expect this bond to be strengthened in the radical cation of **1**. B3LYP calculations confirmed that upon ionization this bond assumes partial double bond character which is also given by the fact that the aziridine and the phenyl rings are nearly coplanar in $1^{+\bullet}$ (Figure 9). In contrast, the length of the bonds in the aziridine moiety are hardly affected by ionization, which indicates that ring-opening will not be much easier in the radical cation than in the neutral aziridine.

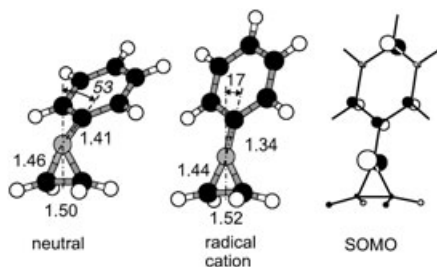
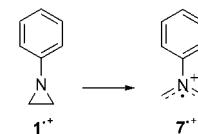


Figure 9. Structural changes on ionization of **1** and shape of the singly occupied MO in the resulting radical cation.

The photoelectron spectrum of **1**^[31,32] shows two more bands within 3 eV of the first, the second of which lies only 1 eV above the first. Hence, the observed absorption bands of $1^{+\bullet}$ at 440 nm (2.8 eV) must correspond to $D_0 \rightarrow D_2$ excitation. Indeed, TD-B3LYP excited state calculations predict another, very weak transition at 690 nm which corresponds to HOMO-1 \rightarrow HOMO excitation (the observed $D_0 \rightarrow D_2$ transition, which involves HOMO-2 \rightarrow HOMO and HOMO \rightarrow LUMO excitation is predicted at 400 nm).

If enforced (e.g., by lengthening the C-C bond in the aziridine), ring opening of the radical cation proceeds in a non-

concerted conrotatory fashion. According to B3LYP, the transition state for this reaction lies 33 kcal mol⁻¹ above $1^{+\bullet}$, but the process leading to the 2-phenylazomethine ylide radical cation $7^{+\bullet}$ (see Scheme 3) is nearly thermoneutral. This contrasts with the parent aziridine radical cation where the same level of theory predicts a barrier of only 10.1 and an exothermicity of 33.6 kcal mol⁻¹.^[28] To understand the influence that



Scheme 3.

the N-phenyl ring has on the thermochemistry and the kinetics of this process we calculated the barriers for rotation of this phenyl ring in $1^{+\bullet}$, at the transition state, and in $7^{+\bullet}$. Whereas in $1^{+\bullet}$ it is 26.3 kcal mol⁻¹—thus testifying to the substantial resonance stabilization of this cation by the phenyl ring—it falls to 9.6 kcal mol⁻¹ at the transition state (i.e., 16.7 kcal mol⁻¹ of resonance energy is lost at this point). In $7^{+\bullet}$ the phenyl ring is already twisted by 53° and bringing it into a perpendicular position requires only 0.6 kcal mol⁻¹. This comes as no surprise, because the phenyl ring is attached to a nodal position of the allylic HOMO of $7^{+\bullet}$ where it cannot exert a stabilizing influence. Thus, our conclusion that **1** retains its ring-closed structure on ionization is fully confirmed by the calculations.

N-Methyl-2-phenylaziridine (2b): If a phenyl ring is attached to a C rather than the N atom of the aziridine, the situation changes completely compared with that in **1**. For reasons of computational economy calculations were carried out on the 1-methyl rather than the 1-butyl derivative (the cations that result from the two compounds have virtually indistinguishable spectra^[28]). Now the HOMO arises through interaction of the benzene moiety with the symmetric Walsh-MO in the three-membered ring (see Figure 10).

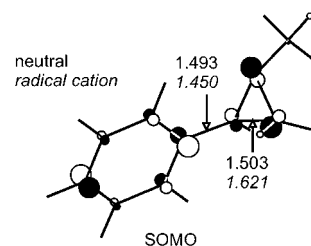


Figure 10. Shape of the singly occupied MO of the radical cation obtained from 1-methyl-2-phenylaziridine **3c** and structural changes on oxidation.

The geometry changes on ionization are in accord with expectations from the nodal properties of the MO from which the electron is removed (Figure 10): The aziridine C-C bond lengthens by 0.12 Å, which will facilitate the cleavage of this bond, whereas the aziridine-phenyl bond shortens by 0.04 Å.

Indeed, the transition state for the ring opening, which occurs again in a conrotatory fashion, was found to lie only 4 kcal mol⁻¹ above **2b**^{•+}, and the process is exothermic by 25 kcal mol⁻¹, that is, almost as much as in the parent compound. An intrinsic reaction coordinate calculation from the transition state leads to the *exo*-isomer of the C-phenyl-N-methyl azomethine ylide radical cation **8**^{•+} although a separate calculation shows that the *endo*-conformer lies even 0.6 kcal mol⁻¹ lower in energy, in spite of the twisting of the phenyl ring that results from steric interactions in this case.

To gain insight into the role of the phenyl ring in **2b** we computed again the barriers for twisting this ring to a position that is perpendicular to that which it assumes at the optimized geometries of **2b**^{•+}, the transition state for ring opening, and **8**^{•+}: this process requires only 7.8 kcal mol⁻¹ in **2b**^{•+} and 8.0 kcal mol⁻¹ in **8**^{•+}, but 18.7 kcal mol⁻¹ at the transition state. Thus, in contrast to **1**^{•+}, the phenyl ring has a 11 kcal mol⁻¹ greater stabilizing effect at the transition state than in the reactant in the case of **2b**^{•+}, which readily explains why the barrier for ring opening is so much lower in this case. Apparently this barrier is too low to even prevent ring opening from occurring at 77 K.

Next we addressed the question whether the spectra shown in Figure 4 are compatible with those expected for **8**^{•+}. In this case, the TD-B3LYP method provided quite unsatisfactory results, so we turned to the CASSCF/CASPT2 method to model the excited states. Thereby we distinguished between the two isomers which are expected to have slightly different spectra. The results of these calculations are summarized in Table 1 which shows that the most important transitions in **8**^{•+} involve the allylic azomethine ylide moiety (MOs 34, 36, and 37 in Figure 11). On the whole, the spectrum that is predicted for the *exo*-isomer is in better accord with the experimental one than that computed for the *endo*-isomer. Together with the IRC calculation mentioned above, this seems to indicate that it is indeed the *exo*-isomer of **8**^{•+} which is formed in the ring-opening of **2b**^{•+}.

N-Methyl-2,3-diphenylaziridine (3c): In view of the above conclusions with regard to 2-phenylaziridine, it certainly comes as no surprise that 2,3-diphenylaziridines undergo almost barrierless ring opening on oxidation. Actually it turned out to be quite tricky to prevent the radical cation of the model system **3c** from relaxing spontaneously to the azomethine ylide radical cation **9**^{•+}, and to find a transition state for this process. On ionization of **3c**, the C–C bond in the aziridine moiety lengthens to 1.86 Å and a barrier of

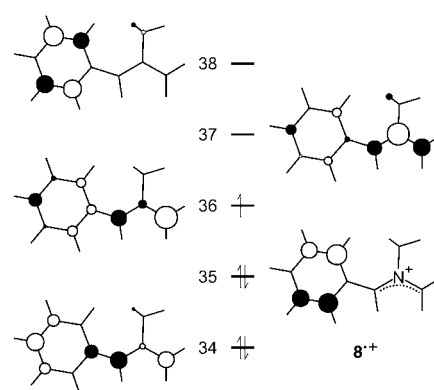


Figure 11. Molecular orbitals of the 1-phenyl-azomethine ylide radical cation **8**^{•+} that are involved in the electronic transitions listed in Table 1.

Table 1. Calculated electronic transitions of **8**^{•+} by using the CASPT2 method.

Isomer	States	Experiment [nm]	Experiment [eV]	CASPT2 [nm]	CASPT2 [eV]	<i>f</i> ^[a]	CASSCF Configurations ^[b]
<i>exo</i>	1 ² A''	–	–	–	–	–	75% (36) ^[c]
	2 ² A''	583	2.12	584	2.12	0.028	44% 36 → 37 20% 34 → 36
	3 ² A''	(440 sh)	(2.82)	484	2.56	0.002	55% 35 → 36 10% 34 → 36
	4 ² A''	398	3.12	396	3.13	0.252	28% 34 → 36 19% 36 → 38 10% 36 → 37
<i>endo</i>	1	–	–	–	–	–	77% (36) ^[c]
	2	583	2.12	566	2.19	0.010	31% 34 → 36 27% 36 → 37 10% 36 → 39
	3	(440 sh)	2.82	485	2.56	0.002	62% 35 → 36
	4	398	3.12	407	3.05	0.129	23% 34 → 36 17% 36 → 37 16% 36 → 40

[a] Oscillator strength for electronic transition. [b] Active space: nine electrons in five occupied + four virtual MOs. The most important of those are shown in Figure 11. [c] The superscripted 1 indicates that orbital 36 (the HOMO) is occupied by a single electron in the ground state.

less than 1 kcal mol⁻¹ remains to effect full cleavage of this bond to yield the *endo-exo* isomer of **9**^{•+} where both phenyl rings are twisted by about 20° relative to the C–N–C plane of the azomethine ylide moiety. Due to the presence of phenyl rings on both aziridine carbon atoms, the SOMO is centered even more strongly in the symmetric Walsh-MO of the three-membered ring than in the 2-phenylaziridine (Figure 12).

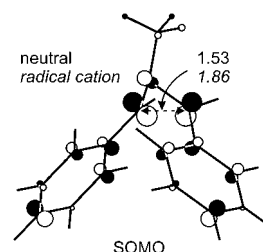
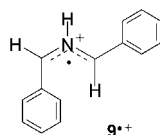


Figure 12. Shape of the singly occupied MO of the radical cation obtained from 1-methyl-, 2,3-diphenylaziridine and structural changes on oxidation.

Unfortunately, $9^{+\bullet}$ proved to be too large to be amenable to CASSF/CASPT2 calculations of its excited states, so we had to resort to the more economical TD-DFT method to model the electronic spectrum of $9^{+\bullet}$. Although the resulting predictions are not in such good quantitative accord with the experimental spectra of ionized **3a** and **3b** shown in Figure 5, they show that the main transitions are of similar nature as those of $8^{+\bullet}$, that is, they also involve mainly MOs that are centered on the allylic azomethine ylide moiety. In agreement with the experimental spectra of ionized **3a** and **3b**, TD-B3LYP predicts those spectra to be dominated by two excitations around 2 and 3 eV, respectively, with the latter being about four times more intense than the former. Perhaps the shoulder at 510 nm is in part due to the two weak transitions that are predicted around 2.6 eV and that correspond to charge transfer from the benzene to the allyl moieties of $9^{+\bullet}$. In any event, the calculations of the potential energy surface and the results in Table 2 leave no doubt that the spectra in Figure 5 are those of $9^{+\bullet}$, although we can make no prediction with regard to the conformations around the allylic N–C bonds in this case.

Table 2. Calculated electronic transitions of *endo-exo-9⁺* by using the TD-B3LYP method.



States	Experiment ^[a]		TD-B3LYP			Configurations ^[b]
	[nm]	[eV]	[nm]	[eV]	<i>f</i> ^[a]	
1	–	–	–	–	–	(56) ^[c]
2	720	1.72	616	2.01	0.134	0.91 × 56 → 57 –0.38 × 53 → 36
3	(510 sh)	(2.43)	474	2.62	0.003	0.96 × 55 → 56 +0.23 × 55 → 57
4			470	2.64	0.002	0.96 × 54 → 56 –0.23 × 54 → 57
5	445	2.79	396	3.13	0.509	0.87 × 53 → 56 +0.25 × 56 → 57

[a] From the spectrum of ionized **3b** shown in Figure 5. [b] MO 56 is the singly occupied HOMO of $9^{+\bullet}$ which corresponds to the allylic NBMO of the azomethine ylide; MOs 53 and 57 are also allylic MOs, whereas the nearly degenerate MOs 53 and 54 are centered on one or the other of the two benzene rings. [c] See Table 1.

1,2-Diphenylaziridine (4a): We have seen above that a phenyl ring attached to the N atom of an aziridine effectively prevents ring opening on ionization, whereas a phenyl ring attached to a C atom promotes it. Therefore we were anxious to see what theory would tell us about the fate of 1,2-diphenylaziridine (**4a**).

As it turned out, the influence of the N-phenyl ring dominates over that of the C-phenyl ring, that is, ionization occurs from an MO that is similar to the HOMO of **1** (Figure 13, see Figure 9). Consequently, the geometry changes on ionization of **4a** are also very similar to those suffered by **1**, that is, a shortening of the N–phenyl bond ac-

companied by an planarization of the N atom (the angle between the plane of the aziridine ring and the C–phenyl bond decreases from 49 to 25°, while the inversion barrier almost disappears). In particular, the distal C–C bond in the aziridine ring is hardly affected by ionization.

Nevertheless the C-phenyl ring does not remain without an effect on the reactivity of **4a**: due to the stabilization of the product, the ring-opening reaction (which had been nearly thermoneutral in $1^{+\bullet}$) becomes exothermic by about 10 kcal mol^{–1} while the barrier decreases to 19.4 kcal mol^{–1} in $4a^{+\bullet}$, that is, it lies almost midway between those in $1^{+\bullet}$ (33 kcal mol^{–1}) and in $2b^{+\bullet}$ and close to that in $3a^{+\bullet}$ (16 kcal mol^{–1}[28]). Thus, at the transition state for ring opening, the effects of the two phenyl rings appear to cancel almost completely.

Due to the great similarity of the spectra observed after ionization of **4a** and of **1**, we refrained from carrying out electronic structure calculations on $4a^{+\bullet}$. Suffice it to say that the “reactive” state where the unpaired electron resides in the symmetric Walsh MO of the aziridine lies almost 1 eV above the state where the SOMO corresponds to that shown in Figure 9, and the transition to that state is very weak, so it does not interfere with the electronic structure of $4a^{+\bullet}$.

1,2,3-Triphenylaziridine (5): The HOMO of **5** from which ionization occurs is once again centered on the N-phenyl moiety, as in **1** and **4a**. Thus, it is not surprising that the structure of the aziridine ring changes very little on ionization. However, the phenyl rings that are attached to the C atoms of the aziridine begin to show their influence on the way to the product in that the activation energy for ring opening is only 5.43 kcal mol^{–1} (up 4.5 kcal mol^{–1} from 2,3-diphenylaziridine radical cation $3c^{+\bullet}$, due to the influence of the N-phenyl ring) and the process is exothermic by 17.9 kcal mol^{–1}[33] halfway between the 1,2-diphenyl- and 2,3-diphenylaziridine radical cations, $4a^{+\bullet}$ and $3c^{+\bullet}$.

Conclusions

In summary we successfully generated and identified the radical cations that are formed on oxidation of different phenyl-substituted aziridines by pulse radiolysis in aqueous solution containing different oxidants or in *n*-butyl chloride at room temperature, and by γ radiolysis in a Freon matrix at 77 K. As it turns out, the position of the phenyl substituent(s) determines the fate of the incipient aziridine radical cations: if the N atom carries a phenyl ring, this effectively protects the aziridine radical cation from decaying to an

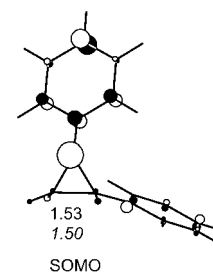


Figure 13. Shape of the singly occupied MO of the radical cation obtained from 1,2-diphenylaziridine and structural changes on oxidation.

azomethine ylide radical cation, due to the benzylic resonance stabilization that prevails in N-phenylaziridine radical cations. The benzylic Ph-N^{•+} chromophore is also responsible for the intense D₀→D₂ transition in the 440–480 nm range that is characteristic for ring-closed aziridine radical cations.

By contrast, phenyl rings attached to the C atoms of the aziridine lower the barrier for ring opening, to the extent that the process becomes nearly activationless in 2,3-diphenylaziridine radical cation. This is mainly due to the preferential stabilization of the resulting allylic azomethine ylide radical cations by phenyl rings attached to their terminal C-atoms. This chromophore gives also rise to intense near-UV transitions, but in addition it distinguishes itself by a weak broad band at 500–800 nm. In addition, the two types of radical cations can be distinguished by their reactivity towards oxygen: In aqueous solution, the ring-opened azomethine ylide radical cations are quenched with a higher rate than the ring-closed aziridine radical cations, and in *n*-butyl chloride the former are not quenchable by O₂ (in contrast to the latter).

Quantum chemical calculations support the above conclusions and helped to assign the observed spectra. They also allow to understand the influence of phenyl rings attached to different positions of aziridine radical cations on their reactivity. In Figure 14 we summarize the results that pertain to the ring-opening reactions of the various types of aziridine radical cations that were investigated in the present study.

The thermochemistry of the ring opening of the different aziridine radical cations is compared with that of the parent aziridine radical cation and the N-methyl derivative, calculated also at the B3LYP/6-31G* level.^[28]

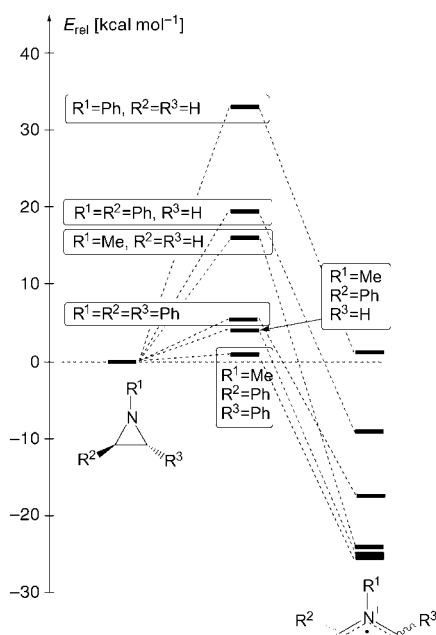


Figure 14. Thermochemistry of the ring-opening reactions of different phenylaziridines from B3LYP/6-31G* calculations.

Upon pulse radiolysis in aqueous solution the radical cation of 2,3-diphenylaziridine was found to undergo spontaneous deprotonation to form an allylic radical, while in *n*-butyl chloride hydrogen abstraction from the aziridine generates the same species. We also provided an additional access to aziridine radical cations upon photolysis of aqueous solutions of aziridines with an excimer laser for **2a**, **3b**, **4a** and **4b**.^[29]

Experimental Section

Starting materials: 1-Phenylaziridine (**1**),^[34] 1,2-diphenylaziridine (**4a**),^[35] 1-(*p*-methoxyphenyl)-2-phenylaziridine (**4b**)^[35] and *trans*-2,3-diphenylaziridine (**3a**)^[36] were prepared by reported procedures.

1-Butyl-2-phenylaziridine (2a):^[11,37] Starting with commercially available styrol oxide the corresponding β-amino alcohol was prepared according to the procedure of Chapman and Triggler.^[38] The formation of 1-butyl-2-phenylaziridine occurred as described by Okada et al.^[37]

1-Butyl-*trans*-2,3-diphenylaziridine (3b):^[11] By using *trans*-stilbene as starting material epoxidation with MCPBA formed the corresponding *trans*-stilbene oxide in yields of 75%. Following the procedure of Deyrup and Moyer^[39] the epoxide was opened to the β-amino alcohol. The cyclization as described above^[37] formed 1-butyl-*trans*-2,3-diphenylaziridine in yields of 58%.

All spectroscopical data of the aziridines have been published elsewhere.^[11]

Pulse radiolysis: For pulse radiolysis, 0.4–2 μs electron pulses from a 3 MeV van de Graaff accelerator were used at dose rates of 30–3000 rad per pulse. N₂O-, argon- or oxygen-saturated solutions containing 0.1 up to 9 mM aziridine were flowed through a quartz cell (20 mm path length) while being irradiated. As precursor of the oxidants we used thallium(I) sulfate, potassium peroxodisulfate and sodium azide in an excess of 10 times of the concentration of the aziridine.

Upon radiolysis in water OH radicals and solvated electrons were generated.^[40–42] By using a N₂O-saturated solution the amount of the OH radicals was increased through the reaction: N₂O + H₂O → N₂ + OH[•] + OH⁻.^[43] The OH radical was important for the formation of the oxidants. In the case of thallium(I) sulfate the oxidizing species was generated according to the reaction: Tl⁺ + OH[•] → TlOH^{•+}.^[21] By using sodium azide, the N₃[•] was formed via N₃⁻ + OH[•] → N₃[•] + OH⁻.^[44] In the measurements with peroxodisulfate, the produced solvated electrons create the sulfate radical anion: S₂O₈²⁻ + e⁻ → SO₄²⁻ + SO₄^{•-}.^[26,27] In this case the OH radicals could disturb, therefore *tert*-butanol was added in order to trap the OH radicals.^[23,45] Pulsing in *n*-butyl chloride, solvent radical cations were formed on direct ionization.^[25,46] All these reactive species can oxidize the substrates in a one electron transfer reaction. The corresponding substrate radical cations were formed.

γ Radiolysis: γ Radiolysis of 10⁻²–10⁻³ M solutions of organic samples in Freons at 77 K constitute a very clean way of generating radical cations under conditions where they persist for hours.^[46] For the present experiments we employed a 1:1 mixture of CFCl₃ and CF₂BrCF₂Br^[47] which formed a transparent glass at 77 K.^[48] Samples were exposed to a total dose of about 5 kSv of ⁶⁰Co radiation (1.173 and 1.332 MeV) in a Gammacell 220 charged with about 450 TBq. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 900 instrument.

Quantum chemical calculations: The geometries of all species except the singlet nitrenes were optimized by the B3LYP density functional method^[49,50] as implemented in the Gaussian program package,^[51,52] using the 6-31G* basis set. All stationary points were characterized by second derivative calculations.

For the ylide radical cation, **8^{•+}** that resulted from oxidative ring opening of 1-methyl-2-phenylaziridine **3c**, excitation energies and oscillator strengths were calculated by the CASSCF/CASPT2 procedure^[53] by using the ANO/S basis set,^[54] at the B3LYP/6-31G* optimized geometries of

the radical cations. The active space that was employed in the CASSCF calculations is indicated in Table 1 where the results are listed. Level shifts^[55] had to be applied to eliminate intruder states in the CASPT2 runs for all excited states under consideration, but we checked carefully that no artefacts were introduced by this technique. Under this condition, the weight of the zero-order CASSCF wavefunction in the PT2 expansion was between 0.7 and 0.72 for all states. All CASSCF/CASPT2 calculations were performed with the Molcas program.^[56]

For the diphenylaziridines, it was impossible to carry out CASSCF/CASPT2 calculations so we resorted to the more economical time-dependent response theory,^[57] where the poles and the residues of the frequency-dependent polarizability are calculated, whereby the former correspond to vertical excitation energies and the latter to oscillator strengths. We employed the density-functional based implementation of this method (TD-DFT)^[58] using again the B3LYP functional and the 6-31G* basis set as described above.

Acknowledgement

Support provided by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. T.B. and B.M. are grateful for support by the Swiss National Science Foundation (project No. 2000-067881.02). C.G. thanks the Studienstiftung des Deutschen Volkes for a scholarship.

- [1] J. Backes in *Methoden der Organischen Chemie Houben-Weyl, Vol. E 16c* (Ed.: D. Klamann), Thieme, Stuttgart, **1992**, pp. 370–677.
- [2] J. A. Deyrup in: *Small Ring Heterocycles, Vol. Part 1* (Ed.: A. Hassner), Wiley, New York, **1983**, pp. 1–214.
- [3] R. Huisgen, *Angew. Chem.* **1963**, 75, 604; *Angew. Chem. Engl. Int. Ed.* **1963**, 2, 656.
- [4] J. W. Lown, *Rec. Chem. Prog.* **1971**, 32, 51.
- [5] R. Huisgen in *1,3-Dipolar Cycloaddition Chemistry, Vol. 1* (Ed.: A. Padwa), Wiley, New York, **1984**, pp. 1–176.
- [6] V. Caer, A. Laurent, E. Laurent, R. Tardevil, Z. Cebulska, R. Bartnik, *Nouv. J. Chim.* **1987**, 11, 351.
- [7] T. Brigaud, E. Laurent, R. Tardevil, Z. Cebulska, R. Bartnik, *J. Chem. Res. Synop.* **1994**, 8, 330.
- [8] C. Gaebert, Diploma Thesis, Westfälische Wilhelms-Universität, Münster (Germany), **1994**.
- [9] C. Gaebert, PhD Thesis, Westfälische Wilhelms-Universität, Münster (Germany), **1997**.
- [10] C. Gaebert, J. Mattay, *J. Inf. Record.* **1996**, 23, 3.
- [11] C. Gaebert, J. Mattay, *Tetrahedron* **1997**, 53, 14297.
- [12] C. Gaebert, C. Siegner, J. Mattay, M. Toubartz, S. Steenken, *J. Chem. Soc. Perkin Trans. 2* **1998**, 2735.
- [13] C. Siegner, C. Gaebert, J. Mattay, S. Steenken, *J. Inf. Record.* **1998**, 24, 253.
- [14] J. L. Holmes, J. K. Terlouw, *Can. J. Chem.* **1976**, 54, 1007.
- [15] A. Maquestiau, Y. van Haverbeke, R. Flammang, A. Menu, *Bull. Soc. Chim. Belg.* **1979**, 88, 53.
- [16] M. H. Lien, A. C. Hopkinson, *Can. J. Chem.* **1984**, 62, 922.
- [17] A. P. Schaap, G. Prasad, S. D. Gagnon, *Tetrahedron Lett.* **1983**, 24, 3047.
- [18] A. P. Schaap, S. Siddiqui, G. Prasad, E. Palomino, L. Lopez, *J. Photochem.* **1984**, 25, 167.
- [19] A. P. Schaap, G. Prasad, S. Siddiqui, *Tetrahedron Lett.* **1984**, 25, 3035.
- [20] X.-Z. Qin, F. Williams, *J. Phys. Chem.* **1986**, 90, 2292.
- [21] P. O'Neill, D. Schulte-Frohlinde, *J. Chem. Soc. Chem. Commun.* **1975**, 387.
- [22] H. Christensen, *Int. J. Radiat. Phys. Chem.* **1972**, 4, 311–333.
- [23] H. Christensen, K. Sehested, E. J. Hart, *J. Phys. Chem.* **1973**, 77, 983.
- [24] P. O'Neill, S. Steenken, D. Schulte-Frohlinde, *J. Phys. Chem.* **1975**, 79, 2773.
- [25] T. Shida, W. H. Hamill, *J. Chem. Phys.* **1966**, 44, 2369.
- [26] E. Heckel, A. Henglein, *Ber. Bunsenges. Phys. Chem.* **1966**, 70, 149.
- [27] L. Dogliotti, E. Hayon, *J. Phys. Chem.* **1967**, 71, 2511.
- [28] B. Müller, PhD Thesis, University of Fribourg, Fribourg (Switzerland), **2000**.
- [29] Interestingly, laser flash photolysis of **3b** in a 1:1 mixture of acetonitrile and water gave also rise to a band at 430 nm (in contrast to the spectra observed previously in pure acetonitrile or methanol), next to those of the azomethine ylide at 500 nm and a 280 nm band that was assigned to an iminium ion obtained by protonation of the azomethine ylide. Thus, it appears that in the presence of water aziridine radical cations and their ring-opening products can also be formed by flash photolysis (see C. Gaebert, C. Siegner, J. Mattay, M. Toubartz, S. Steenken, *Photochem. Photobiol. Sci.* **2004**, 3, 990).
- [30] The bands at 480 and 500 nm persisted on radiolysis of oxygen-saturated BuCl solutions, where the radical cations were not formed. The species responsible for these bands were therefore not very sensitive to molecular oxygen, in accord with their assignment to neutral azomethine ylides.
- [31] R. J. Lichter, K. Crimaldi, D. A. Baker, *J. Org. Chem.* **1982**, 47, 3524.
- [32] K. N. Houk, S. Searles, M. D. Rozeboom, S. E. Seyedrezai, *J. Am. Chem. Soc.* **1982**, 104, 3448.
- [33] An intrinsic reaction coordinate calculation from the transition state for ring opening of **5** leads to the *exo-exo* isomer of the triphenylazomethine ylide radical cation which was, however easily converted into the more stable *exo-endo* isomer.
- [34] H. W. Heine, B. L. Kapur, C. S. Mitch, *J. Am. Chem. Soc.* **1954**, 76, 1173.
- [35] V. Franzen, H. E. Driesen, *Chem. Ber.* **1963**, 96, 1881.
- [36] D. Tanner, C. Birgersson, A. Gogoll, *Tetrahedron* **1994**, 50, 9797.
- [37] I. Okada, K. Ichimura, R. Sudo, *Bull. Chem. Soc. Jpn.* **1970**, 43, 1185.
- [38] N. B. Chapman, D. J. Trigg, *J. Chem. Soc.* **1963**, 1385.
- [39] J. A. Deyrup, C. L. Moyer, *J. Org. Chem.* **1969**, 34, 175.
- [40] A. Henglein, W. Schnabel, J. Wendenburg, *Einführung in die Strahlenchemie*, Verlag Chemie, Weinheim **1969**.
- [41] I. G. Draganic, Z. D. Draganic, *The Radiation Chemistry of Water*, Academic Press, New York, **1971**.
- [42] R. W. T. Spinks, R. J. Woods, *An Introduction to Radiation Chemistry*, Wiley, New York, **1990**.
- [43] J. H. Baxendale, M. A. Rodgers, *Chem. Soc. Rev.* **1978**, 7, 235.
- [44] Z. B. Alfassi, R. H. Schuler, *J. Phys. Chem.* **1985**, 89, 3359.
- [45] E. Bothe, D. J. Deeble, D. G. E. Lemaire, R. Rashid, M. N. Schuchmann, H.-P. Schuchmann, D. Schulte-Frohlinde, S. Steenken, C. von Sonntag, *Radiat. Phys. Chem.* **1990**, 36, 149.
- [46] T. Shida, *Electronic Absorption Spectra of Radical Ions*, Elsevier, Amsterdam, **1988**.
- [47] A. Grimison, G. A. Simpson, *J. Phys. Chem.* **1968**, 72, 1776.
- [48] C. Sandorfy, *Can. J. Spectrosc.* **1965**, 10, 85.
- [49] A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648.
- [50] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, 37, 785.
- [51] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pommelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Repogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.
- [52] B. G. Johnson, P. M. W. Gill, J. A. Pople, *J. Chem. Phys.* **1993**, 98, 5612.

- [53] K. Andersson, B. O. Roos in *Modern Electronic Structure Theory, Vol. Part 1, Vol. 2* (Ed.: D. R. Yarkony), World Scientific Publ., Singapore, **1995**, pp. 55.
- [54] K. Pierloot, B. Dumez, P.-O. Widmark, B. O. Roos, *Theor. Chim. Acta* **1995**, *90*, 87.
- [55] B. O. Roos, K. Andersson, M. P. Fülcher, L. Serrano-Andrés, K. Pierloot, M. Merchan, V. Molina, *J. Mol. Struct.* **1996**, *388*, 257.
- [56] K. Andersson, M. Barysz, A. Bernhardsson, M. R. A. Blomberg, D. L. Cooper, T. Fleig, M. P. Fülcher, C. d. Graaf, B. A. Hess, G. Karlström, R. Lindh, P.-Å. Malmqvist, P. Neogrády, J. Olsen, B. O. Roos, A. J. Sadlej, M. Schütz, B. Schimmelpfennig, L. Seijo, L. Serrano-Andrés, P. E. M. Siegbahn, J. Stålring, T. Thorsteinsson, V. Ver- yazov, P.-O. Widmark, University of Lund (Sweden), **2000**.
- [57] M. E. Casida in *Recent Advances in Density Functional Methods, Part I* (Ed.: D. P. Chong), World Scientific Publ., Singapore, **1995**, pp. 155.
- [58] R. E. Stratmann, G. E. Scuseria, M. J. Frisch, *J. Chem. Phys.* **1998**, *109*, 8218.

Received: June 4, 2004

Published online: January 5, 2005