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Mendeleev Commun., 2016, **26**, 332–334

Mendeleev
Communications

Cyclic form of the aziridine radical cation in a CF_3CCl_3 matrix at 77 K

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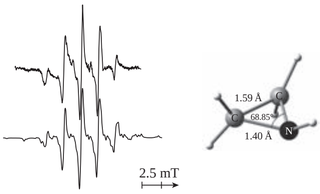
DOI: 10.1016/j.mencom.2016.07.022

The radical cations of aziridine can be stabilized in the matrix of CF_3CCl_3 at 77 K in a cyclic form.



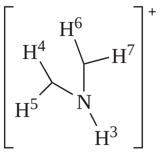
The radical cations (RCs) of three-membered heterocycles (oxiranes, aziridine), yielded in low-temperature matrices upon the action of ionizing radiation at 77 K, can be stabilized in cyclic forms and in open forms, which are isoelectronic to allyl radicals.[1–3] While the possibility of stabilizing the RCs of oxiranes in both open and cyclic forms has been successfully demonstrated, along with the possibility of detecting reversible transformations between those forms (thermally and photochemically induced),[4,5] in the case of aziridine RCs, only the possibility of stabilizing them in $CFCl_3$ at 150 K has been established (merely in their open form).[3]

The aim of this work was to study the stabilization of aziridine RCs in low-temperature matrices in their cyclic form and to compare the reactivity of those species to the reactivities of RCs originating from their closest structural analogues (oxiranes, azetidine), if possible.

$CFCl_3$ (~99%, Aldrich) and CF_3CCl_3 [>99% according to NMR data, obtained from 99% $CF_2ClCFCl_2$ (Aldrich) using a known procedure[6]] were employed as matrices. Aziridine was synthesized in accordance with a published procedure,[7] and its yield was controlled by NMR spectroscopy. The sample preparation procedures, irradiation techniques, detection methodology related to EPR and optical absorption spectra and the procedure of photochemical experiments were described earlier.[4]

Calculations were performed using the unrestricted DFT method and the ORCA 3.0.3 program package.[8] The B3LYP functional with the full-electron TZVP basis set[9] was used to calculate the geometry of potential energy surface minima and transition states; the geometries were additionally checked for the presence or absence of imaginary vibration frequencies. The spin-Hamiltonian parameters were calculated using the B3LYP functional together with the full-electron N07D basis set,[10] dipole contributions to the anisotropic hfc constants were calculated on the UKS/PBE0/def2-QZVPP level. To estimate the solvent effect, the COSMO model was used in all of the calculations.[11]

The quantum chemical calculations demonstrate that, upon photoionization for the aziridine RC, not only the delocalized open form is stable (yielded upon C–C bond dissociation, **1**), but the same can be said about the cyclic form (**2**), which is stable in two conformations that can be differentiated by referring to the mirror symmetry of the α-H atom positions relative to the aziridine ring plane. The height of the barrier along the pathway related to the mutual transformations of these does not exceed ~8 kJ mol^{-1}. Meanwhile, for the transition state lying along this pathway, the α-H atom is positioned within the ring plane of **2a**. While attempting to analyse a cross-section of the PES, which follows the coordinate corresponding to C–N bond cleavage, intramolecular atom transfer was observed for a methylene hydrogen atom in the aziridine RC, resulting in $MeCH{=}NH^{+\bullet}$ **3**.



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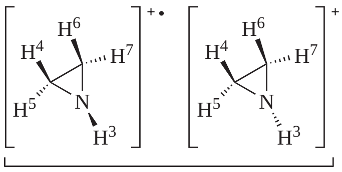

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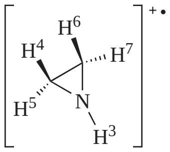
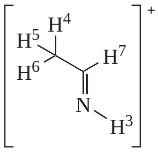


2a



3

The EPR spectrum detected in frozen aziridine/CF_3CCl_3 solutions (0.3–0.5 mol%) at 77 K can be represented as a superposition of an odd and an even signal [Figure 1(*a*)]; the linewidth in the latter notably exceeds the linewidth in the former. At the same time, absorption bands at 420–750 nm arise in the optical absorption spectrum of the sample. Light with λ > 690 nm provokes a decrease in the absorbance of bands with maxima at $\lambda \approx 415$ and 650 nm, which can be attributed to matrix centers of varying nature,[12] while not leading to significant transformations in the shape of the EPR spectrum. The subsequent action of light with $\lambda = 546$ nm results in the disappearance of a complex band that can be depicted as a superposition of two Gauss-shaped bands with their maxima at 425 nm (~23600 cm^{-1}) and 505–510 nm (~19700 cm^{-1}) (Figure 2). The EPR spectrum of paramagnetic species remaining in the sample upon photolysis with visible light [$\lambda = 546$ nm, Figure 1(*b*)] can be suitably simulated when employing a Lorentzian linewidth of ~0.88 mT, measured between

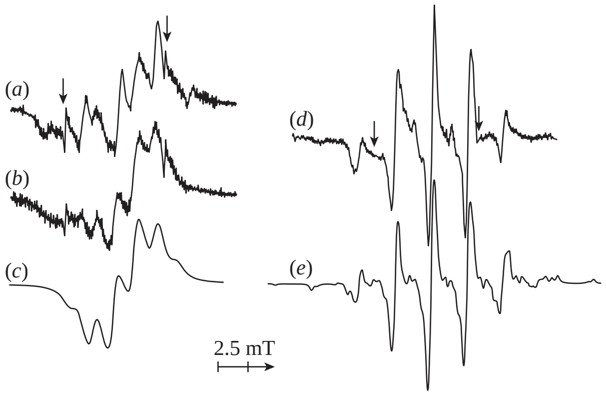


Figure 1 EPR spectra detected in irradiated aziridine/CF_3CCl_3 solutions (*a*) immediately after X-ray irradiation at 77 K and (*b*) after the action of light with λ = 546 nm upon the irradiated sample at 77 K; (*d*) difference EPR spectrum of species transformed upon the action of light; (*c*), (*e*) simulation results for EPR spectra (*a*) and (*d*), respectively (parameters given in Table 1). Arrows point to the third and fourth components of the hyperfine structure of the additional Mn^{2+} ions in MgO powder.

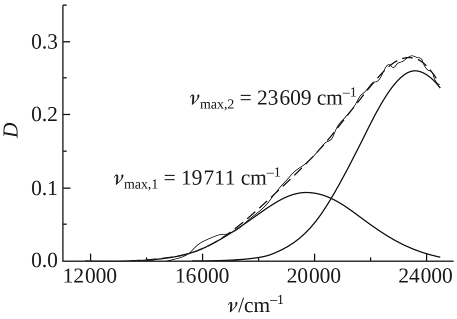


Figure 2 Absorption band disappearing upon the action of light with λ = 546 nm on the irradiated aziridine/CF_3CCl_3 sample at 77 K (thin solid line), and its multi-peak fit (dashed line, Gaussian shape) composed of two peaks (thick solid lines, approximate locations of maxima presented in the figure).

two points of maximum incline, and the following isotropic hfc constants: a_{iso}(4H) = 1.61 mT, a_{iso}(1H) = 0.43 mT and a_{iso}(^{14}N) = = 0.77 mT [Figure 1(*c*)]. The comparison of the fitting results obtained for the experimental spectra with published data[3] and the results of quantum calculations (Table 1) allowed us to conclude that the six-line EPR spectrum should be attributed to the open form of the RC (**1**).

Meanwhile, the difference EPR spectrum obtained upon subtracting the spectrum detected in the sample after the action of light with λ = 546 nm from the spectrum detected upon X-ray irradiation [Figure 1(*d*)] is an odd one. For its interpretation, we had to assess the results of our quantum chemical calculations. Note that the experimentally measured shift of the difference signal center to the region of lower magnetic induction relative to the center of the six-line signal amounts to ~0.3 mT; this value corresponds to a difference between the isotropic *g*-factors of the two paramagnetic species amounting to ~0.002. The integral intensity of the difference signal in the EPR spectrum of the aziridine RC is no higher than 30% of the total integral intensity in the initial EPR spectrum of the RC.

Essentially, the quantum chemical computations for the cyclic RC form (**2**, Table 1) can be used as a source of hfc constants, specifically, *a*(2H) and *a*(^{14}N), which are required for simulating the odd EPR signal. However, this fitting appears rather artificial since it does not address several unanswered questions: namely, those pertaining to small computed values for the two methylene hfc constants, to the unaccounted anisotropy of hfc with the nitrogen atom and to the large value for the hfc constant with the α-H atom, *a*(H^3). The energy barrier that characterizes a transition between the two conformations of the cyclic form of the RC is quite low, essentially denying the possibility of identifying either one of the conformations as preferable. This, combined with the notion of the α-H atom residing in the plane of the cycle for the transition state lying between the two cyclic minima, allows us to treat the calculated hfc constants for the transition state as being qualitatively indicative of averaging along the reaction pathway on the PES: since the reaction profile is symmetrical, averaged parameters and those characterizing the transition state are of a similar order of magnitude. Consequently, this allowed us to use these parameters (see Table 1) as initial when fitting the difference spectrum. These constants were optimized within an isotropic approximation for methylene hydrogen atoms and anisotropically for the α-H and nitrogen atoms. This fitting led us to a reasonable representation of the spectrum with the Lorentzian linewidth of ~0.20 mT, measured between two points of maximum incline, with the following hfc constants: a_{iso}(4H) = 3.19 mT, a_{xx}(1H) = –3.32 mT, a_{yy}(1H) = –3.69 mT, a_{zz}(1H) = –2.01 mT, $a_{||}$(^{14}N) = 7.42 mT and $a_{\perp}$(^{14}N) = 1.70 mT [Figure 1(*e*)].

Table 1 Calculation results for dipole–dipole components and fitting results in regard to hfc constants with hydrogen and nitrogen atoms in various forms of aziridine RCs (H^4, H^5 and H^6, H^7 are hydrogen atoms in methylene groups); as well as calculation results for *g*-tensors.

RC	a_{iso}(H^3)/ mT	a_{iso}(H^4)/ mT	a_{iso}(H^5)/ mT	a_{iso}(H^6)/ mT	a_{iso}(H^7)/ mT	a_{iso}(N)/ mT
1[a]	0.45	–1.79	–1.69	–1.69	–1.79	–0.80
	g_{xx} = 2.0022; g_{yy} = 2.0023; g_{zz} = 2.0026; g_{iso} = 2.0024					
Open, C–C bond cleavage: fitting	0.29	1.63	1.63	1.63	1.63	0.90
2[a]	–1.24	3.69	0.53	0.54	3.68	3.07
	g_{xx} = 2.0021; g_{yy} = 2.0040; g_{zz} = 2.0050; g_{iso} = 2.0037					
2a	–2.42[b] (a_{xx} = –0.29, a_{yy} = –4.26, a_{zz} = –2.72)[b]	3.53[a]	3.53[a]	3.53[a]	3.53[a]	2.80[b] ($a_{\parallel}$ = 5.94, $a_{\perp}$ = 1.23)[b]
	g_{xx} = 2.0047; g_{yy} = 2.0042; g_{zz} = 2.0022; g_{iso} = 2.0037[a]					
Difference spectrum: fitting	–3.01 (a_{xx} = –3.32, a_{yy} = –3.69, a_{zz} = –2.01)	3.19	3.19	3.19	3.19	3.61 ($a_{\parallel}$ = 7.42, $a_{\perp}$ = 1.70)
3[a]	–0.01	–0.02	–0.35	–0.02	7.26	3.64
	g_{xx} = 2.0021; g_{yy} = 2.0024; g_{zz} = 2.0036; g_{iso} = 2.0027					

[a] UKS/B3LYP/NO7D. [b] UKS/PBE0/def2-QZVPP.

In our explanation of the EPR spectra, as compared to the absorption spectra, we attributed the odd EPR spectrum to the cyclic form of the aziridine RC. Note that the absorption band at $\lambda \approx$ 505–510 nm, which disappears in parallel with the decrease of the overall intensity in the above EPR signal, was associated with the same form of the RC. Published data on the absorption spectra of the triethylenediamine RC in a Freon mixture matrix ($\lambda_{max} \approx$ 470 nm[13]), the *N*-methoxy-2,2,6,6-tetramethylpiperidine RC in an *n*-butyl chloride solution ($\lambda_{max} \approx$ 500 nm[14]) and the azetidine RC in CF_3CCl_3 ($\lambda_{max} \approx$ 500 nm[15]) support this interpretation.

In the EPR spectra detected upon the photoinduced transformation of the cyclic RC form, not even trace amounts of the characteristic aziridinyl radical signal can be detected,[3] which excludes deprotonation of the cyclic aziridine RC from the list of possible photochemical mechanisms. Since the integral intensity of the EPR spectrum is roughly preserved upon photolysis, this allows us to interpret the reaction mechanism as a result of C–C bond cleavage with the subsequent formation of the aziridine

RC in its open form (**1**). Accordingly, the photoinduced transformation pathway of the cyclic aziridine RC is identical to the reactions of the cyclic RC forms originating from oxiranes[4,5] while being drastically different from the pathway for the azetidine RC, in which C–N bond cleavage yields a mixture of distonic RCs.[11]

We cannot unambiguously interpret the absence of a cyclic aziridine RC form from the products of X-ray irradiation in aziridine/$CFCl_3$ solutions at 77 K: this behavior is fundamentally different from that observed for the RCs of methyloxiranes under analogous conditions.[4,5] Note that we failed to detect any thermally induced transformations of the cyclic aziridine RC form at $T \leqslant 111$ K, which is close to the softening region of a CF_3CCl_3 matrix (this behavior also distinguishes the aziridine RC in comparison with the RCs of methyloxiranes[4,5]). Since the calculated gas-phase barriers on the pathways of transformation between the cyclic oxirane-derived and aziridine RCs and their open forms (known from literature data[16] and found in this work) are about 38 kJ mol^{-1}, we are forced to assume that significant discrepancies may be discovered for the relaxation mechanisms characteristic of the cyclic RC forms yielded from these compounds upon secondary ionization in various low-temperature matrices.

This work was supported by the Russian Foundation for Basic Research (project nos. 13-03-00099 and 14-03-32014).

The calculations were performed using the resources of the Supercomputing Center of the M. V. Lomonosov Moscow State University.[17]

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Received: 1st February 2016; Com. 16/4828