Transformations of 5-membered heterocyclic radical cations as studied by low-temperature EPR and quantum chemical methods

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Intramolecular transformations of 3-pyrroline (2,5-dihydropyrrole, 2,5-DHP) radical cation radiolytically generated in Freon matrices were investigated using low temperature EPR spectroscopy. DFT quantum chemical calculations made it possible to assign the observed transients and to explain the observed transformations. The primary nitrogen-centred radical cation 2,5-DHP$^{+\bullet}$ is thermally stable, but on illumination with visible light of wavelengths $\lambda > 600$ nm it is transformed by intramolecular H-shift into 2,4-DHP$^{+\bullet}$. The latter is stable at 77 K but its further intramolecular rearrangements through $2 \rightarrow 3$ and $4 \rightarrow 3$ H-shifts can be induced by illumination with visible light of shorter wavelengths (400 nm $< \lambda <$ 600 nm). Both transformations proceed simultaneously, with similar yields of the two isomers of the DHP radical cation, namely 2,3-DHP$^{+\bullet}$ and 3,4-DHP$^{+\bullet}$. The overall transformation pattern is analogous to that established earlier for 2,5-dihydrofuran radical cation. In irradiated F-113 solutions of 2,5-DHP the spectrum of a neutral radical was observed and assigned to one of the two most stable possible structures of pyrrolinyl radicals.

Introduction

Theoretical and experimental results indicate that conventional radical cations are often less stable than their isomers, which do not have a neutral parent molecule. Such isomers may be spontaneously formed by a single intramolecular hydrogen transfer, resulting in a distonic form, characterised by spatially separated charge and radical site.

The technique of low-temperature EPR spectroscopy in a Freon matrix is well established and has been used successfully to investigate a large variety of radical cations, generated radiolytically through positive charge transfer from matrix to solute. In our earlier study,[1] dealing with radical cations of 2,5-dihydrofuran (2,5-DHF), the primary radical cation 2,5-DHF$^{+\bullet}$ was found to be unstable even at 77 K and to undergo irreversible transformation *via* intramolecular $5 \rightarrow 4$ H-shift to the double bond within the molecular ring. The product of this rearrangement, the 2,4-DHF$^{+\bullet}$ radical cation, was quite stable up to temperatures around 145 K; however, its further intramolecular rearrangements through $2 \rightarrow 3$ and $4 \rightarrow 3$ H-shifts could be induced by illumination with visible light.[2]

The present study was aimed at the investigation of radical cations derived from 3-pyrroline (2,5-dihydropyrrole, 2,5-DHP), which is isoelectronic with 2,5-DHF. CF$_3$CCl$_3$ and CFCl$_2$CF$_2$Cl (F-113) were chosen as matrices because of their specific characteristics. CF$_3$CCl$_3$ is more rigid, thus preventing solute diffusion below about 145 K and weaker matrix–solute interaction leads to better resolved spectra. On the other hand the F-113 matrix becomes soft above its phase-transition region around 110 K and migration of molecules then makes ion–molecular reactions possible even at low solute concentrations. However, the F-113 matrix interaction with the solute is often strong and may lead to anisotropic line broadening.[3,4]

Quantum chemical calculations were used to support the interpretation of the experimental results and to assist in the identification of transient species through comparison of the experimental and computed hfs splitting constants.

Experimental and computation methods

The EPR experiments were performed using a Bruker 300E spectrometer (9.5 GHz, 100 kHz modulation) equipped with either a finger Dewar (77 K) or a variable temperature control unit ER 4121 VT (above 95 K). Spectra were recorded at a microwave power of 0.1 mW and modulation amplitude of 0.1 mT. The 3-pyrroline (Lancaster, 97%) and CFCl$_2$CF$_2$Cl (Merck, Uvasol 99.9%) were used as supplied. CF$_3$CCl$_3$ (Acros, 99%) was purified by passing it through a column filled with neutral alumina. Further details on sample preparation and irradiation in liquid nitrogen with the 10-MeV electron beam of a Linac are described elsewhere.[1] A tungsten lamp (250 W) equipped with a water heat-filter and colour glass filters was used for photobleaching of irradiated samples. WinSim software[5] and the SimFonia software package (Bruker) were used for isotropic and anisotropic spectra simulations, respectively.

Quantum chemical calculations were performed using the Gaussian 98, Revision A.11 program.[6] To provide an accurate calculation of hfs splitting constants, the accurate description of the geometrical structure of the molecule, good electron correlation and well-defined basis sets are needed. Molecular and electronic structures of radical cations and neutral radicals were investigated by the density functional theory (DFT) hybrid B3LYP method[7–9] with standard 6-31G(d) basis set, because the hfs splitting constants calculated using the B3LYP method have shown very good agreement with experiment for different transients derived from DHF in a Freon matrix.[1,2] The frequency calculations were also used to locate transition state geometries, to determine the nature of stationary points found by geometry optimisation, and to obtain thermochemical parameters such as zero-point energy, activation energy (height of H-shift barrier) and reaction enthalpy. The electronic transition spectra of transients were calculated with the unrestricted time dependent (UTD) B3LYP/6-31 + G(d,p) method.[10]

Results and discussion

The EPR spectrum recorded with a solution of 2,5-DHP in CF$_3$CCl$_3$ (1 : 700) irradiated at 77 K and warmed to 140 K is
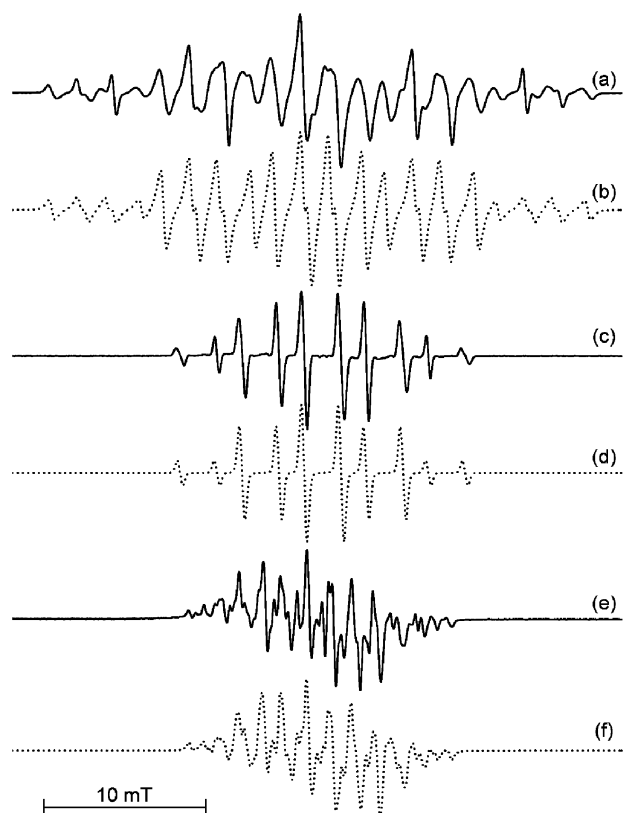
shown in Fig. 1(a); the spectral change between 77 K and 140 K was quite reversible, the spectrum at 140 K being only better resolved. The spectrum is assigned to the primary nitrogen-centred radical cation $1^{+\bullet}$ of 2,5-DHP (2,5-DHP$^{+\bullet}$), characterised by four strongly coupling β-protons (a(4H) = 6.86 mT). The simulated spectrum of $1^{+\bullet}$ is shown in Fig. 1(b) and the hfs splitting constants, together with the calculated values, are given in Table 1. A slight discrepancy between simulation and experiment indicates the presence of a second species, its probable nature will be discussed below. The primary nitrogen-centred 2,5-DHP$^{+\bullet}$($1^{+\bullet}$) is similar to the primary oxygen-centred radical cation of 2,5-DHF, which was however unstable at 77 K and spontaneously transformed into the 2,4-DHF$^{+\bullet}$ radical cation,[1] as is shown in the scheme in Fig. 2(a).

In order to test the stability and possible transformations of the primary radical cation $1^{+\bullet}$, photobleaching experiments were performed. The EPR spectrum measured at 143 K for the sample photobleached at 77 K with visible light of wavelengths $\lambda > 600$ nm is shown in Fig. 1(c). The spectrum is almost identical with that of the 2,4-DHF$^{+\bullet}$ radical cation[1] and is assigned to 2,4-DHP$^{+\bullet}$($2^{+\bullet}$). Its simulated spectrum is shown in Fig. 1(d) and the corresponding hfs splitting constants are given in Table 1. The higher stability of the primary $1^{+\bullet}$ when compared with 2,5-DHF$^{+\bullet}$ is due to the considerably higher energy barrier for the 5 → 4 H-shift (90 and 67 kJ mol^{-1}, respectively, $cf.$ Fig. 2(a) and 2(b)).

It is reasonable to assume that $2^{+\bullet}$ is present at a certain amount already after the irradiation and that it contributes as the second species to the spectrum shown in Fig. 1(a). Indeed, the agreement between simulation and the experiment can be slightly improved if a small contribution ($\sim$10%) of $2^{+\bullet}$ is taken into account. The formation of $2^{+\bullet}$ during the irradiation can be explained under the assumption that the photochemical transformation is induced by the Tscherenkow-light.

The 2,4-DHP$^{+\bullet}$ radical cation ($2^{+\bullet}$) is stable in CF$_3$CCl$_3$ up to the matrix softening point (145 K), but its further

Fig. 1 EPR spectra measured with irradiated 2,5-DHP in CF$_3$CCl$_3$ (1 : 700) (a) at 140 K, (c) at 143 K after photobleaching (77 K) with $\lambda > 600$ nm, (e) at 143 K after further photobleaching (77 K) with 400 nm $< \lambda < 600$ nm. Dotted lines show simulated spectra of (b) 2,5-DHP$^{+\bullet}$, (d) 2,4-DHP$^{+\bullet}$ and (f) a 1 : 1 mixture of 2,3-DHP$^{+\bullet}$ and 3,4-DHP$^{+\bullet}$; the hfs splitting constants are summarized in Table 1.

Table 1 Experimental and calculated hfs splitting constant a (mT) and calculated (B3LYP/6-31G(d)) relative energies ΔE (kJ mol^{-1}) and atomic spin densities ρ of possible isomers of DHP radical cation; λ (nm) are the first two exited states calculated with UTD/B3LYP/6-31+G(d,p) (oscillator strength is in parathenses)

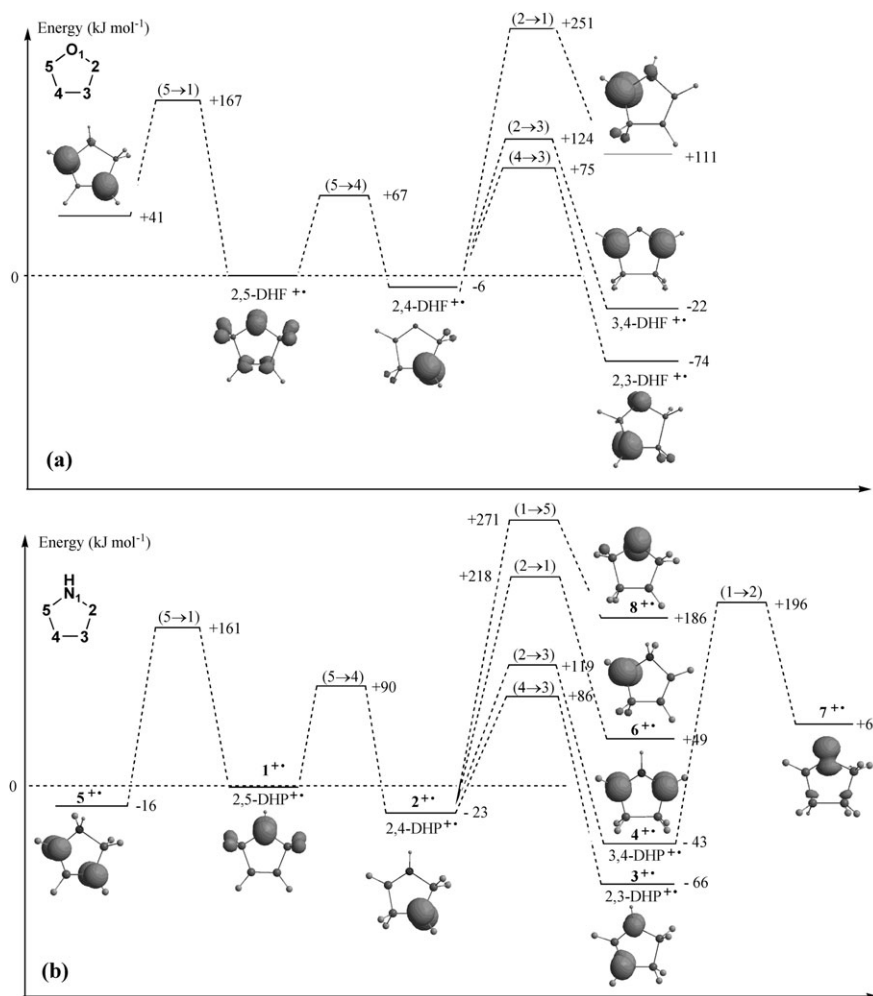| | $1^{+\bullet}$ (2,5-DHP$^{+\bullet}$) | | | $2^{+\bullet}$ (2,4-DHP$^{+\bullet}$) | | $3^{+\bullet}$ (2,3-DHP$^{+\bullet}$) | | $4^{+\bullet}$ (3,4-DHP$^{+\bullet}$) | | $5^{+\bullet}$ | $6^{+\bullet}$ | $7^{+\bullet}$ | $8^{+\bullet}$ |
	Calc.	Exp. CF$_3$CCl$_3$ 140 K	Exp. F-113 77 K	Calc.	Exp. CF$_3$CCl$_3$ 143 K	Calc.	Exp. CF$_3$CCl$_3$ 143 K	Calc.	Exp. CF$_3$CCl$_3$ 143 K	Calc.	Calc.	Calc.	Calc.
ΔE	0.0			−23.4		−65.9		−43.2		−15.5	+49.1	+61.9	+186.3
ρ(N)	0.689			−0.002		0.408		−0.181		−0.030	−0.05	0.823	0.908
ρ(C2)	−0.036			−0.076		−0.017		0.602		−0.049	−0.004	0.026	−0.056
ρ(C3)	0.044			1.028		−0.041		0.125		0.673	0.003	0.101	0.002
ρ(C4)	0.044			−0.077		0.609		0.125		−0.252	−0.078	0.103	0.042
ρ(C5)	−0.036			−0.000		−0.032		0.602		0.639	1.040	−0.088	−0.059
a_{iso}(N)	1.37	1.70		−0.008	—	0.85	0.87	−0.51	−0.61	−0.16	−0.28	3.43	1.53
a_x	0.30		0.35			0.18							
a_y	0.31		0.35			0.20							
a_z	3.51		3.70			2.18							
a(H,N)	−1.87	2.10	2.25	−0.05	—	−1.22	1.17	0.35	0.30	1.51	2.84	—	—
										1.51	2.84		
a(H,C2)	7.30	6.86	6.95	3.81	3.86	2.23	2.19	−1.71	−1.57	2.29	−0.04	0.26	5.82
	7.30	6.86	6.95	3.81	3.86	2.23	2.19			2.29		0.31	2.96
a(H,C3)	−0.15	—	—	−2.56	2.27	3.48	3.54	2.82	2.67	−1.73	−0.07	0.24	0.79
						3.48	3.54	2.82	2.67			0.44	0.11
a(H,C4)	−0.15	—	—	3.74	3.77	−1.56	1.56	2.82	2.67	0.42	4.09	−0.21	−0.18
				3.74	3.77			2.82	2.67		4.09	−0.02	
a(H,C5)	7.30	6.86	6.95	−0.05	0.17	−0.02	—	−1.71	−1.57	−1.75	−2.72	2.36	2.82
	7.30	6.86	6.95										1.27
λ	790(0.018)	Blue		582(0.003)	Yellow	297(0.023)		404(0.062)	Yellow-				
	295(0.002)			257(0.000)		245(0.000)		226(0.000)	Orange				

Fig. 2 Possible transformations and spin density distributions (isospin = 0.01) of different structures of (a) DHF and (b) DHP radical cations.
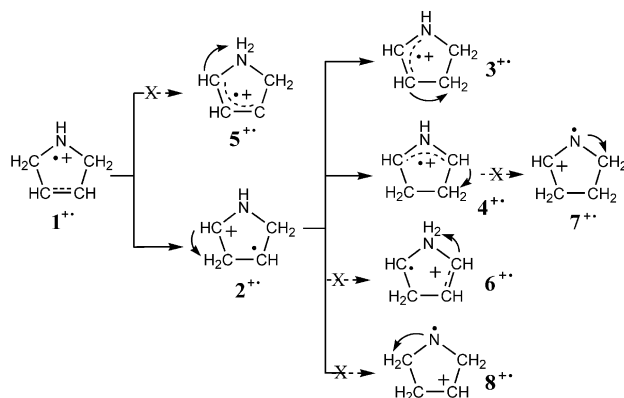
transformation was induced by illumination with the visible light of shorter wavelengths. The EPR spectrum measured at 143 K with irradiated sample photobleached at 77 K first with the light with $\lambda > 600$ nm and then with 400 nm $< \lambda < 600$ nm is shown in Fig. 1(e). This relatively complex spectrum is likely to contain more than one species and in order to explain it, the possible transformations of $2^{+\bullet}$ were quantum chemically investigated. The transformations are shown in Scheme 1 and Fig. 2(b) and the quantum chemical and EPR parameters are given in Table 1.

According to Fig. 2(b), the transformations of the radical cation 2,4-DHP$^{+\bullet}$ by intramolecular $2 \rightarrow 3$ and $4 \rightarrow 3$ H-shifts are feasible, similar to those described in the case of

Scheme 1

2,4-DHF$^{+\bullet}$, where formation of 2,3-DHF$^{+\bullet}$ and 3,4-DHF$^{+\bullet}$ with more-or-less the same yields was observed.[2] The spectrum shown in Fig. 1(f) was simulated as a 1:1 mixture of the 2,3-DHP$^{+\bullet}$($3^{+\bullet}$) and 3,4-DHP$^{+\bullet}$($4^{+\bullet}$), with the sets of hfs splitting constants (Table 1) in good agreement with calculations.

The energy of the light of wavelengths ≥ 400 nm (300 kJ mol^{-1}) is sufficient to induce both the $2 \rightarrow 3$ and $4 \rightarrow 3$ H-shifts (*cf.* scheme in Fig. 2(b)). Transformation then proceeds apparently on a statistical basis and more-or-less the same yields of both isomers can be expected, as was actually observed. When the sample photobleached with 400 nm $< \lambda < 600$ nm light was illuminated with light of shorter wavelengths (350 nm $< \lambda < 400$ nm), no further spectral changes were observed. This complies also with the scheme shown in Fig. 2(b) where all other transformations, which would lead to species $6^{+\bullet}$, $7^{+\bullet}$ or $8^{+\bullet}$, are unlikely to occur, due to the high energy barriers and unfavourable reaction enthalpies. Also, the energetically possible transformation of the primary radical cation $1^{+\bullet}$ *via* $5 \rightarrow 1$ H-shift into species $5^{+\bullet}$ was not observed, apparently due to the energy barrier being higher than that for the $5 \rightarrow 4$ H-shift.

Interestingly, calculations predict that all four detected DHP radical cations ($1^{+\bullet}$, $2^{+\bullet}$, $3^{+\bullet}$ and $4^{+\bullet}$) have planar structures, in agreement with the observed hfs splitting constants. In particular, since the 2,5-DHP radical cation shows 4 equivalent β-protons in contrast to the 2 sets of 2 equivalent β-protons observed for the saturated pyrrolidine radical cation,[11] the double bond in the ring apparently prevents the formation of a twisted structure. However, twisting does not occur in the

case of the saturated 4-membered ring azetidine radical cation.[12] In the latter case the calculations show that the planar structure is the stable one.

It should be mentioned that besides 3-pyrroline (2,5-dihydropyrrole) only 1-pyrroline (3,4-dihydro-2H-pyrrole) is known, however its corresponding radical cation (species $7^{+\bullet}$) was not observed.

The photobleaching of the irradiated sample was accompanied by colour changes. After photobleaching with $\lambda > 600$ nm the sample originally blue became pale yellow and on further photobleaching with 400 nm $< \lambda < 600$ nm it turned orange–yellow. The colour changes comply with the results of the UTD/B3LYP/6-31 + G(d,p) quantum-chemical calculations of the optical absorption spectra of individual DHP cations, which are given in Table 1. The 2,5-DHP$^{+\bullet}$ ($1^{+\bullet}$) and 3,4-DHP$^{+\bullet}$ ($4^{+\bullet}$) have strong absorption bands at 790 nm (blue–green) and at 404 nm (yellow), respectively. The 2,3-DHP$^{+\bullet}$($3^{+\bullet}$) apparently does not absorb in the visible and the observed colour of the sample after photobleaching with 400 nm $< \lambda < 600$ nm corresponds only to $4^{+\bullet}$.

Experiments similar to those with the CF$_3$CCl$_3$ matrix were performed also in F-113, where formation of radicals from radical cations by deprotonation or by H-abstraction can occur. Spectrum measured at 77 K with an irradiated solution of 2,5-DHP in F-113 (1 : 1000) is shown in Fig. 3(a). Spectrum of the primary radical cation ($1^{+\bullet}$) (Fig. 3(b)) was simulated with the set of hfs splitting constants given in Table 1, taking into account the anisotropy of the hfs tensor of nitrogen. On increasing the temperature, the spectrum of $1^{+\bullet}$ gradually disappeared (completely at about 110 K) and at temperatures above ∼120 K a new spectrum developed, which is shown in Fig. 3(c). The final spectrum decayed without further transformation. The spectrum in Fig. 3(c), recorded well above the matrix softening point, was suspected to belong to a radical derived from DHP and in order to assign it, all possible radical structures were investigated quantum chemically. The calculated atomic spin densities, relative stabilities and hfs splitting constants are summarized in Table 2.
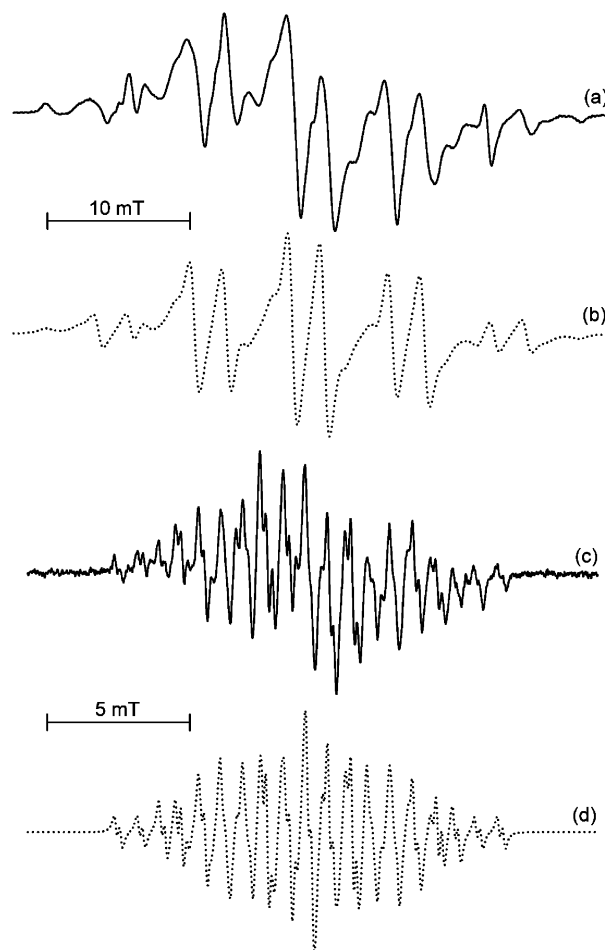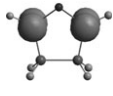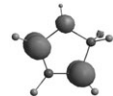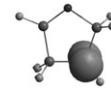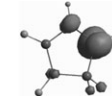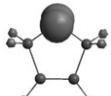

Fig. 3 EPR spectra measured with irradiated 2,5-DHP in F-113 (1 : 1000) at (a) 77 K and (c) 140 K. Dotted lines show simulated spectra of (b) 2,5-DHP$^{+\bullet}$ and (d) 2,3-DHP$^{\bullet}$, the hfs splitting constants are given in Tables 1 and 2.

Table 2 Experimental and calculated hfs splitting constant a (mT) and calculated (B3LYP/6-31G(d)) relative energies ΔE (kJ mol^{-1}) and atomic spin densities ρ of different structures of DHP radical

	9		10	11	12	13	14	
	Calc.	Exp.^{a}	Calc.	Calc.	Calc.	Calc.	Calc.	Exp.^{b}
ΔE	+1.1		0.0	+21.5	+52.8	+60.8	+69.4	
ρ(N)	0.542		−0.221	0.130	−0.004	0.106	0.918	
ρ(C2)	−0.033		0.642	−0.064	−0.080	0.812	−0.066	
ρ(C3)	−0.054		0.176	0.578	1.030	−0.082	−0.002	
ρ(C4)	0.695		0.176	−0.204	−0.083	0.139	−0.002	
ρ(C5)	−0.238		0.602	0.511	0.002	−0.065	−0.066	
a_{iso}(N)	0.90	0.80	−0.37	0.52	−0.03	−0.24	1.53	1.44
a(H,N)	—	—	—	0.56	—	0.50	—	—
a(H,C2)	2.18	2.14	−1.72	4.25	3.65	−0.89	4.34	4.47
	2.18	2.14		3.57	3.65		4.34	4.47
a(H,C3)	2.89	3.00	2.24	−1.45	−2.43	5.12	−0.04	—
	2.89	3.00	2.24			4.67		
a(H,C4)	−1.66	1.55	2.24	0.32	3.95	−0.34	−0.04	—
			2.24		3.95			
a(H,C5)	0.35	0.18	−1.72	−1.32	−0.02	0.11	4.34	4.47
							4.34	4.47

^{a} This work, 140 K, F-113. ^{b} Ref. 13, 241 K, adamantine.

The spectrum shown in Fig. 3(d) was simulated with the set of hfs splitting constants which agree well with those calculated for radical **9** (see Table 2); the letter is also one of the two energetically most stable species (see Table 2).

When an irradiated solution of 2,5-DHP in F-113 (1 : 1000) was photobleached at 77 K with light of $\lambda > 600$ nm, the spectrum of the radical cation 2,4-DHP$^{+\bullet}$ (**2$^{+\bullet}$**) was observed. By increasing the temperature again a transformation occurred and at 145 K, the spectrum of the species **9** was detected. Photobleaching of an irradiated solution of 2,5-DHP in F-113 at 77 K with non-filtered light resulted in a very poorly resolved spectrum, which could not be analysed, but after warming the sample, again the spectrum of the radical **9** was recorded at 145 K. Most likely there are some intermediate species existing between the DHP radical cations and the final radical **9**, but due to the spectral overlap and possible interference with the Freon-derived radicals, the spectra could not be analysed. To our knowledge there is only one paper dealing with pyrrolinyl free radicals, namely generated radiolytically in adamantane matrix.[13] In this case the radical **14** (Table 2) was identified at 241 K and our calculated hfs splitting constants agree well with the reported values. Radical **14** is on the one hand energetically a most unfavourable species; on the other hand its formation by H-abstraction from the N atom is feasible, nevertheless we were not able to see it in our experimental EPR spectra.

Conclusion

The primary nitrogen-centred radical cation 2,5-DHP$^{+\bullet}$(**1$^{+\bullet}$**), radiolytically generated in Freon matrices, is relatively stable (in CF_3CCl_3 up to 140 K), but on illumination with visible light of wavelengths $\lambda > 600$ nm it is transformed by an intramolecular $5 \rightarrow 4$ H-shift into 2,4-DHP$^{+\bullet}$(**2$^{+\bullet}$**). The latter is again thermally stable (up to 143 K), but its further intramolecular rearrangements through $2 \rightarrow 3$ and $4 \rightarrow 3$ H-shifts can be induced by illumination with visible light of shorter wavelengths (400 nm $< \lambda <$ 600 nm). Both transformations proceed simultaneously, with the same yields of the two isomers of the DHP radical cation, namely 2,3-DHP$^{+\bullet}$(**3$^{+\bullet}$**) and 3,4-DHP$^{+\bullet}$(**4$^{+\bullet}$**). These intramolecular H-shifts are most feasible also due to strong localisation of the unpaired electron in position 4 in **2$^{+\bullet}$**. The overall transformation pattern is analogous to that established earlier for the 2,5-dihydrofuran radical cation.

In irradiated F-113 solutions of 2,5-DHP a spectrum of a neutral radical was observed and assigned to one of the two most stable structures of pyrrolinyl radicals. This radical is formed on matrix annealing both directly after irradiation, as well as after transformations of the primary radical cation into other isomers by photobleaching.

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