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A 'magic bridge': effect of methylene chain length on the photochemistry of radical cations produced from bifunctional X–$(CH_2)_n$–Y molecules

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The radical cations of aminoamides $Me_2N(CH_2)_nC(O)NMe_2$ and aminoethers $Me_2N(CH_2)_nOMe$ reveal selective photoinduced intramolecular H transfer from methylene bridge at a specific chain length (n = 3).

The radical cations (RCs) of bridged X–$(CH_2)_n$–Y bifunctional compounds (X and Y are functional groups) represent an interesting class of model systems for molecular electronics, radiation chemistry of macromolecules and radiobiology. It was shown[1,2] that symmetrical RCs of this kind (X = Y) usually exhibited spin and charge delocalization, at least, at $n < 3$. A delocalized structure was also found[3] in methoxyacetone RC, where X and Y are different, but the ionization energy of these groups is close enough (ΔIP_{XY} = 0.33 eV). On the other hand, in the case of amidoesters (X = $CONMe_2$, Y = MeOCO, n = 0–4), spin density is mainly located at the amide nitrogen,[4] which results from substantially lower ionization energy of the amide group (ΔIP_{XY} ~ 1 eV). Nevertheless, the methylene bridge was found to have a remarkable effect on the photochemical reactions of amidoester RC, the most effective and specific intramolecular reaction occurring for n = 3. Here, we report a new striking observation of crucial influence of the bridge length on the photoinduced H transfer in bifunctional RCs containing amino groups.

A series of aminoamides (AA-n; X = Me_2N, Y = $CONMe_2$, n = 1–3) were synthesized by different original methods. AA-1 was obtained from dimethylamine and methyl chloroacetate, AA-2 was synthesized by the reaction of dimethylamine with acrylic acid chloride, and AA-3 was obtained through a three-stage procedure starting from γ-butyrolactone. Aminoethers (AE-n, X = Me_2N, Y = OMe, n = 2, 3) were obtained by known methods. RCs were generated by the X-irradiation of frozen solutions of the corresponding compounds (0.1 to 0.5 vol%) in Freon 113 ($CF_2ClCFCl_2$) at 77 K. Experimental EPR studies were complemented by theoretical DFT analysis (PBE functional,[5] PRIRODA computational code[6,7]).

As revealed by quantum-chemical calculations, spin density in all RCs under investigation is localized at the amino group (at least, 60% of Hirshfeld spin population is located at the amine nitrogen atom). This looks quite logical in view of large ΔIP_{XY} values (~1.9 eV for aminoamides and ~2.1 eV for aminoethers, as estimated from the ionization energies of the corresponding monofunctional molecules). Accordingly, the RCs of aminoamides and aminoethers should exhibit major hyperfine coupling for amine nitrogen nucleus (strongly anisotropic, only weak and broad parallel features can be detected since $a_\perp \sim 0$) and methyl and methylene protons in the β-position to the amine nitrogen atom (well defined and nearly isotropic). RCs with a longer bridge (n = 3) give a large number of computed conformers with close total energy. Meanwhile, in all the cases, the most energetically favourable conformers are folded and correspond to the shortest possible distances between functional groups. The RC conformation manifests itself in variations in methylene β-proton coupling constants and occurrence of extra coupling with a δ-proton for certain folded conformers (assuming free rotation of the methyl groups). The folded conformers are characterized by large coupling with only one of two methylene β-protons. Experimental EPR spectra for all the studied species are in reasonable agreement with the computational results (examples of AA-3 and AE-3 radical cations are shown in Figure 1).

Warming the irradiated sample to 120–145 K results in irreversible changes in the EPR spectra, which are converted to triplets with the hyperfine splittings of 1.8–1.9 mT, which are characteristic of >N–$CH_2^{\cdot}$ type radicals. This can be explained by the ion–molecule reactions:

$$Y(CH_2)_nNMe_2^{+\cdot} + Y(CH_2)_nNMe_2 \longrightarrow Y(CH_2)_nNMeCH_2^{\cdot} + Y(CH_2)_nN^+(H)Me_2$$

where Y = Me_2NCO or MeO. Reactions of this kind typically occur for various RCs in a Freon 113 matrix above 110 K.[8] Note that we did not observe the formation of radicals of the ·RCHNR′ type corresponding to proton abstraction from methylene groups, although such species were calculated to be thermodynamically more stable than the >N–$CH_2^{\cdot}$ type radicals (by 13.35 kcal mol^{-1} for AA-1). This result indicates that the reaction is controlled by steric (kinetic) factors. A similar behaviour was observed previously[9,10] for the methylal RC.

Thus, the structure and thermal reactions of the studied bifunctional RC are similar to those of amine RCs. Also, similar to amine RC, the radical cations of bifunctional compounds with short methylene bridge (n < 3, *i.e.*, AA-1, AA-2 and AE-2) are insensitive to visible light (λ > 370 nm). However, RCs of AA-3 and AE-3 reveal specific and selective photochemical reactions. In particular, the photolysis of AA-3 RC with light at λ = 360–540 nm for ~1 h leads to transformation shown in Figure 1 (spectrum *3*). The resulting spectrum can be described

as a four-line signal with an average splitting of ~2.25 mT (weaker outer lines are probably due to residual primary RC). Such a spectrum should belong to distonic RC, the product of intramolecular H atom transfer from methylene bridge. The presence of three protons with roughly similar coupling constants (2.0–2.5 mT) is possible only for the interior-type radical resulting from H transfer from the central methylene group of the bridge. In this case, one should assume major coupling with two β-protons and one α-proton (the latter one should be essentially anisotropic, which is in agreement with lineshape of the outer components of the quartet). According to the quantum-chemical calculations, the most stable species is a distonic RC, where the H atom is located between amine nitrogen atom and carbonyl oxygen atom, thus forming a seven-membered pseudocyclic structure (Figure 1). The formation of such a structure is favoured by geometry reasons (the shortest distance between H atom to transfer and carbonyl oxygen atom in the primary RC, ~0.277 nm).

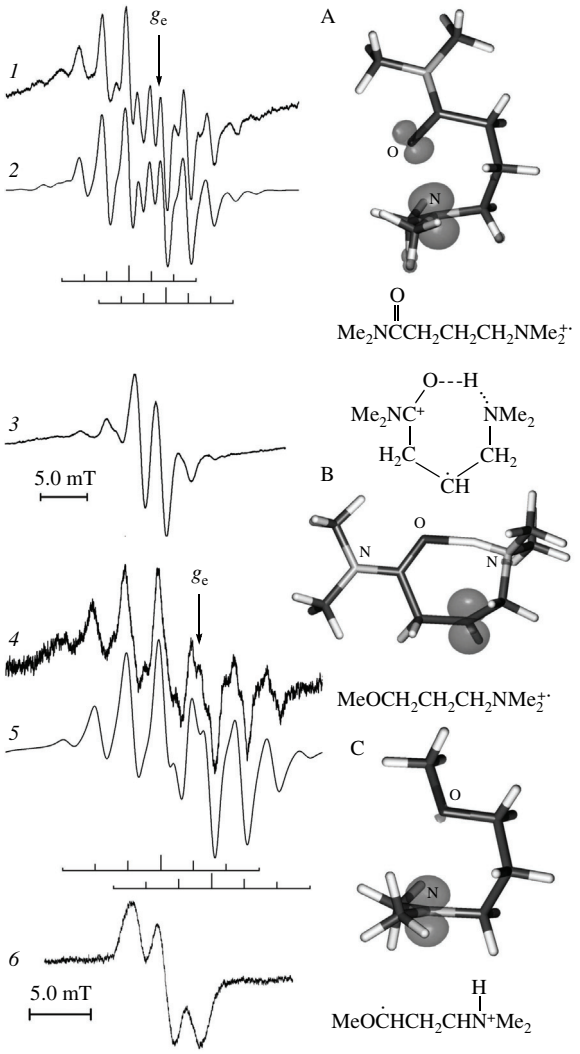

Figure 1 (*1*) Experimental EPR spectrum obtained by X-irradiation of AA-3 frozen solution in Freon 113; (*2*) isotropic simulation of the spectrum of AA-3 RC: a(6H) = 2.45, a(1H) = 3.64 mT; (*3*) EPR spectrum obtained after photolysis of AA-3 RC at λ = 360–540 nm for 1 h; (*4*) experimental EPR spectrum obtained by X-irradiation of AE-3 frozen solution in Freon 113; (*5*) isotropic simulation of AE-3 RC: a(6H) = 2.61, a(1H) = 3.73, a(1H) = = 0.45 mT; (*6*) EPR spectrum obtained after photolysis of AE-3 RC at λ = 360–540 nm for 7 min. Images A, B and C show calculated spin density distribution in optimized conformations of the primary AA-3 RC, distonic RC obtained by its intramolecular transformation, and primary AE-3 RC, respectively.

The most efficient and specific phototransformation is characteristic of AE-3 RC. Photolysis at λ = 380–450 nm for only 7 min leads to the almost complete conversion of initial signal to a three-line spectrum with a non-binomial intensity ratio resulting from two slightly inequivalent protons. This signal can be described reasonably as a doublet of doublets with a(1H) = 1.74 and a(1H) = 2.33 mT (spectrum *6* in Figure 1). Note that the transformation is nearly quantitative (the integrated intensity is retained). The spectrum is clearly different from that of >N–$CH_2^{\cdot}$ type radical, so it originates from the intramolecular H transfer from the methylene bridge. For obvious reasons, it cannot be ascribed to an interior-type radical ($RCH_2^{\cdot}CHCH_2R'$), which should have, at least, three strongly coupling protons. The most probable interpretation is concerned with the formation of distonic RC of the $RCH_2^{\cdot}CHOMe$ type (major hyperfine coupling with one α and one β proton, the second β proton giving a small coupling masked by linewidth):

$$MeO(CH_2)_3NMe_2^{+\cdot} \xrightarrow{h\nu} MeO^{\cdot}CH(CH_2)_2N^+(H)(CH_2)_2.$$

Quantum-chemical calculations show that two lowest electron excited states of the AE-3 RC are characterized by high spin population at $p(\pi)$ or $p(\sigma)$ orbitals of oxygen atom, which implies high probability of H transfer from the adjacent methylene group. An alternative explanation (H transfer from the methylene group adjacent to nitrogen) is unfavourable from both thermodynamic and structural viewpoints.

In summary, we have demonstrated that RC of $Y(CH_2)_nNMe_2$ type compounds underwent efficient and selective intramolecular transformations induced by visible light at n = 3 (a 'magic bridge'). Such reactions do not occur for amine RCs or analogues with a shorter methylene bridge. Most probably, excitation of the primary RC results in electron transfer from remote functional group (amide or ether) to amine nitrogen followed by intramolecular H transfer from the methylene bridge. The process is controlled by favourable folded conformation of RC realized at n = 3. More detailed studies of the mechanism of this unusual class of reactions are in progress.

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