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Reactive Intermediates

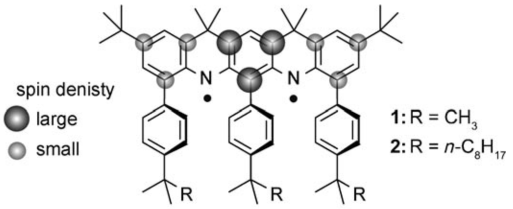
Isolation of the Triplet Ground State Aminyl Diradical**

*Przemysław J. Boratyński, Maren Pink, Suchada Rajca, and Andrzej Rajca**

Nitrogen-centered (aminyl) radicals are typically short-lived, and have been detected as intermediates in a variety of chemical and biological processes.[1,2] To the best of our knowledge, only two known stable aminyl radicals have been reported (more than 30 years ago),[3,4] while a few others have recently been isolated as aminyl metal complexes and as heteroatom (e.g., O, S) stabilized aminyls.[5–7]

Aminyl diradicals, in which the radical centers are connected through *m*-phenylene to form a planar cross-conjugated π system devoid of stabilizing heteroatoms, are predicted by computational studies to possess a strong preference for a high-spin, triplet ($S=1$) ground state, that is, a singlet–triplet energy gap (ΔE_{ST}) that is an order of magnitude greater than the thermal energy (RT) at room temperature.[8,9] Such a nitrogen-centered diradical with large ΔE_{ST} values and persistence at room temperature may be relevant to the design of strongly paramagnetic relaxation reagents[10,11] as well as the development of magnetic materials and devices.[12,13] To date, the two known examples of aminyl diradicals have been examined only at very low temperature. Platz and coworkers first reported an aminyl diradical in a 2-methyltetrahydrofuran (2-MeTHF) matrix at about −195 °C.[14] Recently, we prepared an aminyl diradical with an $S=1$ ground state that was persistent in solution at about −100 °C.[9]

Herein we report the isolation of an $S=1$ ground state aminyl diradical with a large ΔE_{ST} value and persistence at room temperature. The synthesis of the aminyl diradicals **1** and **2** demonstrates the balance between maintaining an effective $2p_\pi$–$2p_\pi$ overlap that enhances electron spin–spin interactions (exchange coupling), and the adequate protection of the carbon and nitrogen atoms with significant spin densities within the diazapentacene backbone in order to achieve the stability required for isolation. This result is significant as the $2p_\pi$–$2p_\pi$ overlap is generally severely perturbed by the increased steric bulk that is required for achieving radical stability, and thus a combination of a large ΔE_{ST} value and persistence at room temperature is not commonly accomplished. In addition, we detected an unexpected self-associated dimer of the $S=1$ aminyl diradical **2** in 2-MeTHF solution; this species appears to resemble a π dimer. Notably, characterization of the dimer is facilitated by its unique zero-field splitting tensor (D). π Dimers of neutral organic radicals in solution are relatively rare and the reports of such phenomena are limited to those of $S=\tfrac{1}{2}$ radicals.[15]



Diradicals **1** and **2** were prepared from the corresponding diamines **5** and **6**, which were obtained from diamine **3** (Scheme 1).[16] The structure of diamine **6** was confirmed by X-ray crystallography, and shows overcrowding of the bulky *tert*-undecyl groups so that the C–C bond axes that connect the two outer pendant benzene rings to the backbone bend outward (Figure 1).[17] This bending creates more space for the pendant benzene rings in order to attain moderate torsion angles of −52.0(4), 61.0(4), and −68.2(3)° with respect to the diazapentacene backbone. Nevertheless, both nitrogen atoms are well-shielded and the diazapentacene backbone remains planar in spite of the steric congestion. The structure of diradical **2**, which differs from its diamine precursor by the absence of two hydrogen atoms, is expected to be similar to that of diamine **6**. Such a sterically shielded, planar structure should have enhanced stability and a strong preference for the $S=1$ ground state.

In spite of hindered access to the NH moieties in the diazapentacene backbone, double deprotonation of diamines **5** and **6** in THF/hexane at about −30 °C, followed by oxidation of the resultant dianions with iodine between −90 and −115 °C provided the corresponding diradicals **1** and **2**, respectively. Generation of **1** is difficult because of its low solubility, and characterization of **1** is possible only by EPR spectroscopy, which gave spectra that are typical of the aminyl diradical in the $S=1$ state (Figure S3 in the Supporting Information).[9] In contrast, the generation of **2** is very efficient, and is facilitated by the good solubility of the diradical and its diamine precursor.

Diradical **2** was prepared on a 1 mg (1 μmol) scale in custom-designed sample tubes, thus enabling sequential measurements by EPR spectroscopy and superconducting quantum interference device (SQUID) magnetometry at low temperatures. The EPR spectra of concentrated purple-blue solutions of **2** in 2-MeTHF at 132 K are strikingly complex,

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[*] Dr. P. J. Boratyński, Prof. Dr. S. Rajca, Prof. Dr. A. Rajca
Department of Chemistry, University of Nebraska
Lincoln, NE 68588-0304 (USA)
Fax: (+1) 402-472-9402
E-mail: arajca1@unl.edu
Homepage: http://www.chem.unl.edu/rajca/rajcahome.html
Dr. M. Pink
Department of Chemistry, Indiana University
Bloomington, IN 47405-7102 (USA)

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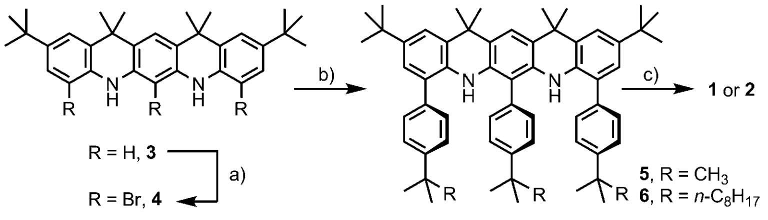

Scheme 1. Synthesis of aminyl diradicals **1** and **2**. a) NBS in chloroform, $NaHCO_3$, Na_2SO_4, −40 °C for 1 h, then 0 °C for 2 h, 35 %. b) 4-*tert*-butylphenylboronic acid or 4-*tert*-undecylphenylboronate, $[Pd(PPh_3)_4]$, Na_2CO_3, benzene/EtOH/water, 90 °C (**5**: 62 % yield, **6**: 43 % yield). c) *n*BuLi (2.4 equiv), THF/hexane, ca. −30 °C for 1 h, then solvent change to THF or 2-MeTHF, and I_2 (1.06 equiv) at −90 °C or titration with I_2 at −90 to −115 °C monitored by EPR spectroscopy. NBS = *N*-bromosuccinimide.

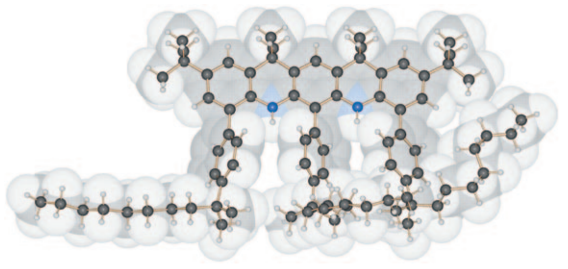

Figure 1. X-ray structure of diamine **6**. Disorder is omitted for clarity. C gray, H white, N blue.

(Figure 2 a ; 4 mM solution of **2**). A similar EPR spectrum was obtained for a 10 mM solution of **2** (Figures S6–S8 in the Supporting Information), which was also examined by SQUID magnetometry (Figure 2 b). In spite of this complexity, SQUID magnetometry unequivocally indicates an approximate $S = 1$ paramagnetic behavior for both magnetization (M) versus magnetic field (H), and magnetic susceptibility (χ) versus temperature (T). The magnetization curves at 1.8–5 K follow the Brillouin plot for $S = 1$ (Figure 2 b), though after correction by a mean-field parameter $\theta \approx -0.3$ K. This value, which is similar for both 10 mM and 50 mM **2** in 2-MeTHF, implies a weak antiferromagnetic exchange coupling between the $S = 1$ ground state diradicals.

We propose that the $S = 1$ diradical **2** assembles to form a dimer $\mathbf{2}_2$ in 2-MeTHF. A numerical fit to the variable-temperature magnetic data, that is, χT versus T, gave a weak antiferromagnetic exchange coupling $J/k \approx -0.2$ K (singlet–quintet energy gap, $6|J| \approx 2\,\mathrm{cal\,mol^{-1}}$), between two $S = 1$ diradicals within the dimer $\mathbf{2}_2$ (Figure 2 b, inset).[18] This exchange coupling implies the presence of two EPR-active states, $S = 2$ and $S = 1$, in addition to the $S = 0$ ground state, for $\mathbf{2}_2$. If $\mathbf{2}_2$ were a centrosymmetric structure with the diradicals oriented similarly to those in a π dimer, the properties of the zero-field splitting tensors (D) would be similar to those in exchange-coupled, symmetric metal ion pairs.[19] Therefore, the largest components of D tensors for the $S = 1$ state (D_1) and $S = 2$ state (D_2), as well as for monomeric **2** (D_d) and exchange contribution (D_{exch}), would be collinear and the corresponding zero-field splitting parameters may be approximately related by Equations (1 a and 1 b):[19] The $S = 2$ and $S = 1$ states of the dimer are expected to be significantly populated in the EPR spectrum (obtained at about 130 K; Figure 2 a) because of weak exchange coupling ($|J/k| \ll 130$ K). The two outermost EPR bands, which are separated by $6|D_2|$ and are not present in the spectra of poorly soluble **1**, are assigned to the $S = 2$ state for the dimer with $|D_2/hc| = 5.49 \times 10^{-3}\,\mathrm{cm^{-1}}$. This assignment is confirmed by dilution experiments, that is, when the concentration of **2** is decreased, the relative intensity of the two outer peaks decreases (Figure 2 a) and the EPR spectra of **2** become increasingly similar to those of **1** with $|D_d/hc| = 8.67 \times 10^{-3}\,\mathrm{cm^{-1}}$ (Figure S3 in the Supporting Information).

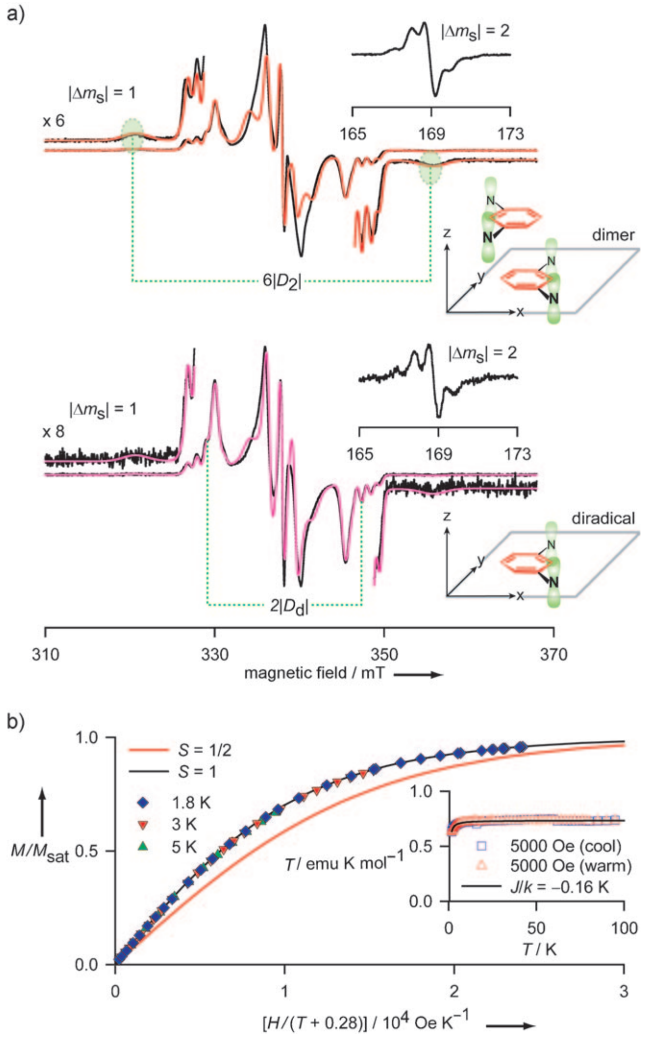

Figure 2. a) EPR (X band) spectra of 4.0 mM (top) 0.5 mM **2** (bottom) in 2-MeTHF at 132 K, and direction of the *z* axis that defines the orientation of the largest components of the D tensor for the aminyl diradical and its dimer. Black line: experimental values, red line: simulated values. b) SQUID magnetometry of ca. 10 mM **2** in 2-MeTHF. Main plot: M/M_{sat} versus $H/(T-\theta)$ with $\theta \approx -0.3$ K, showing curvature corresponding to the value of $S = 0.98$, which is independent of the spin concentration of the sample (M_{sat} = magnetization at saturation). Inset: χT versus T, showing numerical fit to dimer of $S = 1$ diradicals with $J/k \approx -0.2$ K ($R^2 = 0.995$).

$$D_1 = -D_d + D_{exch} \tag{1a}$$

$$D_2 = D_d/3 + D_{exch}/3 \tag{1b}$$

For dilute solutions of **2**, which behave largely like a monomeric $S = 1$ diradical, another pair of outermost EPR bands separated by $2|D_d|$ appears as pentuplets (Figure 2a), which arise from ^{14}N-hyperfine coupling with two nitrogen atoms in the $S = 1$ diradical.[9] Therefore, the largest components of the zero-field splitting tensor (D) and hyperfine tensor (A) are parallel to each other, and to the $2p_\pi$ orbitals on the nitrogen atoms ($2p_z$ in Figure 2a), thus indicating that diradical **2** has an approximately planar diazapentacene backbone, as inferred from the X-ray crystal structure of diamine **6**. This parallel orientation of the largest components for the D and A tensors in **2** is qualitatively different compared to the perpendicular orientation in the recently reported $S = 1$ planar nitroxide diradical derived from diamine **3**,[20] thus precluding the possibility that **2** is a nitroxide diradical.

The orientation of the largest component of the D tensor in **2** indicates that the magnetic dipole–dipole interactions are strongest along the z axis,[21] with the strength qualitatively related to the spectral width $2|D_d|$ (Figure 2a). This observation suggests that the spin density is most pronounced along the z axis in **2**, and even more so in the $S = 2$ state of $\mathbf{2}_2$, which has an approximately centrosymmetric π-dimer-like structure (Figure S54 in the Supporting Information). Thus, the magnetic dipole–dipole interactions in the $S = 2$ state of $\mathbf{2}_2$ are expected to be even stronger along the z axis, therefore leading to the relatively large spectral width $6|D_2|$ (Figure 2a), which both enables the spectroscopic detection of the $S = 2$ state and provides evidence for a structure of the dimer.

Based upon values of D_2 and D_d, and assuming that these values have the same signs, we can estimate from Equation (1) that $|D_1/hc|$ is on the order of 1×10^{-3} cm^{-1}, which is smaller than $|D_d/hc|$, as qualitatively expected for the more spin-dilute $S = 1$ state of the dimer. This approximate value is reasonably consistent with the value of $|D_1/hc| \approx 1.8 \times 10^{-3}$ cm^{-1}, which was obtained from numerical simulations of EPR spectra (Figure 2a and Figure S13 in the Supporting Information). These results provide further support for the structure of $\mathbf{2}_2$. The association constant of $\mathbf{2}_2$ is $K_{assoc} \approx 3 \times 10^2$ M^{-1} at 132 K ($\Delta G \approx -1.5$ kcal mol^{-1}),[22] estimated from numerical simulations of EPR spectra for three samples of 0.5–4.0 mM **2** in 2-MeTHF.

One of the possible structures of $\mathbf{2}_2$ is modeled using a simplified centrosymmetric dimer without long alkyl chains, that is, $\mathbf{1}_2$, for which the geometry of $S = 2$ state is optimized using the standard density functional level of theory (UB3LYP/6-31G(d)).[23] This model structure possesses a relatively long plane-to-plane distance (5.73 Å) between the diazapentacene backbones of bulky $S = 1$ diradicals; this distance is consistent with the weak exchange coupling between the diradicals (Figure S53 in the Supporting Information).

EPR spectroscopy of **2** in 2-MeTHF shows that the diradical is inert toward an excess of iodine and oxygen at temperatures as low as −108 °C, however a brief warming to −26 °C and −78 °C, respectively, resulted in almost complete disappearance of the diradical. In the absence of iodine and oxygen, EPR spectra of **2** in 2-MeTHF show only slight changes in intensity upon sequential warming to −26, 0, and 22 °C. This remarkable persistence of **2** prompted us to explore the isolation of the diradical.

We devised a stringent procedure for the isolation of diradical **2**. The procedure involves generation of 30–65 mg of diradical, followed by precipitation and filtration at low temperature in a Schlenk vessel under an inert atmosphere. After diradical **2** was generated from the diamine as described above, the solvent was removed under vacuum at −78 °C. Then, methanol was added by vacuum transfer in order to dissolve salts and any excess iodine, and to precipitate the diradical. Because of its reactivity towards methanol above −78 °C, the dark blue solid aminyl diradical was filtered at low temperature to minimize decomposition. The solid sample (7:3 diradical/monoradical) could be stored in a glovebox at −20 °C for seven months, during which time only slight decomposition occurred. At room temperature, the concentration of the $S = 1$ diradical decreased to 60 % after five days (Figure S21 in the Supporting Information).

The properties of **2**, that is, a solid diradical that is persistent at room temperature, facilitate the magnetic measurements that provide an estimated ΔE_{ST} value with significantly greater precision compared to low-temperature measurements in solution. In particular, the χT versus T plot for solid **2** is flat from 30 K to 290 K, which is the highest temperature of the SQUID measurement (Figure S22 in the Supporting Information), thus indicating that $\Delta E_{ST} \geq 2$ kcal mol^{-1}. This limiting value is in qualitative agreement with the value of $\Delta E_{ST} \approx 7$ kcal mol^{-1} calculated for diradical **1** using the UB3LYP/6-31(d) level of theory.[23,24]

The isolation of diradical **2** also allows a more in-depth study of kinetic stability of the aminyl diradical and the derived monoradical. The stability of **2** in 2-MeTHF was monitored by EPR spectroscopy at room temperature. The first-order decay kinetics of diradical and monoradical corresponds to a half-life of about 3 and 7 hours, respectively (Figure 3); after several days, ^{1}H NMR spectra showed that the isolated sample was predominantly diamine **6** (Figures S23–S29 in the Supporting Information). These results suggest that the process of conversion of **2** to **6** proceeds by a hydrogen abstraction mechanism, which is facilitated by the

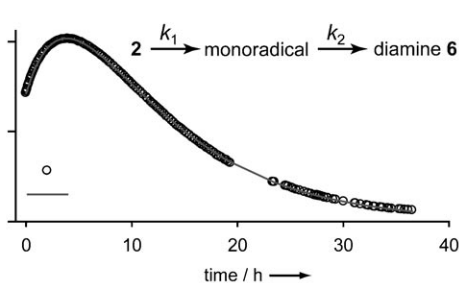

Figure 3. Decay kinetics of diradical and monoradical in 2-MeTHF at 294 K (○: experimental values, ——: numerical fit). The four-parameter fit to the first-order decay kinetics ($R^2 = 0.9999$) gives rate constants $k_1 = 6.8 \times 10^{-5}$ and $k_2 = 2.9 \times 10^{-5}$ s^{-1} (additional details are given in Figures S23–S31 in the Supporting Information).

low C–H bond dissociation energy of solvents such as THF.[25] This mechanism is analogous to that observed for matrix-isolated dialkyl aminyl radicals.[26]

The diradical **2** reacts with oxygen at room temperature both in the solid state and in solution to result in a new diamagnetic product as well as variable amounts of diamine **6** (see the Supporting Information). This reactivity is in contrast to that of other aminyl radicals, which were reported to react with oxygen to form nitroxide radicals (N–O$^\bullet$) via peroxy radicals (N–O–O$^\bullet$).[26,27]

In summary, we isolated a triplet ground state aminyl diradical that is persistent at room temperature and possesses a singlet–triplet energy gap that is significantly greater than the thermal energy at room temperature. The diradical assembles in solution to form a weakly exchange coupled π-dimer-like structure that was detected spectroscopically in its thermally populated $S=2$ state. Both the magnitude of the exchange coupling ($|J/k| \approx 0.1$–$1\ \mathrm{K}$)[28] and relatively large zero-field splitting in the dimer suggest that electron spin relaxation rates could be enhanced by an order of magnitude.[29] Such diradicals may have potential in the design of paramagnetic relaxation reagents and spin-transport devices.[10,11,13]

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[1] K. Piech, T. Bally, A. Sikora, A. Marcinek, *J. Am. Chem. Soc.* **2007**, *129*, 3211–3217.

[2] H. Quast, W. Nüdling, G. Klemm, A. Kirschfeld, P. Neuhaus, W. Sander, D. A. Hrovat, W. T. Borden, *J. Org. Chem.* **2008**, *73*, 4956–4961.

[3] F. A. Neugebauer, H. Fischer, S. Bamberger, H. O. Smith, *Chem. Ber.* **1972**, *105*, 2694–2713.

[4] N. Ballester, J. Castaner, S. Olivella, *Tetrahedron Lett.* **1974**, *15*, 615–616.

[5] T. Büttner, J. Geier, G. Frison, J. Harmer, C. Calle, A. Schweiger, H. Schönberg, H. Grützmacher, *Science* **2005**, *307*, 235–238.

[6] N. P. Mankad, W. E. Antholine, R. K. Szilagyi, J. C. Peters, *J. Am. Chem. Soc.* **2009**, *131*, 3878–3880.

[7] Y. Miura, T. Tomimura, *Chem. Commun.* **2001**, 627–628.

[8] S. Amiri, P. R. Schreiner, *J. Phys. Chem. A* **2009**, *113*, 11750–11757.

[9] A. Rajca, K. Shiraishi, M. Pink, S. Rajca, *J. Am. Chem. Soc.* **2007**, *129*, 7232–7233.

[10] G. M. Clore, J. Iwahara, *Chem. Rev.* **2009**, *109*, 4108–4139.

[11] A. J. Maliakal, N. J. Turro, A. W. Bosman, J. Cornel, E. W. Meijer, *J. Phys. Chem. A* **2003**, *107*, 8467–8475.

[12] A. Rajca, J. Wongsriratanakul, S. Rajca, *Science* **2001**, *294*, 1503–1505.

[13] C. Herrmann, G. C. Solomon, M. A. Ratner, *J. Am. Chem. Soc.* **2010**, *132*, 3682–3684.

[14] K. Haider, N. Soundararajan, M. Shaffer, M. S. Platz, *Tetrahedron Lett.* **1989**, *30*, 1225–1228.

[15] D. Small, V. Zaitsev, Y. Jung, S. V. Rosokha, M. Head-Gordon, J. K. Kochi, *J. Am. Chem. Soc.* **2004**, *126*, 13850–13858.

[16] K. Shiraishi, A. Rajca, M. Pink, S. Rajca, *J. Am. Chem. Soc.* **2005**, *127*, 9312–9313.

[17] CCDC 758072 (**6**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[18] A. Rajca, M. Takahashi, M. Pink, G. Spagnol, S. Rajca, *J. Am. Chem. Soc.* **2007**, *129*, 10159–10170.

[19] A. Bencini, D. Gatteschi, *EPR of Exchange Coupled Systems*, Springer, Berlin, **1990**, pp. 48–85.

[20] A. Rajca, K. Shiraishi, S. Rajca, *Chem. Commun.* **2009**, 4372–4374.

[21] The spin–orbit coupling contribution to the D tensor may be neglected in the N-centered diradicals: Z. Havlas, M. Kývala, J. Michl, *Mol. Phys.* **2005**, *103*, 407–411.

[22] J. Wu, A. Fechtenkötter, J. Gauss, M. D. Watson, M. Kastler, C. Fechtenkötter, M. Wagner, K. Müllen, *J. Am. Chem. Soc.* **2004**, *126*, 11311–11321.

[23] M. J. Frisch et al., Gaussian 03, revision E.01, Gaussian, Wallingford, CT, **2004** (full citation: see Supporting Information).

[24] This level of theory, which is based upon the broken-symmetry wave function, tends to overestimate the value of ΔE_{ST} for triplet ground state molecules: see refs [2] and [8].

[25] S. J. Blanksby, G. B. Ellison, *Acc. Chem. Res.* **2003**, *36*, 255–263.

[26] J. R. Roberts, K. U. Ingold, *J. Am. Chem. Soc.* **1973**, *95*, 3228–3235.

[27] S. F. Nelsen, R. T. Landis, L. H. Kiehle, T. H. Leung, *J. Am. Chem. Soc.* **1972**, *94*, 1610–1614.

[28] A. Rajca, S. Mukherjee, M. Pink, S. Rajca, *J. Am. Chem. Soc.* **2006**, *128*, 13497–13507.

[29] H. Sato, V. Kathirvelu, G. Spagnol, S. Rajca, A. Rajca, S. S. Eaton, G. R. Eaton, *J. Phys. Chem. B* **2008**, *112*, 2818–2828.