Cinnolino[5,4,3][c,d,e][1,2]benzothiazin-4-yl: A New Persistent Radical

Vladimir Benin and Piotr Kaszynski*

Organic Materials Research Group,
Department of Chemistry, Vanderbilt University,
Nashville, Tennessee 37235

piotr@ctrvax.vanderbilt.edu

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Introduction

Cyclic thioaminy1 radicals have been investigated as molecular magnetic and conductive materials.1,2 Their structural versatility allows for the design of a variety of new heterocyclic radicals including those suitable for structural versatility allows for the design of a variety of new heterocyclic radicals including those suitable for structural elements of liquid crystals.3 In this context, we focused on two radicals, 1a and 2a, as potential components for paramagnetic discogens.4 Here we report the preparation and properties of both radicals with an emphasis on the new persistent heterocyclic sulfenamides 1b.5

Results and Discussion

Synthesis. Dibenzo[c,e][1,2]thiazin-5-yl (1a) and cinnolino[5,4,3][c,d,e][1,2]benzothiazin-4-yl (2a) were generated in about 30% yield by PbO₂/K₂CO₃ oxidation of cyclic sulfenamides 1b and 2b, respectively. This method gave much higher yields of the radicals than the thianthrenium perchlorate/pyridine method previously described for generation of 1a.3

The sulfenamides exhibit markedly different solubility and chromatographic properties despite similarities in their structures. The addition of the azo bridge to 1b makes 2b much less mobile on silica gel and only sparingly soluble in common solvents other than acetone and DMSO. Tetracycle 2b crystallizes with half a molecule of water, as evident from elemental analysis and the ¹H NMR spectrum. Sulfenamides 1b and 2b both undergo slow decomposition upon prolonged storage, which presumably is related to the hydrolysis of the amide bond and the oxidation of the NH group. ESR analysis of one of the less mobile fractions obtained from purification of 2b, which was stored for 1 week in a refrigerator, showed the presence of radical 2a.

ESR Spectra. Radicals 1a and 2a exhibit seven groups of multiplets, as shown in Figure 1. Each multiplet in the spectrum of 1a (Figure 1a) consists of four lines (28 lines total), while in the spectrum of 2a the multiplets are unresolved (Figure 1b).

Both spectra were numerically simulated using initial hyperfine coupling constant (hfcc) values obtained from B3LYP/6-31G* calculations. After a least-squares fit to nine parameters, the correlation between the simulated and the experimental spectra was >0.98, and the resulting hfcc's are shown in Figure 2. The same comparison of the experimental spectrum of 1a with that simulated using the previously published hfcc's (obtained by visual comparison of the spectra),3 shows a correlation of only 0.50.

Figure 1. ESR spectra of 1a (a) and 2a (b) recorded in CH₂Cl₂ at 298 K.

Precursors 1b and 2b were obtained from the corresponding S-propyl sulfilimines 3 and 4,6 by thermal elimination of propene according to the general procedure.5

1H NMR spectra.

(a) 1b

(b) 2b

3. R = H
4. R, R = -N=N-

Both radicals have a similar principal coupling of about 0.85 mT to the thioaminyl nitrogen atom and about 0.4 mT to the hydrogen atoms in the positions ortho and para to the nitrogen. Additional splittings are due to coupling constants of 0.05–0.14 mT to hydrogen atoms meta to the thioaminyl bridge and the azo bridge nitrogen atoms in 2a. The largest differences between 1a and 2a are observed for the hfcc's of hydrogen atoms and spin densities in the positions ortho and para to the nitrogen atoms, which are presumably affected by the electronegativity of the azo substituent.

The observed hfcc's and splitting patterns are consistent with the scaled^6 hfcc's values and spin densities derived from DFT calculations (Figure 2). The mean difference between the calculated and experimental data is 0.007 mT and the estimated standard deviation is 0.024 mT, which is close to the accuracy of the computational protocol.9

The g value measured for 1a (2.0052) is slightly larger than that for 2a (2.0049), which is consistent with the calculated larger spin concentration on the sulfur atom in the former (0.22) as compared with that in 2a (0.21).

Both radicals 1a and 2a have the electronic state 2A" and the unpaired electron resides on the \( \pi \) MO (\(-4.62 \text{ eV} \) and \(-5.12 \text{ eV} \), respectively). The dipole moment \( \mu \) calculated for 1a (2.82 D) is larger than that for 2a (1.82 D), which reflects the contribution of the azo bridge to the total dipole moment of the latter. The vertical ionization potential calculated for 2a and scaled^6 by 0.984 is \( I_0 = 6.68 \text{ eV} \) and is higher by 0.47 eV than that for 1a.

Stability of Radicals. When the radicals were generated with the \( \text{PbO}_2/\text{K}_2\text{CO}_3 \) system, both 1a and 2a showed similar stability. After 3 days, the intensity of the ESR signal of sealed samples decreased by 50%, and the radicals were still detected in the solution after 1 week. The decomposition rate was little affected by the presence of atmospheric oxygen in accordance with the general low oxygen sensitivity of thioaminyl radicals.10 When thianthrenium perchlorate/pyridine was used as the oxidant, however, 1a decayed rapidly within several hours,1 while the relatively strong ESR signal of 2a was still detected after 3 days. This significant difference in stability can be attributed to hydrolytic cleavage of the N=S bond catalyzed by pyridinium salts and accelerated by torsional strain of the two hydrogen atoms in 1 and 10 positions in 1a. Replacement of these two hydrogen atoms with an azo bridge in 2a stabilizes the heterocycle against hydrolysis.

To quantify stability, the toluene solutions were worked up in air and chromatographed. Evaporation of the original mixture to dryness and then redissolving the solid in toluene reduced the spin yield to 1/3 of the original 30%. When the resulting solution was passed through a short Florisil plug, only about 40% of the original amount of material was recovered, with about 10% spin concentration.

The stability of radicals 1a and 2a is remarkable, considering that their acyclic analogue \( \text{PhN}_2\text{P}=\text{NP} \) decomposes completely within 1 h and requires substituents protecting the high spin density sites (positions ortho and para to nitrogen) for increased stability.7 Further substitution of these persistent heterocyclic radicals will certainly increase their stability and perhaps enable their isolation and purification. Judicious choice of substituents will provide new opportunities for controlling bulk structures of solids and liquid crystals.

**Experimental Section**

Melting points are uncorrected. ^1H NMR spectra were referenced to the solvent. Elemental analysis was provided by Atlantic Microlab, Norcross, GA.

X-band ESR spectra were taken on a Bruker 300E instrument in distilled toluene which was degassed by three freeze/pump/thaw cycles. Spin concentration and yields were calculated by double integration of the ESR signal of the sample versus the integral intensity of a measured amount of 4-hydroxy-TEMPO radical purchased from Aldrich and assumed to be 100%. Samples were referenced using strong pitch with \( g = 2.0028 \). Lead dioxide and \( \text{K}_2\text{CO}_3 \) were dried in a vacuum at 100 °C for 24 h, in the presence of \( \text{P}_2\text{O}_5 \).

DFT calculations were carried out on the B3LYP/6-31G* level of theory using the Gaussian 94 package on an SGI R8000 workstation. The calculated Fermi constants were converted to hfcc's and scaled by 0.937 for \( ^{14}\text{N} \) and 0.746 for \( ^{1}\text{H} \), according to a general protocol.9 Simulation of the ESR spectra was done with the PEST program (version 0.96 for Windows; available: http://epr.niehs.nih.gov/pest1.html) using the DFT results for the input. The resulting hfcc were perturbed until the global minimum for the fit was achieved.

**Generation of Radicals. Method A.** Precursor 1b or 2b (0.03 mmol) was dissolved in degassed dry toluene (10 mL, 3 mM solution) and stirred over \( \text{PbO}_2 \) (70 mg, 0.30 mmol) and \( \text{K}_2\text{CO}_3 \) (70 mg, 0.30 mmol) for 15 min. The solution acquired a dark color. A sample of 0.5 mL was transferred to an ESR tube and carefully degassed before the measurement.

**Method B.** Precursor 1b or 2b (0.03 mmol) was dissolved in degassed \( \text{CH}_2\text{Cl}_2 \) (10 mL, 3 mM solution), and pyridine (2 mL) was added. Thianthrenium perchlorate (20 mg, 0.06 mmol) was dissolved in degassed \( \text{CH}_2\text{Cl}_2 \) (10 mL, 6 mM solution), and 0.35 mL of this solution was mixed with 0.35 mL of solution of the

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9 Kaszynski, P.; submitted.

precursor in an ESR tube with a vacuum adapter. The resulting solution acquired a darker color. It was carefully degassed before the measurement.

6H-Dibenzo[d,e][1,2]thiazine (1b). The compound was prepared from 5-propyldibenzo[d,e][1,2]thiazine5 (3) in 36% yield as described for 2b. The crude product was purified on a silica gel column (hexane–CH₂Cl₂, 3:1 ratio) to give a pale yellow oil, which solidified upon standing: mp 44–45 °C; ¹H NMR (C₆D₆) ¤ 3.05 (bs, 1H), 6.90–7.00 (m, 6H), 7.43–7.47 (m, 2H).

5H-Cinnolino[5,4,3][c,d,e][1,2]benzothiazine (2b). 4-Propylcinnolino[5,4,3][c,d,e][1,2]benzothiazine (4, 62 mg, 0.23 mmol) was dissolved in dry benzene (5 mL). The resulting solution was stirred at reflux for 18 h. The solvent was removed and the residue was separated on a silica gel column (hexane–EtOAc, 1:1 ratio, followed by pure EtOAc) to give 35 mg (67% yield) of reddish-brown powder: mp 207–208 °C; ¹H NMR (acetone-d₆) ¤ 5.93 (bs, 1H), 7.52 (d, J = 7.4 Hz, 1H), 7.60 (dd, J₁ = 7.9 Hz, J₂ = 0.9 Hz, 1H), 7.89 (td, J₁ = 8.1 Hz, J₂ = 0.9 Hz, 2H), 8.39 (td, J₁ = 7.4 Hz, J₂ = 0.8 Hz, 2H); IR (neat) νmax 3165, 1577, 1430, 1262, 789 cm⁻¹; MS m/e 225 (M⁺, 100), 196 (40). Anal. Calcd for C₁₂H₇N₃S·0.5H₂O: C, 61.52; H, 3.44; N, 17.94. Found: C, 61.52; H, 3.17; N, 17.65.

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Supporting Information Available: Experimental, simulated, and difference spectra for 1a and 2a and simulation parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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