

Formation of stable 1,2,3-benzodithiazolyl radicals by thermolysis of 1,3,2,4-benzodithiadiazines

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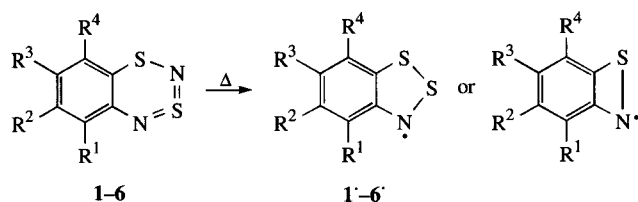
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Mild thermolysis (at 110–150 °C) of 1,3,2,4-benzodithiadiazine **1** and its derivatives **2–6** in hydrocarbon solvents quantitatively yielded stable 1,2,3-benzodithiazolyl π -radicals via a first-order reaction ($E_a = 76.2 \text{ kJ mol}^{-1}$, $k_0 = 4.34 \times 10^5 \text{ s}^{-1}$ for **1**).

The heteroatom reactivity of 1,3,2,4-benzodithiadiazine **1** and its derivatives^{2,3} (Scheme 1) which exhibit formal features of antiaromaticity⁴ (such as a planar or nearly planar geometry, a united molecular 12π -electron system, and low-energy excited states)^{1–3,5,6} is poorly known.^{1,3,7} Reasonably, the first step in studying the chemistry of these compounds is the investigation of their thermal stability and the identification of decomposition products.



- 1, **1'** R¹ = R² = R³ = R⁴ = H
- 2, **2'** R¹ = R² = R⁴ = H, R³ = Me
- 3, **3'** R¹ = R² = R⁴ = H, R³ = OMe
- 4, **4'** R¹ = R² = R³ = R⁴ = F
- 5, **5'** R¹ = R² = R⁴ = H, R³ = F
- 6, **6'** R¹ = R³ = R⁴ = H, R² = F

We found that mild (~110–150 °C) thermolysis of **1–6** in hydrocarbon solvents (squalane, *trans*-decalin, cyclohexane or hexane) resulted with nearly quantitative yields in stable radicals **1'–6'**, which were identified by EPR spectroscopy (Figures 1 and 2, Table 1).[†] The EPR spectra of these radicals generated from **1–3** corresponded to those published earlier for 1,2,3-benzodithiazolyl π -radicals **1'–3'** prepared by other methods,^{8–11} mainly by reduction of corresponding Herz salts (1,2,3-arenodithiazolium chlorides¹²).[‡] Radicals **1'–3'** were initially assigned the 1,2-benzothiazetyl structure^{8,9} (Scheme 1), which was further corrected to 1,2,3-benzodithiazolyl on the basis of EPR experiments with ³³S-enriched species. These experiments indicated the presence of two nonequivalent sulfur atoms.¹¹ The 1,2,3-benzodithiazolyl structure is also consistent with the fact that the radicals can be oxidised into Herz salts by molecular chlorine.¹⁰

Radicals **4'–6'** have been synthesised for the first time; thus, this approach is superior to methods reported previously.^{8–11} In particular, the corresponding Herz salts¹² were not yet described.

The assignment of HFI constants in **1'–6'** (Table 1) was based on earlier data,^{8–11} substitutional effects and the results of the *ab initio* B3LYP/CC-pVDZ calculations of spin density distribution. The calculated constants were consistent with the experimental data (Table 1).

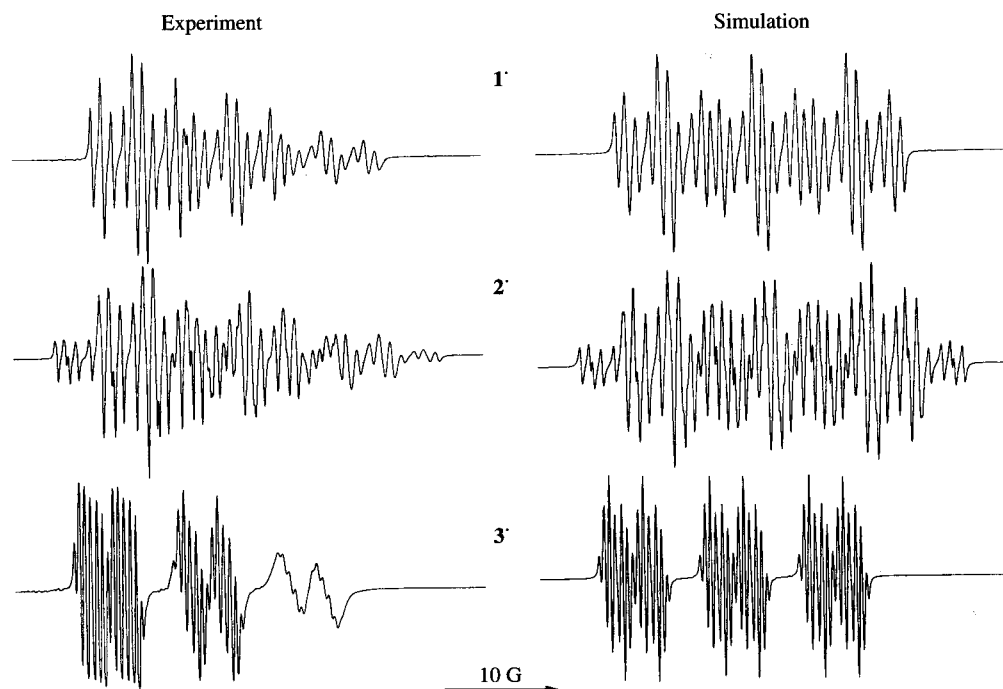


Figure 1 Experimental (in squalane) and simulated EPR spectra of **1'–3'**. Differences in the HF line widths were ignored in simulating the spectra.

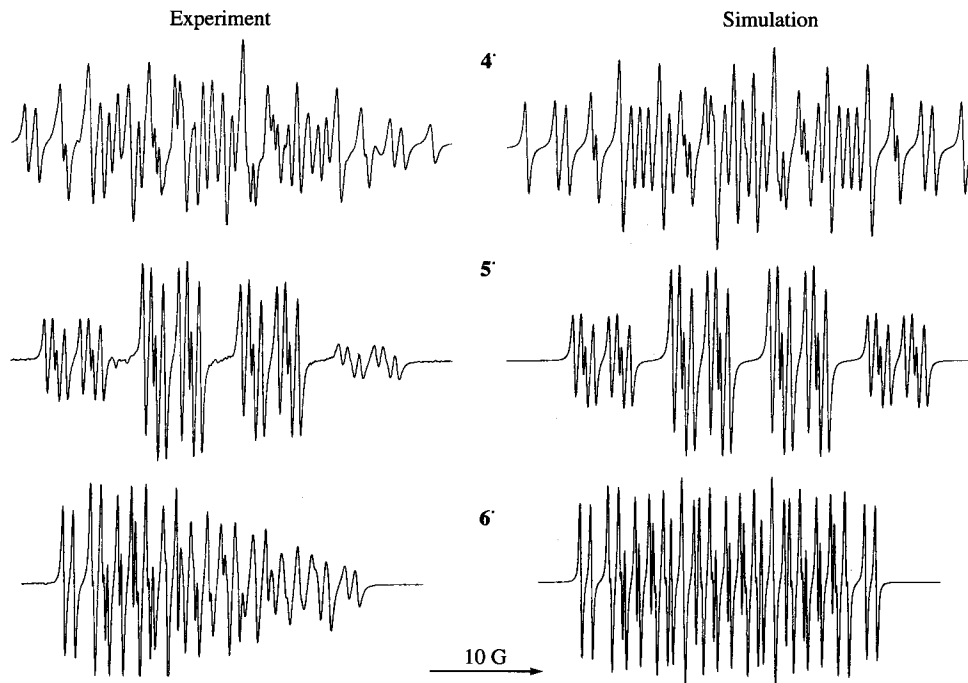


Figure 2 Experimental (in squalane) and simulated EPR spectra of 4–6. Note minor extra lines of an unidentified radical in the spectrum of 5. Differences in the HF line widths were ignored in simulating the spectra.

The kinetic build-up curve of radical 1' in the thermolysis of compound 1 in squalane (Figure 3) was adequately approximated by the first-order equation $A = B(1 - e^{-kt})$ (where B and k are

Table 1 HFI constants (in parentheses, theoretical values), G , and g -factors of radicals 1'–6'.

	N	R ¹	R ²	R ³	R ⁴	g
1'	8.22 (8.1)	2.93 (-2.5)	0.97 (1.2)	3.73 (-2.9)	0.81 (1.2)	2.0080
2'	8.38 (8.2)	2.94 (-2.4)	1.03 (1.1)	3.97 ^a (3.2)	0.75 (1.3)	2.0076
3'	8.67 (8.4)	2.93 (-2.3)	1.08 (0.9)	0.44 ^b (0.7)	0.47 (1.2)	2.0076
4'	8.15 (8.1)	5.67 (7.3)	3.52 (-3.6)	9.96 (10.2)	2.56 (-4.1)	2.0078
5'	8.55 (8.3)	3.15 (-2.6)	1.06 (1.0)	8.55 (9.6)	0.71 (1.3)	2.0079
6'	7.88 (7.7)	2.44 ^c (-2.3)	2.65 ^c (-3.3)	3.87 (-3.0)	0.92 (1.2)	2.0081

^a3H (Me). ^b3H (OMe). ^cInterchangeable values.

† Compounds 1–6 were synthesised and purified as described earlier.^{1–3}

The EPR spectra were recorded on a Bruker EMX spectrometer (MW power, 0.64 mW; modulation frequency, 100 KHz; modulation amplitude, 0.1 G). The spectra simulation was performed with the Simfonia-Bruker program.

The spin density distribution and HFI constants were calculated at the B3LYP/CC-pVDZ level of theory using the Gaussian 94™ program.¹³

In a typical experiment, 10⁻³ M solutions of 1–6 in a hydrocarbon (squalane, *trans*-decalin, cyclohexane or hexane), outgassed by three freeze–pump–thaw cycles, was gradually heated in an EPR valve-equipped quartz capillary up to 150 °C (in squalane, the detectable amounts of radicals appeared at 110 °C, whereas in cyclohexane even at 90 °C). After holding for 1 h at this temperature, the sample was cooled to 20 °C, and the EPR spectrum was measured.

The g -factors of 1'–6' were measured using a DPPH standard.

Nearly quantitative conversion of 1–6 into 1'–6' was determined by a CuCl₂·2H₂O standard with an accuracy of ±15%. At 20 °C, the concentrations of 1'–6' in air-protected solutions decreased only by 30% for 3 weeks. In the presence of oxygen, the radicals are less stable, especially under heating. Thus, in an air-saturated solution at 150 °C, the EPR signal completely decayed in 5 min.

‡ 1,2,3-Benzodithiazolium chloride¹² is readily reduced to 1' with Ph₃Sb in toluene at 20 °C. The EPR spectrum is identical to that of the radical arising from the thermolysis of 1.

the optimised parameters: B is the concentration of radicals at $t = \infty$, k is the reaction rate constant). The results are summarized in Table 2. The activation energy $E_a = 76.2$ kJ mol⁻¹ and the pre-exponential factor $k_0 = 4.34 \times 10^5$ s⁻¹ were calculated from the equation $\ln k = \ln k_0 - E_a/RT$ (Figure 4).

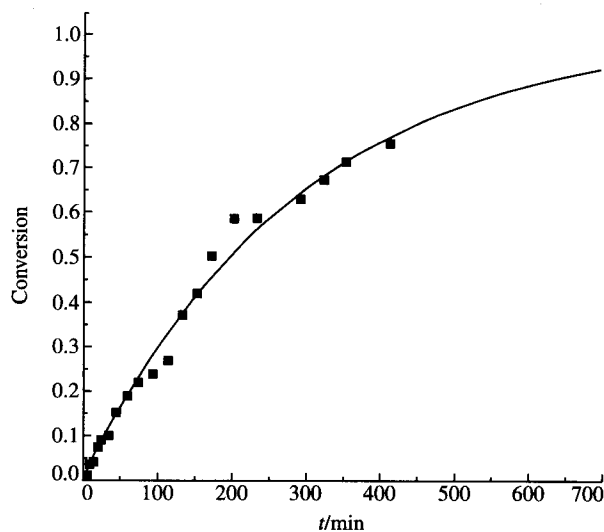


Figure 3 The kinetic build-up curve of 1' by thermolysis of 1 in squalane at 125 °C (initial concentration of 1 was equal to 10⁻³ mol dm⁻³).

Thus, a novel promising approach to the synthesis of thermally stable 1,2,3-benzodithiazolyl radicals was developed. This method provides the basis for further in-depth studies of these interesting species including their individual isolation and structural characterization.

Table 2 Rate constant k of thermolysis of 1 at different temperatures.^a

$T/^\circ\text{C}$	k/s^{-1}	B/N^b
110	1.55×10^{-5}	0.95
125	5.80×10^{-5}	0.92
145	1.42×10^{-4}	0.95
150	1.83×10^{-4}	0.80

^a B is the concentration of 1 at $t = \infty$, and N is the initial concentration of 1. ^b±15%.

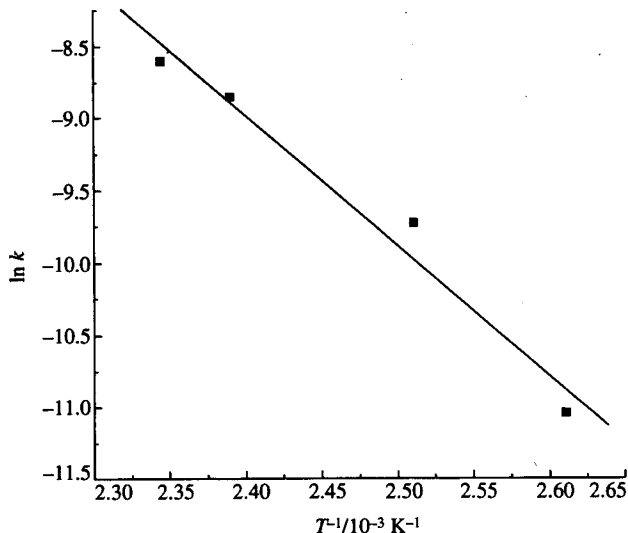


Figure 4 Arrhenius plot of the formation rate constant of 1° in squalane.

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