

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

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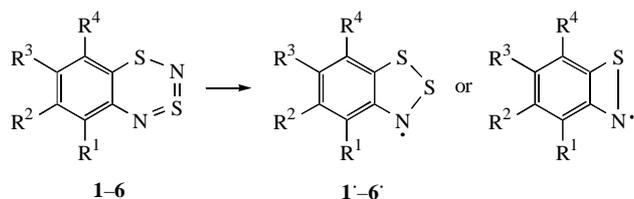
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Mild thermolysis (at 110–150 °C) of 1,3,2,4-benzodithiadiazine **1** and its derivatives **2–6** in hydrocarbon solvents quantitatively yielded stable 1,2,3-benzodithiazolyl radicals *via* a first-order reaction ($E_a = 76.2 \text{ kJ mol}^{-1}$, $k_0 = 4.34 \times 10^5 \text{ s}^{-1}$ 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 12 π -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 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).

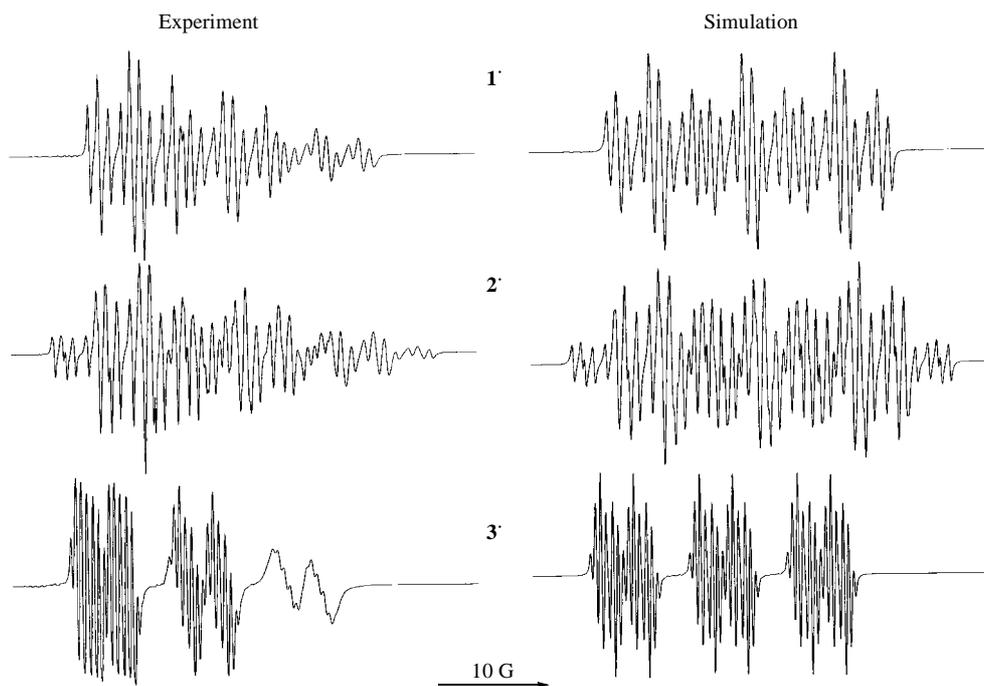


Figure 1 Experimental (in squalane) and simulated EPR spectra of **1'–3'**. Differences in the HF line widths were ignored in simulating the spectra.

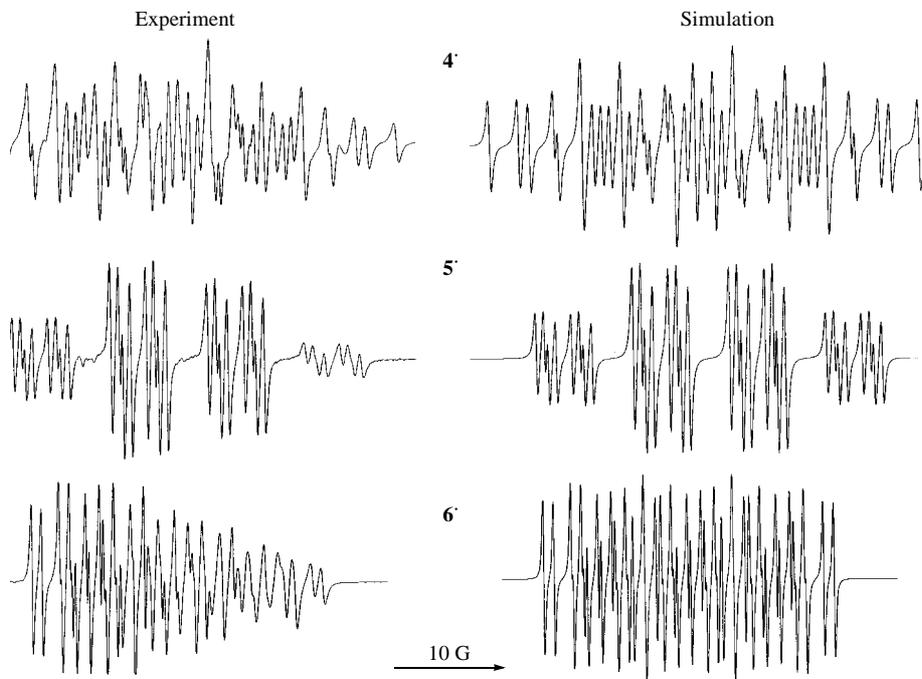


Figure 2 Experimental (in squalane) and simulated EPR spectra of **4**–**6**. Note minor extra lines of an unidentified radical in the spectrum of **5**. Differences in the HF line widths were ignored in simulating the spectra.

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 94TM 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).

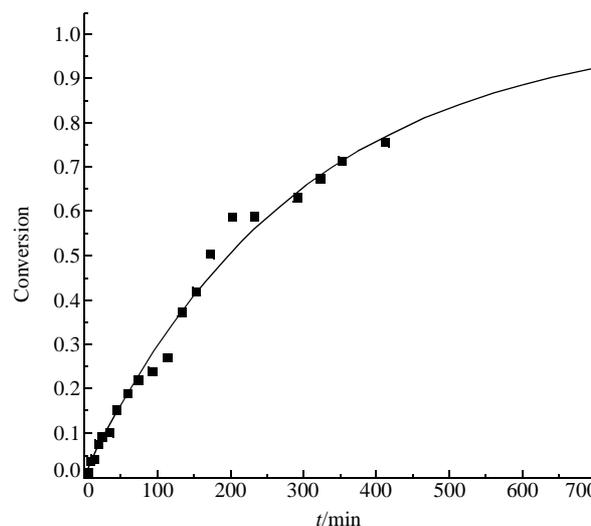


Figure 3 The kinetic build-up curve of **1** by thermolysis of **1** in squalane at 125 °C (initial concentration of **1** was equal to 10^{–3} mol dm^{–3}).

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%.

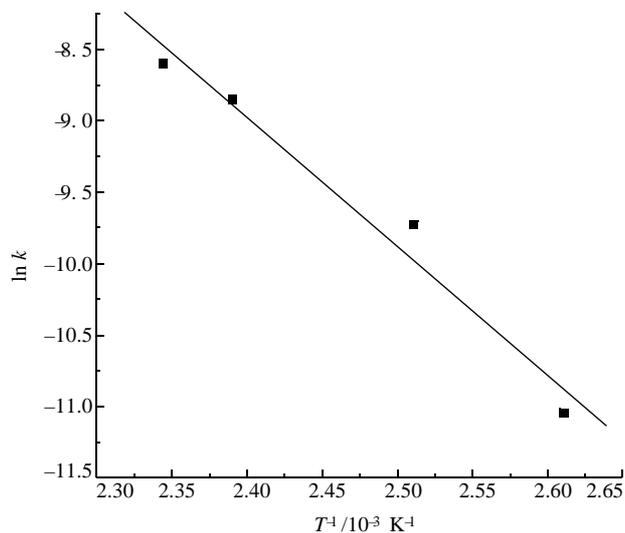


Figure 4 Arrhenius plot of the formation rate constant of 1° in squalane.

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