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

Victor A. Bagryansky,*[a] **Ivan V. Vlasyuk,**[b] **Yuri V. Gatilov,**[c] **Alexander Yu. Makarov,**[c] **Yuri N. Molin,**[a]
Vladimir V. Shcherbukhin[d] **and Andrey V. Zibarev***[c]

[a] *Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk,*
Russian Federation. Fax: +7 3832 34 2350; e-mail: vbag@kinetics.nsc.ru
[b] *Department of Natural Sciences, Novosibirsk State University, 630090 Novosibirsk, Russian Federation*
[c] *N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,*
630090 Novosibirsk, Russian Federation. Fax: +7 3832 34 4752; e-mail: zibarev@nioch.nsc.ru
[d] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 117913 Moscow, Russian Federation.*
Fax: +7 095 135 5328

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 kJ mol^{-1}, k_0 = 4.34×10^5 s^{-1} for **1**).

The heteroatom reactivity of 1,3,2,4-benzodithiadiazine[1] **1** and its derivatives[2,3] (Scheme 1) which exhibit formal features of antiaromaticity[4] (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.

1–6   **1·–6·**
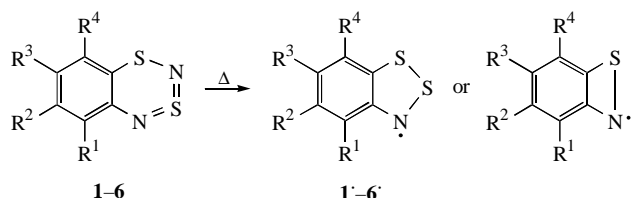
1, **1·** R^1 = R^2 = R^3 = R^4 = H
2, **2·** R^1 = R^2 = R^4 = H, R^3 = Me
3, **3·** R^1 = R^2 = R^4 = H, R^3 = OMe
4, **4·** R^1 = R^2 = R^3 = R^4 = F
5, **5·** R^1 = R^2 = R^4 = H, R^3 = F
6, **6·** R^1 = R^3 = R^4 = H, R^2 = F

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 chlorides[12]).[‡] 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 ^{33}S-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 salts[12] 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).
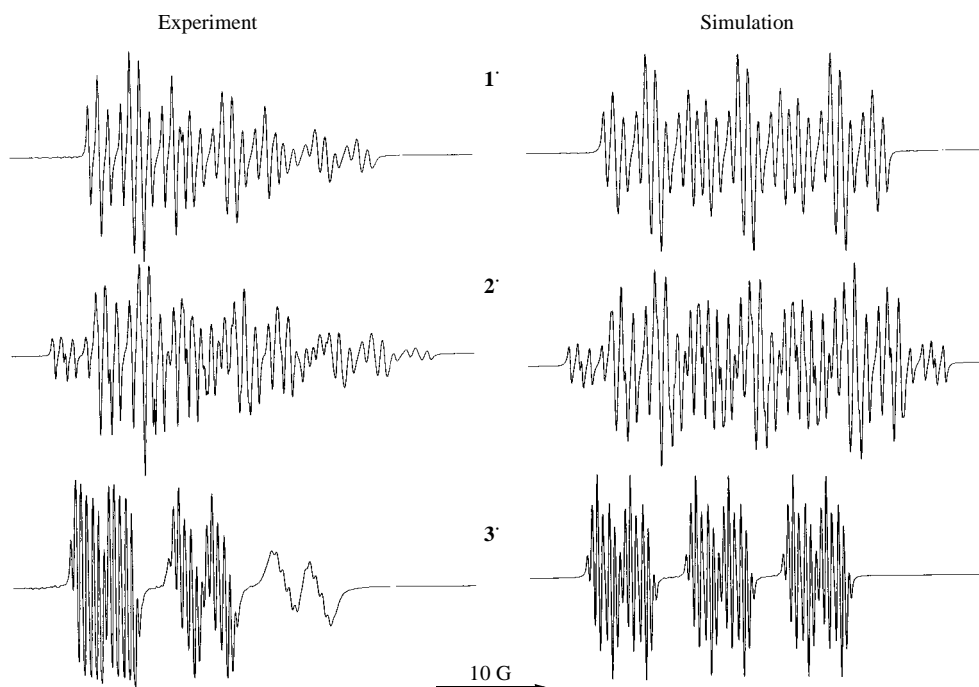
Experiment   Simulation

10 G

Figure 1 Experimental (in squalane) and simulated EPR spectra of **1·–3·**. Differences in the HF line widths were ignored in simulating the spectra.
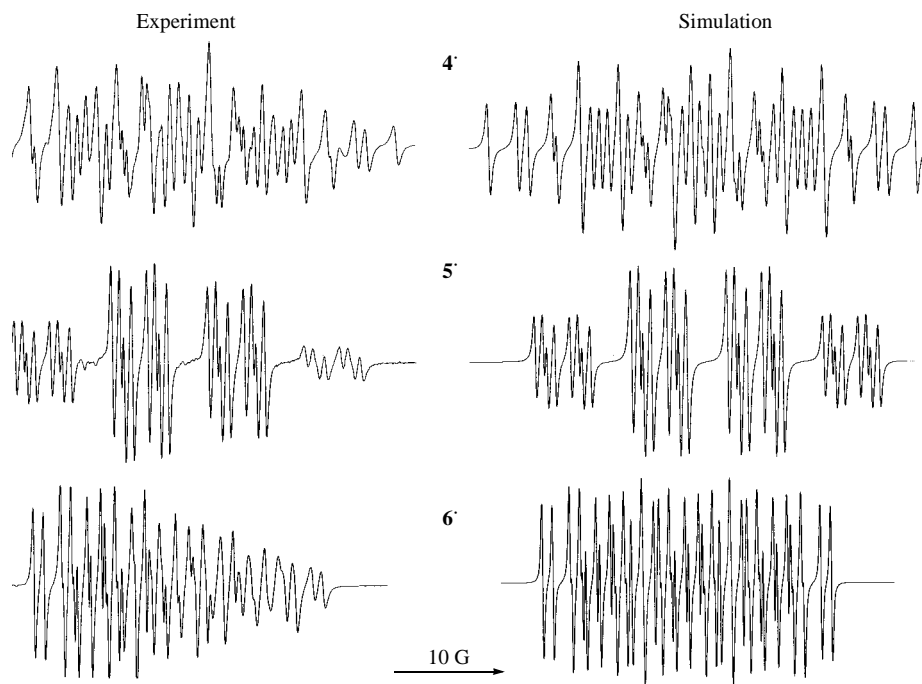
Figure 2 Experimental (in squalane) and simulated EPR spectra of **4**˙–**6**˙. Note minor extra lines of an unidentified radical in the spectrum of **5**˙. Differences in the HF line widths were ignored in simulating the spectra.

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 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).

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

^{a}3H (Me). ^{b}3H (OMe). ^{c}Interchangeable 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 CuCl$_2$·2H$_2$O 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 chloride[12] is readily reduced to **1**˙ with Ph$_3$Sb in toluene at 20 °C. The EPR spectrum is identical to that of the radical arising from the thermolysis of **1**.

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.
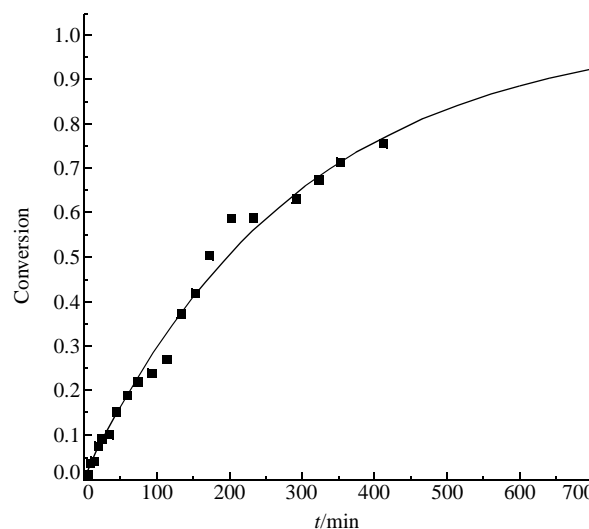

Figure 3 The kinetic build-up curve of **1**˙ by thermolysis of **1** in squalane at 125 °C (initial concentration of **1** was equal to 10^{-3} mol dm^{-3}).

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

T/°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**.
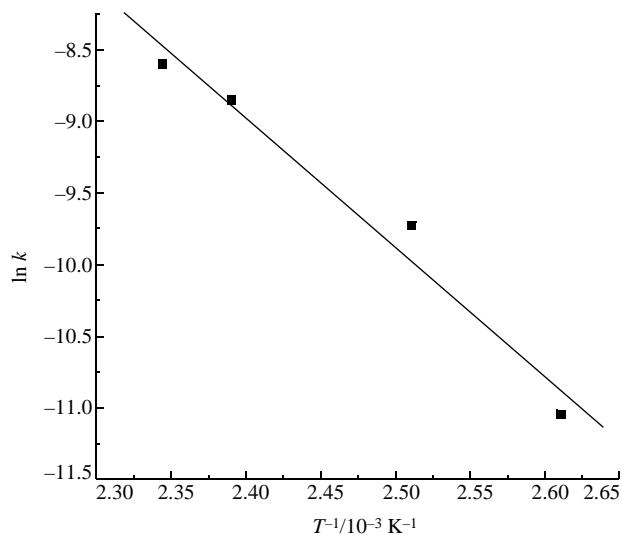^{b}±15%.

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

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