

## Interaction of 1,2,3-benzodithiazolyls (Herz radicals) with dioxygen

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DOI: 10.1070/MC2005v015n01ABEH001984

The interaction of 4,6-di-*tert*-butyl-1,2,3-benzodithiazolyl (Herz radical) **1** with O<sub>2</sub> in a hydrocarbon solution leads to substituted *N,N'*-disulfinyl-2,2'-diaminodiphenyl disulfide **2**, the radical decay kinetics corresponds to a self-termination reaction with a rate constant, which is a linear function of the concentration of dissolved O<sub>2</sub>.

The isomeric 1,2,3- and 1,3,2-benzodithiazolyl  $\pi$ -radicals are of interest for contemporary materials science as potential building blocks in the design and synthesis of molecular magnets or/and molecular conductors.<sup>1,2</sup> However, their instability towards O<sub>2</sub>, especially in solution, represents an impediment to their application. The inhibition of this process, based on an understanding of its chemistry, is obviously necessary to achieve further progress in the field. Although several research groups have observed transformations of these radicals into diamagnetic species in solution under contact with air,<sup>2–6</sup> no products were identified.

We studied the reaction of 1,2,3-benzodithiazolyls (Herz radicals) with O<sub>2</sub> in order to isolate and identify the reaction products and to elucidate the reaction mechanism. Sterically hindered (*i.e.* kinetically stabilised) 4,6-di-*tert*-butyl-1,2,3-benzodithiazolyl **1** (Scheme 1), previously characterised by ESR spectroscopy,<sup>2–4</sup> was chosen for the study.

Radical **1** was obtained by three different techniques (Scheme 1). The reduction of Herz salt **3** with Ph<sub>3</sub>Sb was used in preparative experiments designed to isolate the final products of interaction between **1** and O<sub>2</sub>.<sup>†</sup> Photolysis (313 nm) and mild thermolysis

(140–150 °C) of heterocycle **4** (*i.e.*, a new methodology proposed in refs. 5–8) were employed in the mechanistic studies.<sup>‡,§</sup> In all cases, the formation of **1** and its quantitative yield were assessed

<sup>†</sup> Reaction of 4,6-di-*tert*-butyl-1,2,3-benzodithiazolyl **1** with dioxygen. *N,N'*-Disulfinyl-2,2'-diamino-3,3',5,5'-tetra(*tert*-butyl)diphenyl disulfide **2**. A mixture of 0.30 g (1 mmol) of salt **3**<sup>§</sup> and 0.18 g (0.5 mmol) of Ph<sub>3</sub>Sb in 6 ml of benzene, which was degassed by three freeze–pump–thaw cycles, was stirred under argon for a week at ambient temperature. According to ESR measurements, conversion of **3** into **1** is quantitative under these conditions. When the resulting dark brown-red solution was exposed to dry air, its colour changed to orange-yellow. After pumping off the solvent, the solid residue (0.50 g), consisted of a 1:1 molar mixture of **2** and Ph<sub>3</sub>SbCl<sub>2</sub> (<sup>1</sup>H NMR data), which corresponds to a quantitative yield of **2**. The crude product was recrystallised twice from hexane. Compound **2** was isolated as orange-yellow crystals, 0.16 g (60 %), mp 133–134 °C (lit.,<sup>12</sup> 134 °C). <sup>1</sup>H NMR,  $\delta$ : 7.53, 7.39, 1.38, 1.24. <sup>13</sup>C NMR,  $\delta$ : 149.8, 140.9, 137.7, 128.3, 128.1, 124.7, 35.7, 34.8, 31.0, 29.6. <sup>15</sup>N NMR,  $\delta$ : 330.0. UV-VIS [heptane,  $\lambda_{\max}$ /nm (log  $\epsilon$ ): 382 (3.56). MS,  $m/z$ : 564.1962 (M<sup>+</sup>; calc. for C<sub>28</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub> 564.1973).

<sup>‡</sup> X-ray structure data collected for **2** were in full agreement with published data.<sup>12</sup>

by ESR spectroscopy. Experimental hfc constants are very close to those reported previously<sup>2–4</sup> and agree fairly well with the data calculated at the B3LYP/6-311G\*\* level of theory.<sup>‡</sup>

‡ Photolysis of (2–10) × 10<sup>−4</sup> M solutions of **4** in hexane was performed in a quartz cuvette degassed by bubbling argon, as well as in an ESR quartz tube fitted with a Teflon valve and degassed by three freeze–pump–thaw cycles. The 313 nm line of a DRSh-500 high-pressure mercury lamp equipped with a water filter and a combination of UVS-2 and ZhS-3 glass filters was used. The yields of **1** were quantitative. After photolysis, solutions were saturated with dioxygen by the extensive bubbling of O<sub>2</sub> or air for 3 min. The UV-VIS and ESR spectra were collected.

Thermolysis of a 10<sup>−3</sup> M solution of **4** in squalane (2,6,10,15,19,25-hexamethyltetracosane), degassed as described above, was performed in the same type of ESR tubes. The sample was heated to 145 °C for 1 h, cooled to 20 °C, whereupon a reference ESR spectrum of **1** was measured. The yield of **1** was 95 %.

ESR spectra of radical **1** were recorded on a Bruker EMX spectrometer (MW power of 0.64 mW, modulation frequency of 100 kHz, modulation amplitude of 0.01 mT). The spectral integrations and simulations were performed with the Winsim v1.0 program. The *g*-factor of **1** was measured using DPPH as a standard. The yields of **1** were determined with an accuracy of ±10% by comparison of the radical spectral integrals with the integrals of the spectrum of a single crystal of CuCl<sub>2</sub>·2H<sub>2</sub>O standard containing a known amount of paramagnetic species.

Experimental (calculated by B3LYP/6-311G\*\*, *S*<sup>2</sup> = 0.767 and *S*<sup>2</sup> = 0.750 after annihilation) hfc constants (*G*) and *g*-factor of **1**: *a*<sub>N</sub><sup>3</sup> 8.19 (6.26), *a*<sub>H</sub><sup>5</sup> 0.71 (1.25), *a*<sub>H</sub><sup>7</sup> 0.98 (1.50); 2.0077.

§ 4,6-Di-*tert*-butyl-1,2,3-benzodithiazolium chloride **3** and 5,7-di-*tert*-butyl-1,3,4,δ<sup>2</sup>,2,4-benzodithiadiazine **4**. 2,4-Di-*tert*-butylaniline was converted under standard conditions<sup>13–15</sup> into *N*-sulfinyl-2,4-di-*tert*-butylaniline **9**: orange oil, 78%, bp 123–125 °C/3 Torr. <sup>1</sup>H NMR, δ: 8.43, 7.37, 7.20, 1.44, 1.32. MS, *m/z*: 251 (*M*<sup>+</sup>; calc. for C<sub>14</sub>H<sub>21</sub>NOS 251).

Compound **9** was transformed into 1-(2,4-di-*tert*-butylphenyl)-3-trimethylsilyl-1,3-diaza-2-thiaallene **10** by reaction with LiN(SiMe<sub>3</sub>)<sub>2</sub> (hexane, −30 °C; for typical protocols, see refs. 13–15). Compound **10**: red oil, 72%, bp 135–136 °C/3 Torr. <sup>1</sup>H NMR, δ: 7.97, 7.41, 7.19, 1.52, 1.41, 0.29. UV-VIS [heptane, λ<sub>max</sub>/nm (log ε)]: 363 (3.97). MS, *m/z*: 322.1898 (*M*<sup>+</sup>; calc. for C<sub>17</sub>H<sub>30</sub>N<sub>2</sub>SSi 322.1899).

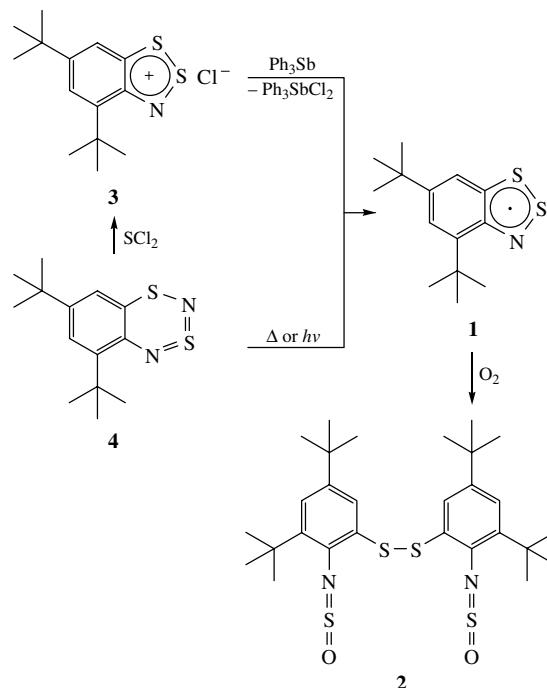
Under argon, solutions of 1.61 g (5 mmol) of **10** and 0.39 g (3.8 mmol) of SCl<sub>2</sub>, each in 30 ml of CH<sub>2</sub>Cl<sub>2</sub>, were mixed by adding them to 150 ml of boiling CH<sub>2</sub>Cl<sub>2</sub> over a period of 1 h. After an additional 1 h, the reaction mixture was cooled to 20 °C, filtered, the solvent was distilled off, and the residue was fractionally sublimed in a vacuum and recrystallised from hexane. Compound **4** was obtained as black crystals, 0.10 g (6% according to SCl<sub>2</sub>), mp 64–65 °C. <sup>1</sup>H NMR, δ: 6.61, 5.61, 1.19, 1.13. <sup>13</sup>C NMR, δ: 156.1, 141.6, 135.9, 125.0, 120.2, 114.5, 35.1, 34.8, 30.4, 30.1. <sup>15</sup>N NMR, δ: 270.5, 266.4. UV-VIS [CHCl<sub>3</sub>, λ<sub>max</sub>/nm (log ε)]: 626 (2.68), 383 (3.34), 302 (4.16), 294 (4.18), 258 (3.81).

At 20 °C, a solution of 0.85 g (3 mmol) of **4** in 10 ml of CH<sub>2</sub>Cl<sub>2</sub> was added to a solution of 0.31 g (3 mmol) of SCl<sub>2</sub> in 10 ml of the specified solvent. The reaction mixture was stirred overnight, filtered, diluted with 100 ml of CCl<sub>4</sub>/hexane (1:1) and kept at −20 °C. Salt **3** was obtained as orange crystals, 0.40 g (44%), mp 248–250 °C (241 °C).<sup>16</sup> <sup>1</sup>H NMR, δ: 9.26, 7.96, 1.42, 1.29. <sup>13</sup>C NMR, δ: 161.8, 161.3, 160.6, 149.3, 127.1, 119.9, 37.0, 36.7, 30.1, 30.0. <sup>15</sup>N NMR, δ: 402.9. UV-VIS [CHCl<sub>3</sub>, λ<sub>max</sub>/nm (log ε)]: 435 (3.45, sh.), 3.77 (3.84), 353 (3.86), 253 (3.65). MS, *m/z*: 266.1043 (*M*<sup>+</sup> − Cl, calc. for C<sub>14</sub>H<sub>20</sub>NS<sub>2</sub> 266.1037).

X-ray structure data for **4**: C<sub>14</sub>H<sub>20</sub>N<sub>2</sub>S<sub>2</sub>, *M* = 280.44, triclinic, *a* = 10.234(1), *b* = 11.597(1) and *c* = 14.922(1) Å, α = 107.066(9)°, β = 105.473(9)°, γ = 102.981(9)°, *V* = 1540.8(3) Å<sup>3</sup>, space group *P*1̄, *Z* = 4, *d*<sub>calc</sub> = 1.209 g cm<sup>−3</sup>, μ(MoKα) = 0.331 mm<sup>−1</sup>. The final indices are *wR*<sub>2</sub> = 0.1453, *S* = 1.025 for all 5270 *F*<sup>2</sup>, *R*<sub>1</sub> = 0.0505 for 3734 *F*<sub>0</sub> > 4σ (486 parameters).

The data were measured on a Bruker P4 diffractometer with graphite-monochromated MoKα radiation (0.71073 Å) using θ/2θ scans (2θ < 50°). A correction for absorption was made by an empirical method based on ψ scans (transmission of 0.90–0.96). The structure was solved by direct methods using the SHELXS-97 program and refined in the full-matrix anisotropic (isotropic for H atoms) approximation using the SHELXL-97 program. The H atoms positions were located from a difference Fourier map.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 234303. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2005.



Scheme 1

The preparative experiments showed that, at room temperature in concentrated (~0.15 M) benzene solution, **1** reacts with dissolved O<sub>2</sub> to give *N,N'*-disulfinyl-2,2'-diaminodiphenyl disulfide **2** (Scheme 1), whose structure was confirmed by X-ray diffraction, in quantitative yield.<sup>†</sup> Thus, the reactivity of Herz radicals towards O<sub>2</sub> seems different from that of the related 4-aryl-1,2,3,5-dithiazolyl radicals, which are known to produce 1,5,2,4,6,8-dithiatetrazocines in contact with air.<sup>9</sup>

The kinetics of decay of **1** was followed by UV-VIS (Figures 1, 2) and ESR spectroscopy, which showed that the reaction can be described as a second-order self-termination reaction  $dR/dt = -kR^2$ , where the time dependence of radical concentration *R* is expressed by the equation  $R(t) = R_0/(1 + kR_0t)$ . The product  $kR_0$  in the denominator is equaled to a fitting parameter α, which depends linearly on the initial radical concentration *R*<sub>0</sub> (Figure 3), whilst the rate constant *k* is proportional to the concentration of dissolved O<sub>2</sub> (Figure 2). Solutions saturated with O<sub>2</sub> (concentration of 1.56 × 10<sup>−2</sup> mol dm<sup>−3</sup>)<sup>10</sup> or air (O<sub>2</sub> concentration 4.8 times lower) were used in all of the experiments.

The kinetics and products of the decay of radical **1** can be reproduced by assuming that the reaction begins with reversible

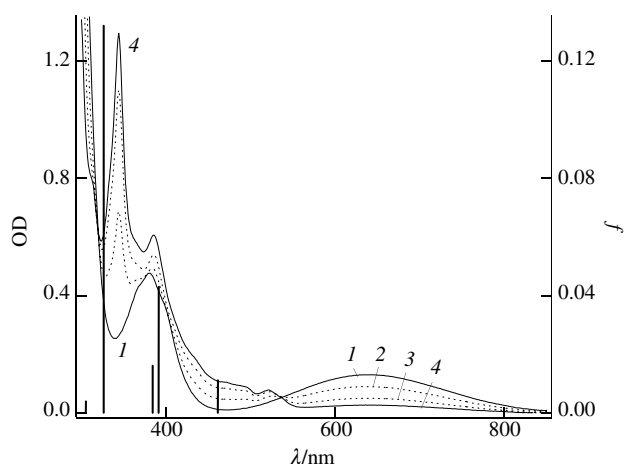
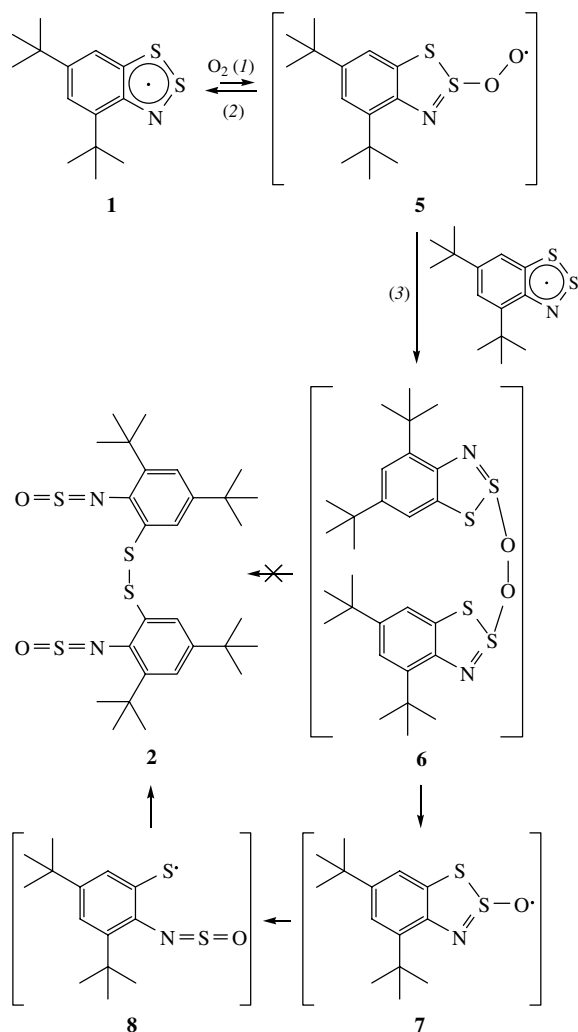


Figure 1 UV-VIS spectrum of (*I*) compound **4** (*c* = 0.17 × 10<sup>−3</sup> M) in hexane and its changes upon 313 nm photolysis for (2) 5, (3) 20 and (4) 40 min. The TD-B3LYP/6-311+G\*\* positions and oscillator strengths (*f*) of the absorption bands of the parent 1,2,3-benzodithiazolyl are depicted as solid bars.



Scheme 2

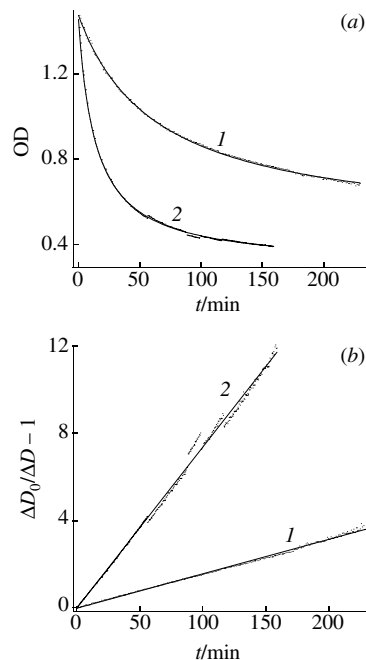
addition of  $O_2$  to **1**, giving peroxy radical **5**, whereby the equilibrium is shifted significantly towards **1**. Peroxy radical **5** may then add **1** to give peroxide **6** (Scheme 2), which is an isomer of final product **2**.

The value of  $k$  can be expressed in terms of the rate constants of the above elementary reactions (1–3, Scheme 2) by the equation  $k = (k_1 k_3 / k_2) [O_2] = k_3 K_{12} [O_2]$ . From the value of  $k$  measured for two  $O_2$  concentrations, the value of  $k_3 K_{12}$  was deduced to be  $(3.5 \pm 0.5) \times 10^2 \text{ dm}^3 \text{ mol}^{-2} \text{ s}^{-1}$ . Assuming that the rate constant of radical recombination  $k_3$  is close to the typical value of  $\sim 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , the equilibrium constant  $K_{12}$  can be estimated to be as low as  $\sim 4 \times 10^{-7} \text{ dm}^3 \text{ mol}^{-1}$ . Therefore, reaction (1) is endothermic and its enthalpy can be roughly estimated at  $\sim 50 \text{ kJ mol}^{-1}$ . UMP2/6-311G\*\* single point energy calculations at geometries optimised at the UHF level predict a value of  $111 \text{ kJ mol}^{-1}$ .

Two possible mechanisms may be considered for the transformation of **6** into **2**: (1) peroxide bond splitting to form O-centered radicals **7**, which may subsequently undergo ring-opening isomerization to give S-centered radicals **8**, whose recombination affords **2**, and (2) a [3,3] sigmatropic shift resembling a Cope rearrangement (Scheme 2).

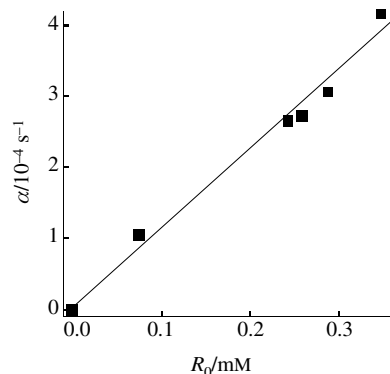
Model B3LYP/6-311G\*\* calculations performed for non-benzo-fused archetypes of the species presented in Scheme 2 failed to yield a transition state for a concerted Cope-like rearrangement of **6** to **2**. At the same time, the calculations revealed that the homolytic cleavage of the peroxide bond followed by rearrangement and recombination of the resulting radicals is a thermodynamically favourable process.

Thus, the final products of the reaction of Herz radicals with  $O_2$  were identified for the first time as substituted diphenyl disulfides bearing two  $-N=S=O$  groups. The reaction begins with the reversible formation of peroxy radicals while its final



**Figure 2** (a) The kinetics of decay of radical **1** absorption at 344 nm (points) in hexane at ambient temperature and  $O_2$  concentrations (1)  $3.28 \times 10^{-3}$  and (2)  $1.56 \times 10^{-2}$  M, and their fitting (solid lines) to the equation  $D_t = D_\infty + \Delta D / (1 + \alpha t)$ . (b) Linear plot of  $\Delta D_0 / \Delta D_t - 1$  vs. time.

products most likely originate from the recombination of thiyl radicals. However, intermediate stages of this interesting new reaction, which obviously requires a hetero ring-opening rearrangement of one of its early products, are unclear.







**Figure 3** Concentration dependence of the fitting parameter  $\alpha = kR_0$  on the initial radical concentration  $R_0$ .

In contrast to  $R-N=S=O$  compounds,  $R-N=Se=O$  derivatives are highly unstable,<sup>11</sup> which seemingly reflects thermodynamic non-attractiveness of the  $-N=Se=O$  function. On this basis, it might be possible to suppress, or at least to attenuate, the instability of Herz radicals towards  $O_2$  by going to their 2-Se counterparts (*i.e.*, 1,2,3-benzothiaselenazolyls), which have so far received little attention.<sup>2</sup>

We are grateful to Professor Yuri N. Molin, Dr. Victor A. Bagryansky and Professor Matthew S. Platz for helpful discussions. This work was supported by the Russian Foundation for Basic Research (grant no. 04-03-32259), the Federal Ministry for Education and Science (project no. UR.05.01.022) and the Division of Chemistry and Materials Science of the Russian Academy of Sciences.

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Received: 17th June 2004; Com. 04/2309