# **Physical Chemistry**

# Electron spin and electron nuclear double resonances of the stable 1-(4-nitrophenyl)-3-phenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl free radical

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The <sup>1</sup>H and <sup>14</sup>N hyperfine structure constants for the stable 1-(4-nitrophenyl)-3-phenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl free radical obtained by the oxidation of 1-(4-nitrophenyl)-3-phenyl-1,4-dihydro-1,2,4-benzotriazine or *N*-phenylbenzamide 4-nitrophenylhydrazone were determined by the ESR and <sup>1</sup>H electron nuclear double resonance methods.

**Key words:** electron spin resonance, <sup>1</sup>H electron nuclear double resonance, stable free radical, 1-(4-nitrophenyl)-3-phenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl, 1-(4-nitrophenyl)-3-phenyl-1,4-dihydro-1,2,4-benzotriazine, amidrazone, oxidation.

The 1,3-diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl radical (1), its selectively isotope-substituted analogs, and 1-(4-chlorophenyl) and 3-*tert*-butyl derivatives have previously been studied by the ESR method.<sup>1–3</sup>



The electron nuclear double resonance (ENDOR) spectra of radical **1** in the mineral oil were recorded for the first time in our previous work.<sup>4</sup> The high-quality <sup>1</sup>H and <sup>15</sup>N electron nuclear triple resonance spectra of radical **1** and its isotope-substituted analogs in toluene have also been measured.<sup>5</sup> This paper is devoted to the ESR and <sup>1</sup>H ENDOR study of spectral characteristics of the stable 1-(4-nitro)-3-diphenyl-1,4-dihydro-1,2,4-benzo-triazin-4-yl free radical (**2**).

The new compound  $\mathbf{2}$  was synthesized according to Scheme 1.

#### Experimental

IR spectra were recorded using a UR-20 instrument for a suspension in Nujol between KBr plates. UV spectra were mea-

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sured with a Specord UV-VIS spectrometer. <sup>1</sup>H NMR spectra were recorded using Varian T-60 and Bruker WM-250 spectrometers using Me<sub>4</sub>Si as the internal standard. The reaction course and the purity of the synthesized compounds were monitored by TLC on Silufol UV-254 plates using an  $Et_2O$ —hexane—methanol (6 : 3 : 1) system as the eluent.

N-Phenylbenzamide 4-nitrophenylhydrazone (3). A solution of 4-nitrophenylhydrazone benzoyl chloride (1.38 g, 5 mmol), freshly distilled aniline (0.47 g, 5 mmol), and triethylamine (0.7 mL, 5 mmol) in ethanol (200 mL) was stirred in a nitrogen atmosphere for 15 h at 18-20 °C. After the solution was stored for 27 days, amidrazone 3 (1.5 g, 90%) precipitated. Fast recrystallization from ethanol by small portions produced brick-red fine needles of compound 3 with m.p. 193-195 °C (decomp., Boetius stage; cf. Ref. 6: 180-181 °C)\* without admixtures of azoimine 4, benzotriazine 5, and benzotriazinyl 2. A similar result was obtained for the reaction in dioxane. An increase in the reaction temperature results in a mixture of products 2, 3, 4, and 5, whose ratio depends, as a rule, on the duration and temperature of the reaction and the method used for the isolation of the target product. It is fairly difficult to separate this mixture, because oxidative transformations of compounds 3 and 5 and heterocyclization of azoimine 4 occur in any solvent (see Refs. 7 and 8). Found (%): C, 68.54; H, 4.72; N, 16.77. C<sub>19</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>. Calculated (%): C, 68.67; H, 4.82; N, 16.86. UV,  $\lambda$ /nm (loge), EtOH: 250 (4.31), 293 (4.09), 427 (4.54); dioxane: 406 (4.48); CCl<sub>4</sub>: 282, 395. IR (Nujol), v/cm<sup>-1</sup>: 3394, 3292, 1608, 1544, 1512, 1348, 1323, 1307, 1280. <sup>1</sup>H NMR, δ, HMFA: 10.53 (s, 1 H, N(1)H); 8.97 (s, 1 H, N(3)H); 8.23 (d, 2 H,  $C_6H_4NO_2$ , J = 9 Hz); 7.80–6.70 (w.m, 12 H, 2 Ph + 2 H, C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>); DMSO: 10.03 (s, 1 H, N(1)H); 8.29 (s, 1 H, N(3)H); 8.01 (d, 2 H,  $C_6H_4NO_2$ , J = 9 Hz); 7.60–6.50 (w.m, 12 H, 2 Ph + 2 H,  $C_6H_4NO_2$ ; 1,4-dioxane: 8.73 (s, 1 H, N(1)H); 8.01 (d, 2 H,  $C_6H_4NO_2$ , J = 9 Hz); 7.70–6.50 (w.m, 13 H,  $2 Ph + N(3)H + 2 H, C_6H_4NO_2$ ).

1-(4-Nitrophenyl)-3-phenyl-1,4-dihydro-1,2,4-benzotriazine (5). Freshly prepared silver oxide (5 g) was added to a solution of amidrazone 3 (1.66 g, 5 mmol) in THF (150 mL), and the suspension was stirred for 3 days in a nitrogen atmosphere. The slime was thoroughly separated, and the solvent was removed in vacuo without heating. Dark green needles of benzotriazine 5 were obtained in 63% yield (1.05 g), m.p. 216-218 °C (decomp., Boetius stage). The substance is well soluble in benzene, dioxane, and acetone and is moderately soluble in alcohols. Found (%): C, 69.42; H, 4.25; N, 16.58. C<sub>19</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>. Calculated (%): C, 69.09; H, 4.24; N, 16.97. UV ( $Pr^{i}OH$ ),  $\lambda/nm$  (loge): 254 (4.42), 470 (4.32). IR (Nujol), v/cm<sup>-1</sup>: 3365, 1650, 1598, 1530 w, 1512, 1498. <sup>1</sup>H NMR (DMSO, δ: 9.47 (s, 1 H, NH); 8.07 (d, 2 H,  $C_6H_4NO_2$ , J = 9 Hz); 7.52 (d, 2 H,  $C_6H_4NO_2$ , J =9 Hz); 7.46 (m, 3 H, H(5)–H(7)); 7.93 (m, 1 H, H(8)); 7.00 (m, 5 H, Ph).

1-(4-Nitrophenyl)-3-phenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (2). A solution of amidrazone 3 in ethanol or dioxane was refluxed for 5—6 days without oxidants or for 1—2 days in the presence of AgO or HgO (methods *A* and *B*), or solutions of benzotriazine 5 were refluxed in ethanol or treated similar to the treatments described in methods *A* and *B*. After the slime was separated and solvents were distilled off, dark violet, almost black needles of compound 2 with m.p. 179—181 °C (decomp., Boetius stage) were obtained. They are well soluble in diethyl ether and acetone and are moderately soluble in benzene and alcohols. The yield of compound 2 was 40—50%. Found (%): C, 68.57; H, 4.06; N, 17.11. C<sub>19</sub>H<sub>13</sub>N<sub>4</sub>O<sub>2</sub>. Calculated (%): C, 69.30; H, 3.95; N, 17.02. UV,  $\lambda$ /nm (loge), Et<sub>2</sub>O: 273 (4.83), 370 (4.10), 492 (3.98), 565 (3.75); CCl<sub>4</sub>, 370, 489, 590. IR (Nujol), v/cm<sup>-1</sup>: 1598, 1521, 1485, 1409, 1359, 1310.

**Spectroscopic studies.** Product **2** was dissolved in toluene in a concentration of  $10^{-3}$  mol L<sup>-1</sup>. The freezing—thawing procedure was performed three times to remove oxygen from the sample. ESR and ENDOR spectra were recorded using a Bruker-ER200D radiospectrometer (Germany) using an ENDOR/TRIPLE attachment and a B-VT-1000 temperature variator.

<sup>\*</sup> The reaction of aniline with  $\alpha$ -nitrobenzaldehyde 4-nitrophenylhydrazone in ethanol, which was carried out by Ponzio and co-authors,<sup>6</sup> should yield the oxidant (the nitrite anion). The melting point of the reaction product decreases due to oxidative processes (m.p. 179–181 °C). Perhaps, in this case, the reaction product is radical **2** rather than amidrazone **3**.

The HFS constants for product 2, which were obtained from the <sup>1</sup>H ENDOR and ESR spectra and by the calculation of the theoretical ESR spectra, are presented in Table 1. The program for ESR spectra simulation produced the theoretical spectrum in the isotropic or anisotropic medium with the chaotic distribu-

Magnetic nuclei	1 <sup>6</sup>	2	Magnetic nuclei	1 <sup>6</sup>	2
N(1)	7.51	6.8	H(2´), H(6´)	0.75	0.55
N(2)	4.78	5.4	H(3'), H(5')	0.51	0.55
N(4)	5.05	5.6	N(4′)	0.61	0.66
H(5)	1.36	1.40	H(2"), H(6")	0.23	0.25
H(6)	1.19	0.95	H(3"), H(5")	0.14	0.13
H(7)	1.84	1.99	H(4")	0.23	0.35
H(8)	0.87	0.95			

Table 1. Absolute values of the HFS constants (in G) of benzotriazinyl radicals 1 and 2

tion of paramagnetic species. The resonance fields and probabilities of transitions were calculated using the theory of firstorder perturbations.

### **Results and Discussion**

The ESR spectrum of radical **2** in toluene is shown in Fig. 1. Despite a very low concentration  $(10^{-3} \text{ mol } \text{L}^{-1})$  of radical **2**, we could not achieve a satisfactory resolution of the ESR spectrum.

The study of radical 2 in toluene at 193 K by <sup>1</sup>H ENDOR spectroscopy was more successful. The ENDOR spectra (Fig. 2) distinctly demonstrate the splittings from protons of the aryl rings bound to both the nitrogen atom in position 1 and the carbon atom in position 3.

A comparison of the spectral characteristics of compounds 1 and 2 shows that the introduction of the nitro group to position 4 of the 4 *N*-phenyl fragment has an



**Fig. 1.** ESR spectrum of a  $10^{-3}$  *M* solution of compound **2** in toluene at 298 K.

insignificant effect on the spin density distribution. The spin density is mainly concentrated in the triazine cycle of both radical 1 and 1-(4-chlorophenyl)-3-phenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (6).<sup>1-4</sup>

We examined and calculated the spectra assuming the free rotation of the aryl substituents around the N—C and C—C bonds in the ESR time scale.<sup>2–4</sup> The N(1) atom has a considerable spin density and  $a_{N(1)}$  is by an order of magnitude higher than  $a_{H(2')}$ ,  $a_{H(6')}$ ,  $a_{H(3')}$ ,  $a_{H(5')}$ , and  $a_{N(4')}$ . The observed splittings from the protons of the 3-phenyl ring are insignificant:  $a_{H(4'')} = 0.35$  G,  $a_{H(2'')} = a_{H(6'')} = 0.13$  G.

Taking into account the stereochemical peculiarities of radical 2, we can assume that in radical 2, like in radicals 1 and 6, the steric interaction between the H(8) proton and H(2<sup>'</sup>) and H(6<sup>'</sup>) protons is hindered due to



Fig. 2. <sup>1</sup>H ENDOR spectrum of a  $10^{-3}$  M solution of compound 2 in toluene at 193 K.

the coplanar arrangement of the N-aryl substituent and 1,4-dihydro-1,2,4-benzotriazinyl entity. The nonplanar arrangement of the fragments impedes the spin density delocalization in the N-aryl fragment, and the character of orbital interactions hinders the spin density delocalization in the C-phenyl fragment. The assumption about steric hindrances in the molecules and 1,4-dihydro-1,2,4benzotriazinyl radicals<sup>5</sup> was experimentally confirmed. The X-ray diffraction studies of 1-(4-chlorophenyl)-3phenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl<sup>3</sup> (6), radical 1,<sup>9</sup> and 1,3,5,8-tetraphenyl-1,2,4,5,7,8-hexazaanthracene-4,6-diyl<sup>10</sup> (7) showed that the phenyl rings bound to the nitrogen atoms are substantially noncoplanar, unlike the *C*-phenyl rings. For example, in radical **1** the turning angle of the phenyl ring about the Ph-N(1) bond is  $-54^{\circ}$ . and that about the Ph-C(3) bond is only 8°. In radical 6, the corresponding angles are 56.9 and 15.9°, and the bonds of the N(1) nitrogen atom have the planar trigonal configuration, which is not characteristic of nitrogen atoms in 8pπ-heterocycles,<sup>11</sup> including 1,4-dihydro-1,2,4-benzotriazine. The N(2)–C(3) and C(3)–N(4) bonds are equal to 1.336(2) and 1.333(2) Å in radical 1 and 1.327(2) and 1.315(3) Å in radical 6, respectively. It is likely that the same situation is retained in radical 2 under study.



The available data<sup>1-5,9,10</sup> indicating that the spin density is mainly delocalized in the amidrazonyl fragment of the 1,4-dihydro-1,2,4-triazinyl cycle, regardless of the nature of substituents in the 1-phenyl fragment, suggest that resonance structure **8** is most preferential for radicals of the 1,4-dihydrobenzo-1,2,4-triazinyl series. Structure **8** is close to structure **9**, which was considered<sup>12</sup> as a possible resonance structure.



Based on the results obtained in this work, we can conclude that the complex use of different methods of magnetic resonance allows one to identify free radicals and obtain a detailed information on HFS constants of free radicals with bulky and low-symmetry structures.

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