Thermal transformations of 2*H*-benzimidazole 1,3-dioxides

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Thermal transformations of 2*H*-benzimidazole 1,3-dioxides represented by spiro[2*H*-benzimidazole-2,1´-cyclohexane] 1,3-dioxide and its 5-nitro derivative were studied. Their heating resulted in reversible isomerization to spiro[3*H*-[2,1,4]benzoxadiazine-3,1´-cyclohexane] 4-oxides. More prolonged heating of 2*H*-benzimidazole 1,3-dioxides caused sequential elimination of the first and then (at higher temperature) the second N-oxide oxygen atom to form 2*H*-benzimidazole derivatives, which upon further heating were transformed to 7,8,9,10-tetrahydro-6*H*-azepino[1,2-*a*]benzimidazoles. A scheme of the process was suggested, which described the experimental data obtained. Spiro[3*H*-[2,1,4]benzoxadiazine-3,1´-cyclohexane] 4-oxides on exposure to the sunlight were quantitatively transformed to 2*H*-benzimidazole 1,3-dioxides.

Key words: 2*H*-benzimidazoles, 2,1,4-benzoxadiazines, heterocyclic N-oxides, rearrangements, phototransformation, oxidation.

2*H*-Benzimidazoles are known and relatively well studied heterocyclic compounds,[1,2] while 2*H*-benzimidazole 1,3-dioxides are studied considerably less. It was also noted[3] that these compounds possess unusual reactivity. Recently,[4—6] it was published that some 2*H*-benzimidazole 1,3-dioxides display high biological activity against tripanosomic parasites (*Tripanosoma cruzi* and *Leishmania spp*), whose action is comparable with that of known drugs used for the treatment of diseases caused by these parasites. In this connection, studies of properties of 2*H*-benzimidazole 1,3-dioxides is an actual problem.

It is known[7] that 2*H*-benzimidazoles upon heating undergo 1,5-sigmatropic rearrangement to 2,3-disubstituted 1*H*-benzimidazoles. Information on the behavior of 2*H*-benzimidazole 1,3-dioxides on heating is absent. The purpose of the present work is to study thermal transformations of 2*H*-benzimidazole 1,3-dioxides.

Heating of spiro[2*H*-benzimidazole-2,1´-cyclohexane] 1,3-dioxide (**1**) in the inert solvent, chlorobenzene, at 110 °C results in the reaction mixture, from which spiro[3*H*-[2,1,4]benzoxadiazine-3,1´-cyclohexane] 4-oxide (**2**) and already known spiro[2*H*-benzimidazole-2,1´-cyclohexane] 1-oxide (**3**)[3] were isolated (Scheme 1). Benzoxadiazine **2** has proved very unstable (especially in solutions) and was easy transformed to the starting dioxide **1** on heating and in the light, that made difficult its isolation from the reaction mixture and handling. The structure of compound **2** was established based on the spectral and analytical data (see Experimental). The TLC data show that more prolonged heating of compound **1** in chlorobenzene leads to the formation of the intermediate spiro[2*H*-benzimidazole-2,1´-cyclohexane] (**4**), and already known 7,8,9,10-tetrahydro-6*H*-azepino[1,2-*a*]benzimidazole (**5**)[8] was the only final product of the reaction (demonstrated on the thermolysis of compound **3** in *o*-dichlorobenzene taken as an example).

Thus, it can be suggested that upon heating of compound **1**, elimination of the N-oxide oxygen atoms occurs initially to form 2*H*-benzimidazole **4**, and then its 1,5-sigmatropic rearrangement leads to compound **5**.

Earlier,[9] we have shown that the reaction of benzofuroxanes with alcohols or alkyl halides in sulfuric or perchloric acids smoothly gives 2*H*-benzimidazole 1,3-dioxides. 5-Nitrobenzofuroxane easy leads to 5-nitrospiro[2*H*-benzimidazole-2,1´-cyclohexane] 1,3-dioxide (**6**). Upon heating of compound **6** in chlorobenzene, the initially dark blue solution rapidly turns bright red. Chromatographic separation of the reaction mixture yielded, in addition to the starting compound **6**, four products: isomeric 2,1,4-benzoxadiazine 4-oxides **7** and **8** and 2*H*-benzimidazole 1-oxides **9** and **10**. The structure of compound **7** has been established earlier[9] based on the ^{1}H and ^{13}C NMR data. We confirmed the structure of this compound by X-ray crystallography. The structure of molecule **7** in the crystal is shown in Fig. 1. Data on similar oxadiazines are absent in the Cambrige Structural Database. Distribution of the bond lengths corresponds to the conjugated system of double bonds. The nitro group comes out of the plane of the benzene ring by 2.1(1)°. The heterocycle is characterized by the twisted boat conformation with the atoms N(1)

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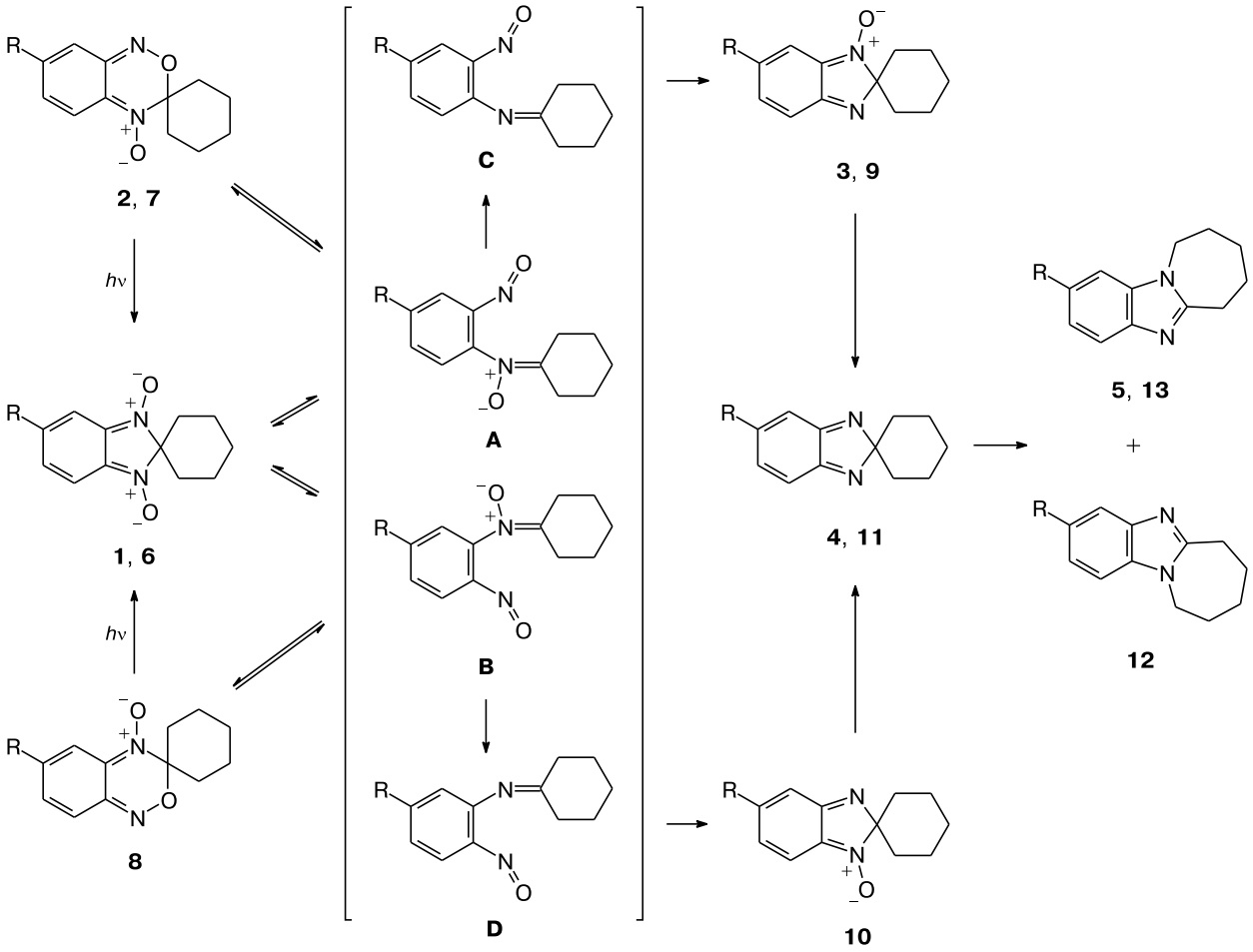
Scheme 1



R = H (**1**—**5**), NO_2 (**6**—**13**)

and O(2) coming out of the plane C(3)N(4)C(4a)C(8a) by 0.382 and 0.782 Å, respectively, whereas, the cyclohexane ring has the chair conformation. Molecules in the crystal form layers by the weak hydrogen bonds C(8)—H(8)...N(1) (H...N, 2.46(2) Å; C—H...N, 167(2)°), C(5)—H(5)...O(1) (H...O, 2.54(2) Å; C—H...O, 145(2)°),

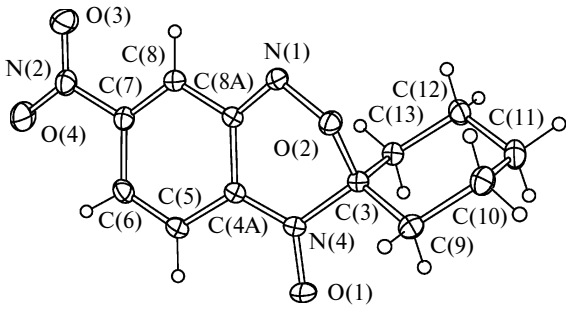


Fig. 1. The spatial structure of 7-nitrospiro[3*H*-[2,1,4]benzoxadiazine-3,1′-cyclohexane] 4-oxide (**7**) molecule according to the X-ray crystallographic data.

C(13)—H(13A)...O(4) (H...O, 2.55(2) Å; C—H...O, 160(2)°) and by the interaction O(2)...π (C(4a)C(5)C(6)—C(7)C(8)C(8a)) with the distance O—centroid equal to 3.248 Å.

The structure of compound **9** was also established by us by X-ray crystallography. The spatial structure of the molecule of compound **9** is shown in Fig. 2. The atoms of the 6-nitrobenzimidazole 1-oxide fragment are on the mirror plane. The cyclohexane fragment spiro-jointed with it is divided by this plane along the atoms C(2) and C(10) to the two dependent parts and has the chair conformation. The Cambrige Structural Database[10,11] has only three structures with similar tricyclic framework: 5,6-(*N*,*N*′-dipiperidino)isobenzimidazole-2-spirocyclohexane,[12] dispiro-[2*H*-benzimidazole-2,1′-cyclohexane-4′,2″-[2*H*]benzimidazole] 1,1″-dioxide,[13] and 4-bromo-6-(2,3-dichlorophenoxy)-2*H*-benzimidazole-2-spirocyclohexane.[14] Analysis of geometry of compound **9** showed that its bond lengths and bond angles are close to the corresponding values in the found compounds and agree with the literature data.[15]

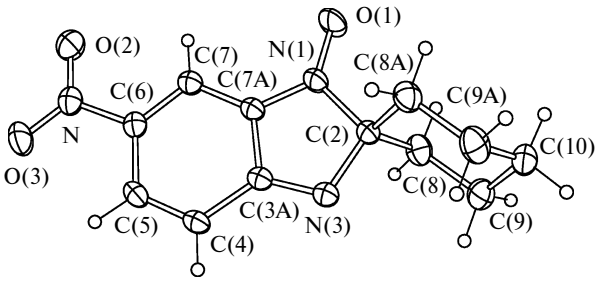


Fig. 2. The spatial structure of 6-nitrospiro[2*H*-benzimidazole-2,1´-cyclohexane] 1-oxide (**9**) molecule according to the X-ray crystallographic data.

The X-ray crystallographic results together with other spectral and analytical data also confirm the structures of compounds **8** and **10**, which are isomeric to compounds **7** and **9**.

We studied how composition of the reaction products changes with time. For this, we collected aliquots during reflux of 2*H*-benzimidazole 1,3-dioxide **6** in chlorobenzene through the certain periods of time and recorded ^{1}H NMR spectra for them (Fig. 3). Composition of the mixture was calculated based on the relative integral intensities of the signals for the aromatic protons characteristic of each compound. The data obtained are shown in Fig. 4. It is seen that the amount of the starting compound **6** monotonously decreases during reflux of the solution (see Fig. 4) with simultaneous accumulation of 2*H*-benzimidazole mono-*N*-oxides **9** and **10** in the reaction mixture. The amount of 2,1,4-benzoxadiazine 4-oxides **7** and **8** rapidly grows in the initial period, reaches the maximum, and then gradually decreases until complete disappearance after the dioxide **6** was consumed. Proceeding from these data, it would have been suggested that 2*H*-benzimidazole 1-oxides **9** and **10** are formed through the intermediate 2,1,4-benzoxadiazine 4-oxides **7** and **8**. However, heating of compounds **7** or **8** in chlorobenzene shows the presence of products **6**—**10** in the reaction mixture (TLC data). Apparently, 2,1,4-benzoxadiazine 4-oxides are not the intermediate compounds in the elimination reaction of oxygen.

Heating of 2*H*-benzimidazole 1-oxides **9** and **10** in *o*-dichlorobenzene at higher temperature furnished 2-spirocyclohexyl-2*H*-benzimidazole **11** and a mixture of azepino[1,2-*a*]benzimidazoles **12** and **13** (see Scheme 1).

Based on the facts mentioned above, we suggested the following scheme describing the transformations observed. It is possible that heating of 2*H*-benzimidazole 1,3-dioxides **1** and **6** forms nitroso nitrones **A** and **B** as the intermediates (see Scheme 1), which are able either to reversibly cyclize to 1,2,4-benzoxadiazine 4-oxides **2**, **7**, and **8** or lose oxygen with the formation of nitroso imines **C** and **D** as the intermediates. The latter, in turn, can irreversibly cyclize to 2*H*-benzimidazole 1-oxides **3**, **9**, and **10**. Further heating of compounds **3**, **9**, and **10** at higher temperature eliminates another oxygen atom to furnish 2*H*-benzimidazoles **4** and **11**, which are transformed to azepino[1,2-*a*]benzimidazoles **5**, **12**, and **13** by the known 1,5-sigmatropic rearrangement[7] (see Scheme 1).

The oxygen atoms in heterocyclic N-oxides in the absence of oxygen acceptors can be removed by heating, but this occurs at high temperature.[15,16] At the same time, it is known[17,18] that all the nitrones are more or less thermally labile, for which the Cope rearrangement, *i.e.*, transformation of nitrones to the oxime ethers on heating, was described.[19—22] Apparently, in this case 2,1,4-benzoxadiazine 4-oxides **2**, **7**, and **8** are formed as a result of rearrangement similar to the Cope rearrangement, which is

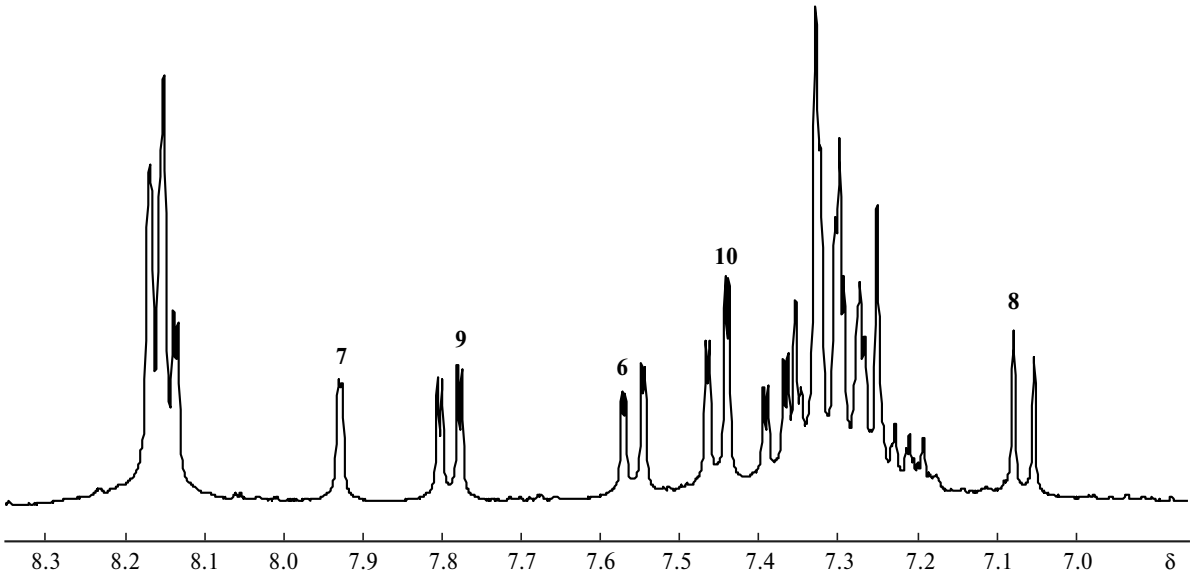


Fig. 3. The fragment of the ^{1}H NMR spectrum of the reaction mixture during thermolysis of 5-nitrospiro[2*H*-benzimidazole-2,1´-cyclohexane] 1,3-dioxide (**6**) in chlorobenzene after 1.5 h. Characteristic signals for the protons of each component of the mixture are marked.

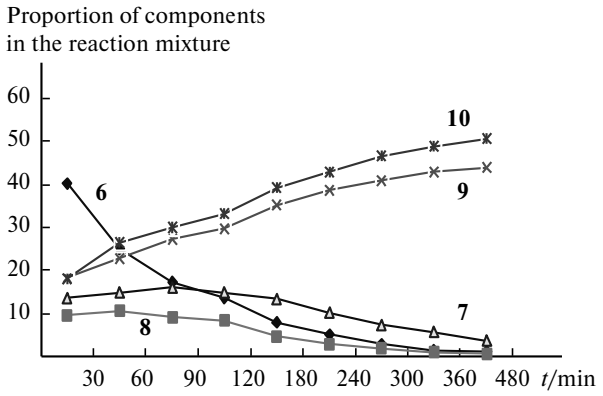


Fig. 4. The changes in the concentration of the reaction products **7**—**10** with time during reflux of 5-nitrospiro[2*H*-benzimidazole-2,1´-cyclohexane] 1,3-dioxide (**6**) in chlorobenzene.

characteristic of nitrones. The easy enough elimination of the N-oxide oxygen atom in 2*H*-benzimidazole 1,3-dioxides upon moderate heating also indicates that these compounds resemble nitrones in their properties. Thus, 2*H*-benzimidazole 1,3-dioxides **1** and **6** on heating display properties typical of nitrones.

It should be noted that exposure of solutions or powders of benzoxadiazines **2**, **7**, or **8** to the sunlight leads to 2*H*-benzimidazole 1,3-dioxides **1** or **6**, respectively. The photochemical isomerization of benzoxadiazines can be formally called the retro-Cope rearrangement (transformation of the oxime ether to the nitrone). We have no information on such transformations, and, apparently, this is the first example of such a rearrangement. Earlier,[9] we have reported that compound **7** is converted to compound **6** on keeping in sulfuric acid.

It is known[17,23] that N-oxides of heterocyclic compounds are oxidants. 2*H*-Benzimidazole 1,3-dioxides are no exception. Heating of compound **6** in benzene with hydroquinone in the equivalent amount gives benzoquinone in 60% isolated yield.

In conclusion, elimination of the oxygen atoms from 2*H*-benzimidazole 1,3-dioxides takes place sequentially. The first step presumably includes formation of a nitroso nitrone as the intermediate (the evidence is formation of 2,1,4-benzoxadiazines), which then eliminate the oxygen atom to furnish 2*H*-benzimidazole 1-oxides. Further, the second oxygen atom is eliminated at higher temperature to yield 2*H*-benzimidazole. Apparently, elimination of the second oxygen atom follows the mechanism similar to that characteristic of heterocyclic compound N-oxides.[16]

Experimental

IR spectra were recorded on a Bruker Vector-22 spectrometer in KBr pellets (the concentration was 0.25%), UV spectra were recorded on a Hewlett-Packard 4853 instrument in ethanol. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-300 spectrometer in $CDCl_3$ and DMSO-d_6 for 10% solutions at 25 °C. Chemical shifts were measured relatively to the residual signals of the solvents: $CHCl_3$ (δ_H 7.24, δ_C 76.90) and DMSO-d_6 (δ_H 2.50, δ_C 39.50). Splitting of the signals in the ^{13}C NMR spectra was determined using *J*-modulation (JMOD) and ^{13}C—H correlations. Mass spectra were recorded on a Thermo—Scientific DFS instrument (70 eV, a direct injection of compounds, the temperature of the source of ions was 180 °C); the peaks whose intensities are higher than 10% are reported. The reaction progresses and individuality of compounds were monitored by TLC on Sorbfil UV-254 plates (Sorbpolimer, Krasnodar, Russia); the plates were visualized by UV light and in iodine vapors. Compounds **1** and **6** were synthesized according to the known procedure.[9] Chlorobenzene and *o*-dichlorobenzene were freshly distilled. Melting points were determined on a Kofler microheating stage. Elemental analysis was performed in the Laboratory of Microanalysis of the Novosibirsk Institute of Organic Chemistry SB RAS.

Thermolysis of spiro[2*H*-benzimidazole-2,1´-cyclohexane] 1,3-dioxide (1). A solution of di-N-oxide **1** (2.54 g, 0.012 mol) in chlorobenzene (50 mL) was heated for 2.5 h at 110 °C. The solvent was evaporated *in vacuo*, the residue was subjected to chromatography on SiO_2 (hexane—ethyl acetate (10 : 1)) to obtain three fractions. The first fraction was for the second time subjected to chromatography on SiO_2 (hexane) to isolate spiro[3*H*-[2,1,4]benzoxadiazine-3,1´-cyclohexane] 4-oxide (**2**) (0.09 g, 3.5%). The second fraction yielded spiro[2*H*-benzimidazole-2,1´-cyclohexane] 1-oxide (**3**) (1.6 g, 63.0%). The third fraction (0.6 g, 23.6%) was the starting compound **1**.

Spiro[3*H*-[2,1,4]benzoxadiazine-3,1´-cyclohexane] 4-oxide (2). M.p. 78—80 °C (from hexane). Found (%): C, 66.06; H, 6.42; N, 12.84. $C_{12}H_{14}N_2O_2$. Calculated (%): C, 66.03; H, 6.47; N, 12.84. UV, λ_{max}/nm (logε): 379 (3.55), 440 (3.53). IR, ν/cm^{-1}: 1612 (C=N). ^{1}H NMR ($CDCl_3$), δ: 1.20—1.32 (m, 1 H, CH); 1.68—2.05 (m, 9 H, CH, 4 CH_2); 6.55—6.68 (m, 2 H, 2 CH); 6.81—6.85, 7.11—7.15 (both m, 1 H each, 2 CH). ^{13}C NMR ($CDCl_3$), δ: 28.30, 24.19, 21.60 (all CH_2); 118.06, 123.88, 127.88, 128.86 (all CH); 96.08 (C(3)); 128.86 (C(8a)); 150.77 (C(4a)). MS, *m*/*z* (I_{rel} (%)): 218 $[M]^+$ (76), 202 (18), 201 (13), 185 (44), 171 (13), 164 (10), 148 (18), 147 (19), 127 (20), 131 (21), 120 (33), 98 (100). HRMS, found: *m*/*z* 218.1052 $[M]^+$. $C_{12}H_{14}N_2O_2$. Calculated: M = 218.1050.

Spiro[2*H*-benzimidazole-2,1´-cyclohexane] 1-oxide (3). M.p. 84—86 °C (from benzene) (*cf.* Ref. 3: m.p. 86 °C).

Thermolysis of spiro[2*H*-benzimidazole-2,1´-cyclohexane] 1-oxide (3). A solution of mono-N-oxide **3** (0.57 g, 0.0028 mol) in *o*-dichlorobenzene (10 mL) was heated for 3 h at 165 °C. The solvent was evaporated *in vacuo*, the residue was subjected to chromatography on SiO_2 (benzene—acetone (10 : 1)) to isolate the starting compound **3** (0.1 g, 17.5%), spiro[2*H*-benzimidazole-2,1´-cyclohexane] (**4**) (0.07 g, 12.5%), and 7,8,9,10-tetrahydro-6*H*-azepino[1,2-*a*]benzimidazole (**5**) (0.2 g, 35%).

Spiro[2*H*-benzimidazole-2,1´-cyclohexane] (4). M.p. 63—65 °C (from benzene) (*cf.* Ref. 3: m.p. 65 °C).

7,8,9,10-Tetrahydro-6*H*-azepino[1,2-*a*]benzimidazole (5). M.p. 125—126 °C (from benzene) (*cf.* Ref. 8: m.p. 125—126 °C). ^{1}H NMR ($CDCl_3$), δ: 1.70—1.95 (m, 6 H, 3 CH_2); 3.00—3.10, 4.05—4.15 (both m, 2 H each, 2 CH_2); 7.12—7.22 (m, 3 H, 3 CH); 7.62—7.70 (m, 1 H, CH). ^{13}C NMR ($CDCl_3$), δ: 25.43, 28.56, 29.97, 30.79, 44.27 (all CH_2); 108.61, 119.07, 121.30, 121.70 (all CH); 135.68, 142.28, 157.36 (all C).

Thermolysis of 5-nitrospiro[2*H*-benzimidazole-2,1´-cyclohexane] 1,3-dioxide (6). ***A.*** A solution of di-N-oxide **6** (6.18 g, 0.023 mol) in chlorobenzene (150 mL) was refluxed for 6 h, the solvent was evaporated *in vacuo*. The residue was subjected to chromatography on SiO_2 (hexane—ethyl acetate (5 : 1)) to sequentially isolate 7-nitrospiro[3*H*-[2,1,4]-benzoxadiazine-3,1´-cyclohexane] 4-oxide (**7**) (0.25 g, 4%), 6-nitrospiro[3*H*-[2,1,4]-benzoxadiazine-3,1´-cyclohexane] 4-oxide (**8**) (0.5 g, 8%), 6-nitrospiro[2*H*-benzimidazole-2,1´-cyclohexane] 1-oxide (**9**) (1.50 g, 26%), and 5-nitrospiro[2*H*-benzimidazole-2,1´-cyclohexane] 1-oxide (**10**) (2.6 g, 46%). On the TLC plates, the following spots were also visualized (hexane—ethyl acetate (5 : 1)): the dark blue one with R_f 0.23 (the starting compound **6**), the orange one with R_f 0.25 (compound **9**), the yellow one with R_f 0.42 (compound **10**), the orange one with R_f 0.53 (compound **8**), and the yellow one with R_f 0.61 (compound **7**).

Compound 6. ^{1}H NMR ($CDCl_3$), δ: 1.50—1.52 (m, 2 H, CH_2); 1.80—2.10 (m, 8 H, 4 CH_2); 7.32 (d, 1 H, H(7), $J_{7,6}$ = = 10.0 Hz); 7.59 (dd, 1 H, H(6), $J_{6,7}$ = 10.0 Hz, $J_{6,4}$ = 1.7 Hz); 8.18 (dd, 1 H, H(4), $J_{4,6}$ = 1.9 Hz, $J_{7,4}$ = 1.7 Hz).

7-Nitrospiro[3*H*-[2,1,4]-benzoxadiazine-3,1´-cyclohexane] 4-oxide (7). M.p. 171—173 °C (from benzene) (*cf.* Ref. 9: m.p. 171—173 °C). ^{1}H NMR ($CDCl_3$), δ: 1.10—1.40 (m, 1 H, CH); 1.70—2.10 (m, 9 H, CH, 4 CH_2); 7.28 (dd, 1 H, H(6), $J_{6,5}$ = 10.0 Hz, $J_{6,8}$ = 2.0 Hz); 7.35 (d, 1 H, H(5), $J_{5,6}$ = 10.0 Hz); 7.94 (d, 1 H, H(8), $J_{8,6}$ = 2.0 Hz). MS, *m/z* (I_{rel} (%)): 263 $[M]^+$ (49), 247 (19), 230 (48), 209 (13), 192 (23), 184 (27), 176 (19), 98 (100), 80 (26). HRMS, found: *m/z* 263.0896 $[M]^+$. $C_{12}H_{13}N_3O_4$. Calculated: M = 263.0901.

6-Nitrospiro[3*H*-[2,1,4]benzoxadiazine-3,1´-cyclohexane] 4-oxide (8). M.p. 118—120 °C (from ethyl acetate—hexane (1 : 3)). Found (%): C, 55.09; H, 4.96; N, 16.13. $C_{12}H_{13}N_3O_4$. Calculated (%): C, 54.75; H, 4.98; N, 15.96. UV, λ_{max}/nm (logε): 260 (3.98), 332 (3.68), 493 (3.30). IR, ν/cm^{-1}: 1611 (C=N), 1359, 1550 (NO_2). ^{1}H NMR ($CDCl_3$), δ: 1.45—1.68 (m, 1 H, CH); 1.70—2.40 (m, 9 H, CH, 4 CH_2); 7.06 (dd, 1 H, H(8), $J_{8,7}$ = 10.0 Hz, $J_{8,5}$ = 0.8 Hz); 7.38 (dd, 1 H, H(7), $J_{7,8}$ = 10.0 Hz, $J_{7,5}$ = 2.0 Hz); 8.15 (dd, 1 H, H(5), $J_{5,7}$ = 2.0 Hz, $J_{5,8}$ = 0.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 21.75, 24.31, 28.47 (all CH_2); 117.30, 122.46, 126.88 (all CH); 98.15, 128.34, 146.81, 150.24 (all C). MS, *m/z* (I_{rel} (%)): 263 $[M]^+$ (7), 230 (11), 186 (13), 185 (16), 98 (22), 85 (65), 83 (100). HRMS, found: *m/z* 263.0899 $[M]^+$. $C_{12}H_{13}N_3O_4$. Calculated: M = 263.0901.

6-Nitrospiro[2*H*-benzimidazole-2,1´-cyclohexane] 1-oxide (9). M.p. 132—135 °C (from hexane). Found (%): C, 58.12; H, 5.30; N, 16.95. $C_{12}H_{13}N_3O_3$. Calculated (%): C, 58.29; H, 5.30; N, 17.00. UV, λ_{max}/nm (logε): 278 (4.06), 447 (3.55). IR, ν/cm^{-1}: 1608 (C=N); 1326, 1513 (NO_2). ^{1}H NMR ($CDCl_3$), δ: 1.25—1.34 (m, 2 H, CH_2); 1.40—1.65 (m, 1 H, CH); 1.80—2.10 (m, 7 H, 3 CH_2, CH); 7.34 (dd, 1 H, H(4), $J_{4,5}$ = 10.0 Hz, $J_{4,7}$ = 0.8 Hz); 7.83 (dd, 1 H, H(5), $J_{5,4}$ = 10.0 Hz, $J_{5,7}$ = 1.9 Hz); 8.21 (dd, 1 H, H(7), $J_{7,4}$ = 1.9 Hz, $J_{7,5}$ = 0.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 23.42, 24.42, 35.17 (all CH_2); 118.58, 120.85, 123.18 (all CH); 108.64, 135.26, 153.48, 160.75 (all C). MS, *m/z* (I_{rel} (%)): 247 $[M]^+$ (58), 230 (100), 218 (10), 193 (14), 192 (10), 184 (42), 176 (30). HRMS, found: *m/z* 247.0958 $[M]^+$. $C_{12}H_{13}N_3O_3$. Calculated: M = 247.0951.

5-Nitrospiro[2*H*-benzimidazole-2,1´-cyclohexane] 1-oxide (10). M.p. 172—175 °C (from hexane). Found (%): C, 58.21; H, 5.41; N, 17.01. $C_{12}H_{13}N_3O_3$. Calculated (%): C, 58.29; H, 5.30, N, 17.00. UV, λ_{max}/nm (logε): 272 (4.13), 329 (3.68), 453 (3.50). IR, ν/cm^{-1}: 1607 (C=N); 1326, 1513 (NO_2). ^{1}H NMR ($CDCl_3$), δ: 1.19—1.26 (m, 2 H, CH_2); 1.43—1.52 (m, 1 H, CH); 1.75—2.10 (m, 7 H, 3 CH_2, CH); 7.30 (dd, 1 H, H(7), $J_{7,6}$ = 10.0 Hz, $J_{7,4}$ = 0.8 Hz); 7.44 (dd, 1 H, H(6), $J_{6,7}$ = 10.0 Hz, $J_{6,4}$ = 1.9 Hz); 8.16 (dd, 1 H, H(4), $J_{4,6}$ = 1.9 Hz, $J_{4,7}$ = 0.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 23.35, 24.32, 35.18 (all CH_2); 115.20, 126.79, 128.24 (all CH); 109.29, 133.40, 146.45, 160.64 (all C). MS, *m/z* (I_{rel} (%)): 247 $[M]^+$ (65), 230 (100), 218 (16), 202 (12), 193 (14), 192 (11), 184 (42), 176 (30), 143 (10). HRMS, found: *m/z* 247.0954 $[M]^+$. $C_{12}H_{13}N_3O_3$. Calculated: M = 247.0951.

B. A solution of di-N-oxide **6** (0.8 g, 0.003 mol) in chlorobenzene (30 mL) was refluxed for 8 h, collecting aliquots (2 mL) through the certain periods of time. Each portion was concentrated *in vacuo*, followed by recording an ^{1}H NMR spectrum. The composition of the mixture was calculated based on the ratio of integral intensities of signals for the protons of aromatic rings characteristic of each compound (see Figs 3 and 4).

Thermolysis of 2,1,4-benzoxadiazine 4-oxides 7 and 8. A solution of 2,1,4-benzoxadiazine **8** (0.1 g, 0.00038 mol) in chlorobenzene (5 mL) and a solution of 2,1,4-benzoxadiazine **7** (0.15 g, 0.00057 mol) in chlorobenzene (5 mL) was refluxed for 1 h. According to the TLC data, each reaction mixture contained a combination of compounds **6—10**.

Thermolysis of 6-nitrospiro[2*H*-benzimidazole-2,1´-cyclohexane] 1-oxide (9). A solution of mono-N-oxide **9** (0.45 g, 0.0018 mol) in *o*-dichlorobenzene (15 mL) was refluxed for 30 min. The solvent was evaporated *in vacuo*, the residue was subjected to chromatography on SiO_2 (hexane—ethyl acetate (3 : 1), then ethyl acetate) to obtain a mixture of compounds **9** and **11** (0.06 g) in the ratio 10 : 4 (^{1}H NMR data) and a mixture of azepino[1,2-*a*]benzimidazoles **12** and **13** (0.25 g) in the ratio 10 : 3 (^{1}H NMR data).

Thermolysis of 5-nitrospiro[2*H*-benzimidazole-2,1´-cyclohexane] 1-oxide (10). A solution of mono-N-oxide **10** (0.8 g, 0.0032 mol) in *o*-dichlorobenzene (30 mL) was refluxed for 2 h. The solvent was evaporated *in vacuo*, the residue was subjected to chromatography on SiO_2 (hexane—ethyl acetate (3 : 1), then ethyl acetate) to isolate the starting compound **10** (0.1 g, 12.5%), 5-nitrospiro[2*H*-benzimidazole-2,1´-cyclohexane] (**11**) (0.03 g, 4.0%), and a mixture of 6*H*-azepino[1,2-*a*]benzimidazoles **12** and **13** (0.45 g) in the ratio 10 : 3 (^{1}H NMR data). The mixture of 6*H*-azepino[1,2-*a*]benzimidazoles **12** and **13** was separated by chromatography on SiO_2 (ethyl acetate) to obtain 3-nitro-7,8,9,10-tetrahydro-6*H*-azepino[1,2-*a*]benzimidazole (**12**) (0.12 g, 16%) and 2-nitro-7,8,9,10-tetrahydro-6*H*-azepino[1,2-*a*]benzimidazole (**13**) (0.3 g, 40%).

5-Nitrospiro[2*H*-benzimidazole-2,1´-cyclohexane] (11). M.p. 100 °C (from benzene) (*cf.* Ref. 7: m.p. 100 °C).

3-Nitro-7,8,9,10-tetrahydro-6*H*-azepino[1,2-*a*]benzimidazole (12). M.p. 173—175 °C (*cf.* Ref. 8: m.p. 174—175 °C). UV, λ_{max}/nm (logε): 241 (4.23), 311 (3.88). IR, ν/cm^{-1}: 1334, 1472 (NO_2). ^{1}H NMR ($CDCl_3$), δ: 1.72—2.00 (m, 6 H, 3 CH_2); 3.07—3.11 (m, 2 H, CH_2); 4.15—4.19 (m, 2 H, CH_2); 7.24 (d, 1 H, H(1), $J_{1,2}$ = 9.0 Hz); 8.08 (dd, 1 H, H(2), $J_{1,2}$ = 9.0 Hz, $J_{2,4}$ = 2.0 Hz); 8.47 (d, 1 H, H(4), $J_{2,4}$ = 2.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 25.44, 28.71, 30.38, 30.87, 45.43 (all CH_2); 108.81, 115.98, 118.13 (all CH); 140.10, 141.91, 143.34, 161.59 (all C). MS, *m/z* (I_{rel} (%)): 231 $[M]^+$ (100), 230 (10), 201 (24), 185 (18), 184 (10). HRMS, found: *m/z* 231.1004 $[M]^+$. $C_{12}H_{13}N_3O_2$. Calculated: M = 231.1002.

2-Nitro-7,8,9,10-tetrahydro-6*H*-azepino[1,2-*a*]benzimidazole (13). M.p. 196—198 °C (*cf.* Ref. 8: m.p. 196—197 °C). UV,

λ_{max}/nm (logε): 237 (4.19), 313 (4.05). IR, ν/cm^{-1}: 1334, 1518 (NO_2). ^{1}H NMR ($CDCl_3$), δ: 1.70—2.00 (m, 6 H, 3 CH_2); 3.07—3.11 (m, 2 H, CH_2); 4.15—4.20 (m, 2 H, CH_2); 7.26 (d, 1 H, H(4), $J_{3,4}$ = 9.0 Hz); 8.06 (dd, 1 H, H(3), $J_{3,4}$ = 9.0 Hz, $J_{1,3}$ = 2.0 Hz); 8.46 (d, 1 H, H(1), $J_{1,3}$ = 2.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 25.23, 28.55, 30.39, 30.73, 45.25 (all CH_2); 105.93, 117.69, 119.13 (all CH); 135.18, 143.15, 147.17, 162.86 (all C). MS, *m/z* (I_{rel} (%)): 231 $[M]^+$ (100), 230 (8), 201 (26), 185 (27), 184 (10). HRMS, found: *m/z* 231.0994 $[M]^+$. $C_{12}H_{13}N_3O_2$. Calculated: M = 231.1002.

Exposure of compound 7 to the light. A solution of compound **7** (0.3 g, 0.0012 mol) in benzene (20 mL) was exposed to the scattered sunlight (June, 55 latitude). The starting orange solution rapidly turned dark and the starting compound **7** disappeared within ~4 h (TLC data). The solvent was evaporated, the residue was triturated with small amount of pentane and filtered to obtain a dark blue compound **6** (0.29 g, 97%), m.p. 122—124 °C (*cf.* Ref. 9: m.p. 122—124 °C). The IR spectrum of the compound was identical to that of compound **6** synthesized earlier. Benzoxadiazine 4-oxides **2** and **8** reacted with the light similarly.

Oxidation of hydroquinone with compound 6. Hydroquinone (1.10 g, 0.01 mol) was added to a solution of compound **6** (2.63 g, 0.01 mol) in benzene (50 mL) and the mixture obtained was refluxed until the starting compound **6** was completely consumed (~4 h). The solvent was evaporated to 10 mL in volume. The residue was subjected to chromatography on SiO_2 (benzene). Benzoquinone (0.60 g, 60%) was isolated from the first fractions.

X-ray diffraction experiment was performed on a Bruker P4 diffractometer (Mo-Kα radiation, graphite monochromator, 2θ/θ-scanning). The structures were solved by the direct method using the SHELXS-97 program.[24] Parameters of the structure were refined by the least squires method on all the reflections in the full-matrix anisotropic approximation using the SHELXL-97 program.[24]

The crystals of compound **9** were obtained by crystallization from the AcOEt—hexane (1 : 4) solvent mixture, the crystals of compound **7**, by recrystallization from hexane.

The crystallographic data for compound **7** are as follows: a triclinic crystal system, a = 5.8845(3) Å, b = 9.1128(6) Å, c = 11.6075(8) Å, α = 104.285(5)°, β = 93.013(6)°, γ = 101.271(4)°, V = 588.23(6) Å^3, a $P\bar{1}$ space group, $C_{12}H_{13}N_3O_4$, Z = 2, d_{calc} = 1.486 g cm^{-3}, μ = 0.114 mm^{-1}, 2θ < 55°, the sample size 0.24×0.43×0.66 mm. Intensities of 2675 independent reflections were measured. Allowance for the absorption was made by the method of integration on the crystal faceting (transmission 0.957—0.979). Parameters of the hydrogen atoms were refined in the isotropic approximation. The results of refinement are as follows: wR_2 = 0.1123, S = 1.038, 225 parameters, R = 0.0391 for 2429 reflections with $F > 4\sigma_F$.

The crystallographic data for compound **9** are as follows: an orthorhombic crystal system, a = 21.119(1) Å, b = 6.5679(4) Å, c = 8.3401(4) Å, V = 1156.9(1) Å^3, a *Pnma* space group, $C_{12}H_{13}N_3O_3$, Z = 4, d_{calc} = 1.420 g cm^{-3}, μ = 0.105 mm^{-1}, 2θ < 52°, the sample size 0.2×0.2×0.5 mm. Intensities of 1241 independent reflections were measured. No allowance was made for the absorption. Parameters for the hydrogen atoms were calculated in each cycle of refinement using coordinates of the corresponding carbon atoms (the riding model). The results of refinement are as follows: wR_2 = 0.1071, S = 1.021, 103 parameter, R = 0.0429 for 947 reflections with $F > 4\sigma_F$.

Crystallographic data for compounds **7** and **9** were deposited with the Cambrige Structural Database (CCDC 821921 and CCDC 821922, respectively).

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