Synthesis and structures of spiro-σ-complexes based on 2-(2-benzylaminophenyl)-5,6-dimethylbenzimidazole*

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The reactions of 2-(2-benzylaminophenyl)-5,6-dimethylbenzimidazole with electrophilic 8-chloro-5,7-dinitroquinoline and 7-chloro-4,6-dinitrobenzofuroxan afforded two new bipolar spiro-σ-complexes. The structure of the complex prepared by the latter reaction was established by X-ray diffraction analysis. The activation parameters of the stereodynamic rearrangement of quinoline spirane were determined by dynamic NMR spectroscopy.

Key words: 2-(2-benzylaminophenyl)-5,6-dimethylbenzimidazole, 8-chloro-5,7-dinitroquinoline, 7-chloro-4,6-dinitrobenzofuroxan, bipolar spiro-σ-complex, rearrangement.

Various bipolar spirocyclic σ-complexes **1** have been prepared earlier based on the tropolone ligands and have been characterized in detail by X-ray diffraction analysis.[1—6] It appeared that it is possible to synthesize such compounds with highly variable structures of tautomeric systems, and the spiro-σ-complexes thus prepared serve as models of transition states for nucleophilic aromatic substitution reactions. These compounds can also exhibit solvatochromic and thermochromic properties due to reversible ring-chain rearrangements.[6]

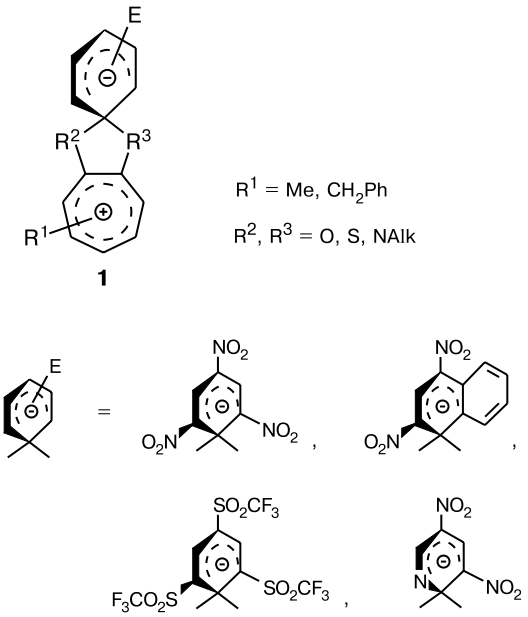
For example, the kinetic and activation parameters of the reversible cleavage—formation of the C_{ipso}—R^2 (C_{ipso}—R^3) bonds and degenerate $R \rightleftharpoons S$ enantiomerization for a series of chiral spiranes **1** were determined by dynamic ^{1}H NMR spectroscopy.[7—9]

In the present study, we investigated new bipolar spiro-σ-complexes based on 2-(2-benzylaminophenyl)benzimidazole (**2**).

The reactions of ligand **2** with electrophilic 8-chloro-5,7-dinitroquinoline (**3a**) and superelectrophilic 7-chloro-4,6-dinitrobenzofuroxan (**3b**)[10] afforded bipolar spiro-σ-complexes (**4**) (Scheme 2).

In the ^{1}H NMR spectra of these compounds, the signals for the protons of the electron-withdrawing fragment

Scheme 1



are substantially shifted upfield compared to the haloarene reagent, which is indicative of an excess of electron density on this fragment. The signals for the H(2″) and H(3″) protons in the quinoline moiety of spirane **4a** are characterized by the largest shifts. Below are given the chemical shifts of the protons of 8-chloro-5,7-dinitroquinoline **3a**,

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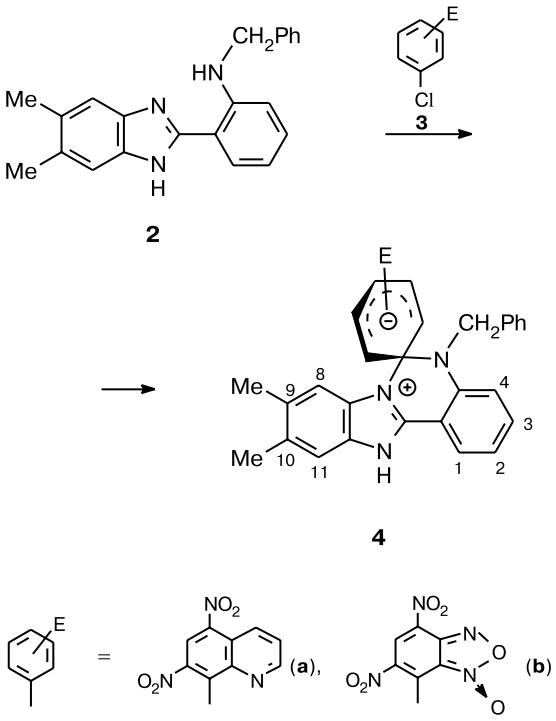
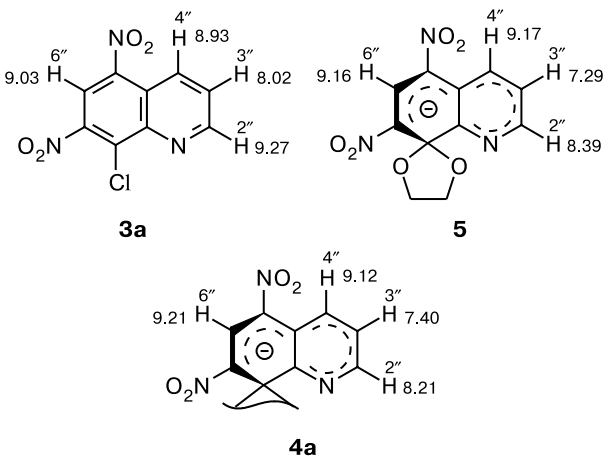
Scheme 2



its ethylene glycol-derived anionic σ-complex **5**,[11] and spiro complex **4a**.



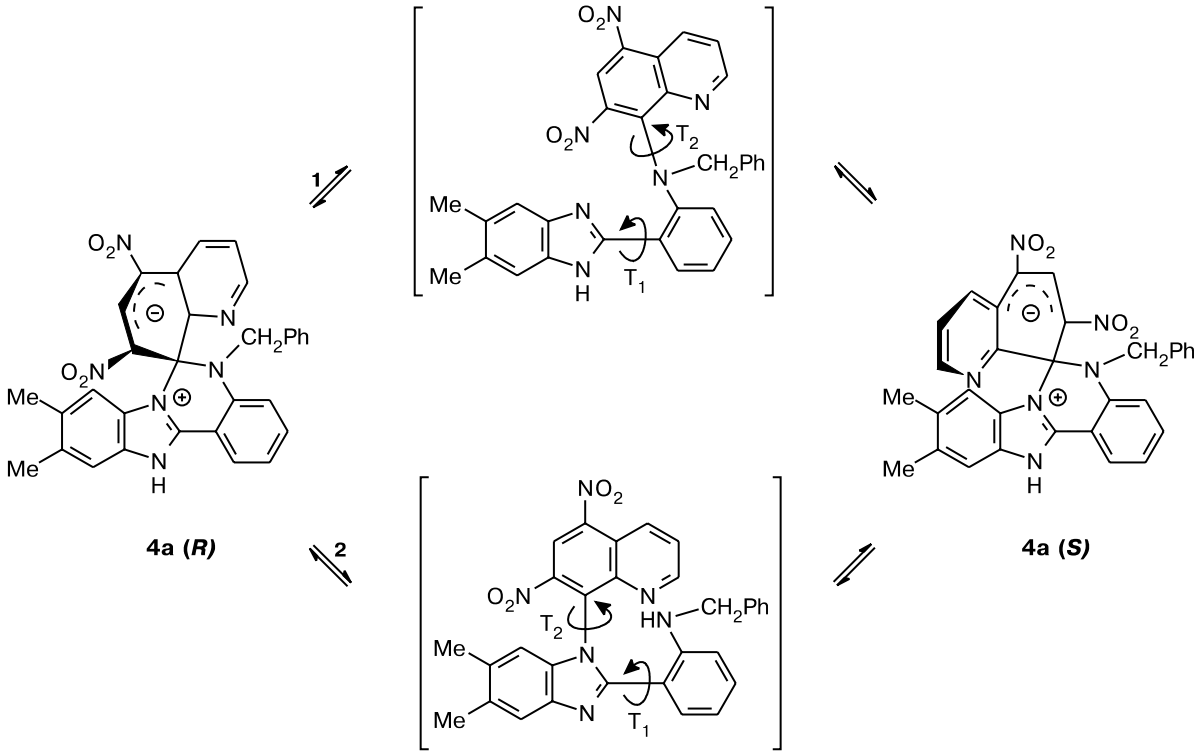
The signal for the H(1) proton in the benzimidazole fragment of spiro complexes **4a** and **4b** is shifted downfield by 0.63 and 0.67 ppm, respectively, compared to the signal in the spectrum of the starting ligand **2**, which is indicative of an electron deficiency. It should be noted that the signals of two methyl groups, which are isochronic in ligand **2** due to free rotation about the benzimidazolyl—phenyl bond and fast N(1) ⇌ N(3) proton exchange, become anisochronic in spiro-σ-complexes **4**. The signal for the protons of the CH_2 group of the diastereotopic benzyl substituent is transformed into an AB quartet.

A reversible evolution of the signals for the protons of the methylene and methyl groups into singlets is observed on heating in the NMR spectra of a solution of compound **4a** in DMSO-d_6, which is evidence for the occurrence of the ring-chain rearrangement (Scheme 3). The kinetic and activation parameters extracted from analysis of the temperature dependence of the line shapes of the methyl and methylene indicator signals demonstrate that the rearrangement **4a(*R*)** ⇌ **4a(*S*)** can follow two paths. One path involves the cleavage of the C_{ipso}—N(7) bond and torsional rotations about the benzimidazolyl—aminophenyl (T_1) and quinolyl—N(5) (T_2) bonds. An alternative path involves the cleavage of the quinolyl—N(5) bond and rotations about the quinolyl—benzimidazolyl (T_2) and benzimidazolyl—aminophenyl (T_1) bonds.

Heating of a solution of spirane **4b** in DMSO-d_6 up to 170 °C causes neither exchange broadening nor collapse of indicator signals, which is characteristic of spirane **4a**. This fact indicates that the activation barrier of the ring-chain rearrangement sharply increases (see Scheme 3) upon the replacement of dinitroquinoline with superelectrophilic[12] dinitrobenzofuroxan.

Since data on the structures of bipolar spiro-σ-complexes based on 4,6-dinitrobenzofuroxan are lacking in the literature, we studied compound **4b** by X-ray diffraction analysis (Fig. 1). The benzimidazole and quinazoline fragments of molecule **4b** are virtually coplanar. These fragments are twisted with respect to each other about the C(14)—C(15) bond by 175.1° (the C(5)—C(15)—C(14)—N(12) torsion angle). The spiro-annelated dinitrobenzofuroxan fragment is almost orthogonal to the tetracyclic benz[4,5]imidazo[1,2-*c*]quinazoline system (the dihedral angle between the N(5)—C(6)—N(7) and C(6′)—C(6)—C(8′) planes is 90.1°). Both nitro groups are coplanar with the benzofuroxan moiety (the torsion angles are no larger than 3°). Six bond angles in the spiro unit vary in a range of 106.4—111.8°. The C(6′)—C(6)—C(8′) and C(6′)—C(6)—N(5) angles have the smallest and largest values (106.4° and 111.8°, respectively). The *N*-benzyl substituent is twisted with respect to the quinazoline fragment by 83.4° so that its benzene ring is located in the vicinity of the 6′-nitro group (*syn* position) and is far removed from the furoxan fragment (*anti* position). The distances between the C(22) atom of the benzene ring of the $PhCH_2$ group and the N(6) and O(6′) atoms of the nitro group are 3.23 and 3.21 Å, respectively (van der Waals contacts). The dihedral angle between the planes of the benzene rings of the benzyl and benzofuroxan fragments approximates 43°.

Scheme 3



Fragment	k_{298}/s^{-1}	$\Delta G^{\neq}_{298}$	$\Delta H^{\neq}$	$-\Delta S^{\neq}$/e.u.
		kcal mol^{-1}		
CH_3	0.9	17.5	8	32
CH_2	4.4	16.7	8.6	27

Experimental

^{1}H NMR spectra were recorded on a Varian Unity 300 spectrometer (300 MHz). The rate constants of the ring-chain tautomeric rearrangement were determined with an accuracy of ±10% by computer simulation of the signal shapes for the indicator protons (CH_3 and CH_2) and visual fitting to the line shapes recorded at a particular temperature using the gNMR V 4.1.0 program (Copyright © 1995—1998 IvorySoft). The activation parameters were determined according to a standard procedure of linearization of $\ln k$—$1/T$ with a regression coefficient of no smaller than 0.98.

X-ray diffraction study. Single crystals of compound **4b** were grown by keeping its solution in DMSO in open air for one month. Yellow needle-like crystals of $C_{28}H_{21}N_7O_6 \cdot 2DMSO \cdot H_2O$ (M = 725.79) belong to the triclinic system, space group $P\bar{1}$, at 110 K, a = 10.424(3), b = 10.694(3), c = 15.497(4) Å, α = 81.068(8), β = 78.292(8), γ = 82.492(7)°, V = 1662.2(8) Å^3, Z = 2, d_{calc} = 1.450 g cm^{-3}. A total of 14616 reflections were collected on a Bruker SMART 1000 CCD diffractometer at 110 K (Mo-Kα radiation, λ = 0.71073 Å, ω scanning technique with a step of 0.3°, exposure time per frame was 20 s, $2\theta_{max}$ = 56°) from a single crystal of dimensions 0.55×0.10×0.07 mm^3. Merging of the equivalent reflections gave 8022 independent reflections (R_{int} = 0.0459), which were used in the structure solution and refinement. The structure was solved by direct methods and refined by the full-matrix least-squares method against F^2 with anisotropic thermal parameters for nonhydrogen atoms. All hydrogen atoms were revealed from difference electron density maps and refined isotropically. The final reliability factors were R_1 = 0.0544 (based on F_{hkl} for 3617 reflections with $I > 2\sigma(I)$), wR_2 = 0.1230 (based on F^2_{hkl} for all independent reflections), GOOF = 0.738, 599 parameters were refined. All calculations were carried out using the SHELXTL v.5 program package.[13] The atomic coordinates for the structure of compound **4b** and the complete tables of the bond lengths and bond angles were deposited with the Cambridge Structural Database. Selected bond lengths and bond angles are given in Tables 1 and 2, respectively.

2-(2-Benzylaminophenyl)-5,6-dimethylbenzimidazole (2). 2-(2-Aminophenyl)-5,6-dimethylbenzimidazole[14] (2.37 g, 0.01 mol) and anhydrous AcONa (0.82 g, 0.01 mol) were dissolved in MeOH (60 mL). Then $PhCH_2Cl$ (1.15 mL, 0.01 mol) was added and the reaction mixture was refluxed for 15 h. The solution was poured into water (100 mL) and kept for one day until precipitation was completed. The reaction product was filtered off, crystallized from CCl_4, chromatographed on Al_2O_3 ($CHCl_3$), and crystallized from CCl_4. The yield was 1 g (30.5%). M.p. 168—170 °C. Found (%): C, 80.83; H, 6.56; N, 12.95.

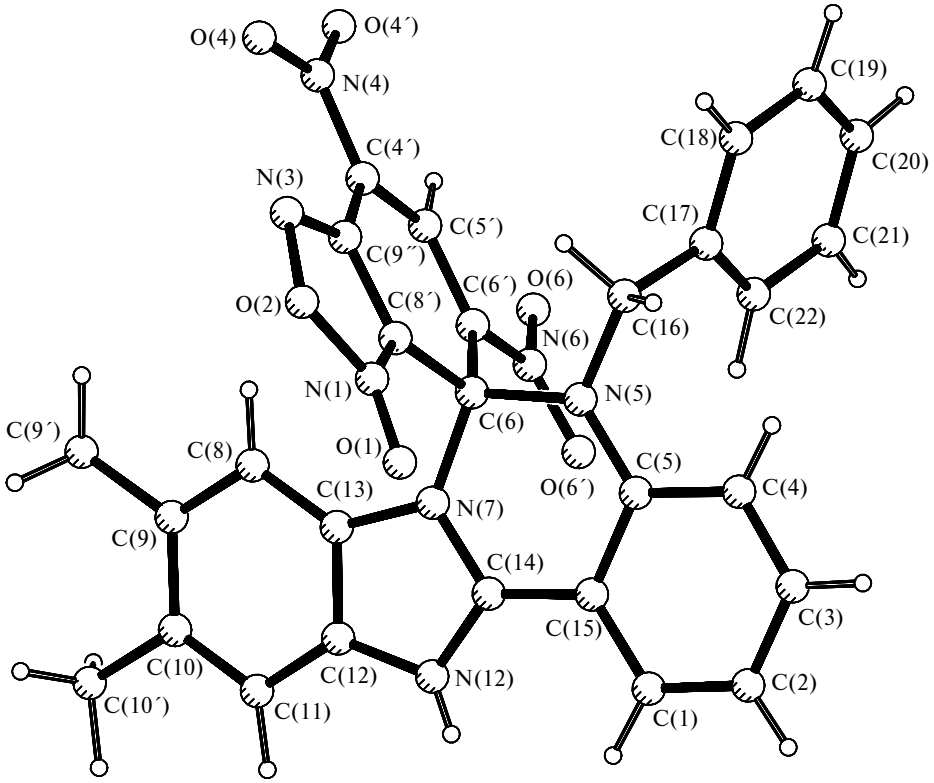


Fig. 1. Molecular structure of compound **4b**.

Table 1. Selected bond lengths (*d*) in the structure of **4b**

Bond	*d*/Å	Bond	*d*/Å
O(1)—N(1)	1.221(3)	C(9)—C(9′)	1.503(4)
O(2)—N(3)	1.413(5)	C(10)—C(11)	1.369(4)
O(2)—N(1)	1.434(4)	C(10)—C(10′)	1.494(4)
O(4)—N(4)	1.240(3)	C(11)—C(12)	1.398(4)
O(4′)—N(4)	1.235(3)	C(15)—C(1)	1.388(4)
O(6′)—N(6)	1.241(3)	C(15)—C(5)	1.410(4)
O(6)—N(6)	1.282(8)	C(1)—C(2)	1.366(4)
N(12)—C(14)	1.333(3)	C(2)—C(3)	1.386(4)
N(12)—C(12)	1.375(4)	C(3)—C(4)	1.375(4)
N(7)—C(14)	1.339(3)	C(4)—C(5)	1.402(4)
N(7)—C(13)	1.398(3)	C(6)—C(8′)	1.497(4)
N(7)—C(6)	1.478(3)	C(6)—C(6′)	1.503(4)
N(5)—C(5)	1.372(3)	C(8′)—C(9″)	1.408(4)
N(5)—C(16)	1.457(3)	C(9″)—C(4′)	1.417(4)
N(5)—C(6)	1.480(3)	C(4′)—C(5′)	1.384(4)
N(1)—C(8′)	1.327(4)	C(5′)—C(6′)	1.377(4)
N(3)—C(9″)	1.338(4)	C(16)—C(17)	1.516(4)
N(4)—C(4′)	1.410(4)	C(17)—C(22)	1.382(4)
N(6)—C(6′)	1.400(4)	C(17)—C(18)	1.385(4)
C(14)—C(15)	1.416(4)	C(18)—C(19)	1.366(4)
C(13)—C(8)	1.383(4)	C(19)—C(20)	1.385(4)
C(13)—C(12)	1.390(4)	C(20)—C(21)	1.375(4)
C(8)—C(9)	1.386(4)	C(21)—C(22)	1.385(4)
C(9)—C(10)	1.415(4)		

$C_{22}H_{21}N_3$. Calculated (%): C, 80.70; H, 6.46; N, 12.83. ^{1}H NMR ($CDCl_3$), δ: 2.34 (s, 6 H, C(5)Me, C(6)Me); 4.55 (s, 2 H, CH_2); 6.64 (dd, 1 H, H(5′), J = 7.3 Hz, J = 7.3 Hz); 6.71 (d, 1 H, H(3′), J = 8.4 Hz); 7.10—7.45 (m, 8 H, Ar); 7.49 (d, 1 H, H(6′), J = 7.8 Hz); 9.38 (br.s, 2 H, NH).

5-Benzyl-9,10-dimethyl-5′,7′-dinitro-5,12-dihydro-6*H*-spiro(benz[4,5]imidazo[1,2-*c*]quinazoline-6,8′-quinoline) (4a). Benzimidazole **2** (0.4 g, 1.22 mmol) and 8-chloro-5,7-dinitroquinoline (**3a**)[11] (0.32 g, 1.22 mmol) were dissolved in MeCN (7 mL). The reaction mixture was kept at room temperature for 7 days. The precipitate that formed was filtered off, suspended in MeOH (5 mL), brought to reflux, and filtered without cooling. The operation was repeated three times. Then the reaction product was dissolved in DMSO (20 mL) and poured into water (120 mL). After 12 h, the precipitate that formed was filtered off, twice washed with MeOH (5 mL), and once washed with diethyl ether (5 mL). The yield was 0.19 g (57%). M.p. 278 °C (with decomp.). Found (%): C, 68.54; H, 4.63; N, 15.61. $C_{31}H_{24}N_6O_4$. Calculated (%): C, 68.37; H, 4.44; N, 15.43. ^{1}H NMR (DMSO-d_6), δ: 2.06 and 2.26 (both s, 3 H each, C(9)Me, C(10)Me); 4.11 and 4.22 (both d, 1 H each, CH_2, J = 18.1 Hz); 6.31 (s, 1 H, H(11)); 6.40 (d, 1 H, H(4), J = 8.6 Hz); 6.91 (dd, 1 H, H(2), J = 7.5 Hz, J = 7.5 Hz); 6.95—7.01 (m, 2 H, Ar)); 7.03—7.20 (m, 3 H, Ar); 7.30—7.40 (m, 2 H, H(3), H(3′)); 7.53 (s, 1 H, H(8)); 8.12 (d, 1 H, H(1), J = 7.8 Hz); 8.21 (dd, 1 H, H(2′), J = 1.4 Hz, J = 4.4 Hz); 8.99—9.05 (m, 2 H, H(4′), H(6′)).

5-Benzyl-9,10-dimethyl-4′,6′-dinitro-5,12-dihydro-6*H*-spiro[(benz[4,5]imidazo[1,2-*c*]quinazoline)-6,7′-(2,1,3-benz-

Table 2. Bond angles (ω) in the structure of **4b**

Angle	ω/deg	Angle	ω/deg
N(3)—O(2)—N(1)	109.4(3)	N(12)—C(12)—C(13)	107.5(2)
C(14)—N(12)—C(12)	109.3(2)	N(12)—C(12)—C(11)	131.3(3)
C(14)—N(7)—C(13)	109.4(2)	C(13)—C(12)—C(11)	121.1(3)
C(14)—N(7)—C(6)	125.6(2)	C(1)—C(15)—C(5)	120.8(3)
C(13)—N(7)—C(6)	124.6(2)	C(1)—C(15)—C(14)	123.0(3)
C(5)—N(5)—C(16)	120.2(2)	C(5)—C(15)—C(14)	116.2(3)
C(5)—N(5)—C(6)	125.6(2)	C(2)—C(1)—C(15)	120.8(3)
C(16)—N(5)—C(6)	114.1(2)	C(1)—C(2)—C(3)	119.2(3)
O(1)—N(1)—C(8′)	131.7(3)	C(4)—C(3)—C(2)	121.1(3)
O(1)—N(1)—O(2)	122.8(3)	C(3)—C(4)—C(5)	120.9(3)
C(8′)—N(1)—O(2)	105.4(3)	N(5)—C(5)—C(4)	121.6(2)
C(9″)—N(3)—O(2)	105.0(3)	N(5)—C(5)—C(15)	121.2(2)
O(4′)—N(4)—O(4)	123.3(2)	C(4)—C(5)—C(15)	117.2(3)
O(4′)—N(4)—C(4′)	118.6(3)	N(7)—C(6)—N(5)	108.6(2)
O(4)—N(4)—C(4′)	118.0(3)	N(7)—C(6)—C(8′)	109.0(2)
O(6′)—N(6)—O(6)	119.5(4)	N(5)—C(6)—C(8′)	109.9(2)
O(6′)—N(6)—C(6′)	120.6(3)	N(7)—C(6)—C(6′)	111.1(2)
O(6)—N(6)—C(6′)	119.9(4)	N(5)—C(6)—C(6′)	111.8(2)
N(12)—C(14)—N(7)	108.6(2)	C(8′)—C(6)—C(6′)	106.3(2)
N(12)—C(14)—C(15)	128.7(3)	N(1)—C(8′)—C(9″)	109.7(3)
N(7)—C(14)—C(15)	122.6(2)	N(1)—C(8′)—C(6)	122.1(3)
C(8)—C(13)—C(12)	121.0(3)	C(9″)—C(8′)—C(6)	128.0(3)
C(8)—C(13)—N(7)	133.8(3)	N(3)—C(9″)—C(8′)	110.5(3)
C(12)—C(13)—N(7)	105.2(2)	N(3)—C(9″)—C(4′)	131.2(3)
C(13)—C(8)—C(9)	118.1(3)	C(8′)—C(9″)—C(4′)	118.3(3)
C(8)—C(9)—C(10)	120.7(3)	C(5′)—C(4′)—N(4)	120.3(3)
C(8)—C(9)—C(9′)	119.4(3)	C(5′)—C(4′)—C(9″)	118.3(3)
C(10)—C(9)—C(9′)	119.8(3)	N(4)—C(4′)—C(9″)	121.4(3)
C(11)—C(10)—C(9)	120.8(3)	C(6′)—C(5′)—C(4′)	123.2(3)
C(11)—C(10)—C(10′)	119.5(3)	C(5′)—C(6′)—N(6)	116.9(3)
C(19)—C(18)—C(17)	121.3(3)	C(5′)—C(6′)—C(6)	125.2(3)
C(18)—C(19)—C(20)	119.7(3)	N(6)—C(6′)—C(6)	117.9(3)
C(21)—C(20)—C(19)	120.0(3)	N(5)—C(16)—C(17)	116.8(2)
C(20)—C(21)—C(22)	119.9(3)	C(22)—C(17)—C(18)	118.6(3)
C(17)—C(22)—C(21)	120.5(3)	C(22)—C(17)—C(16)	124.4(2)
C(9)—C(10)—C(10′)	119.7(3)	C(18)—C(17)—C(16)	117.0(3)
C(10)—C(11)—C(12)	118.2(3)		

oxadiazole)] 1′-oxide (4b). Benzimidazole **2** (0.2 g, 0.61 mmol) and 7-chloro-4,6-dinitrobenzofuroxan **3b** [15] (0.16 g, 0.61 mmol) were dissolved in MeCN (5 mL). The reaction mixture was kept at room temperature for 24 h. The precipitate that formed was filtered off and purified analogously to compound **4a**. The yield was 0.1 g (60%). M.p. 256 °C (with decomp.). Found (%): C, 61.12; H, 3.93; N, 17.94. $C_{28}H_{21}N_7O_6$. Calculated (%): C, 60.98; H, 3.84; N, 17.78. ^{1}H NMR (DMSO-d_6), δ: 2.20 and 2.33 (both s, 3 H each, C(9)Me, C(10)Me); 4.46 and 4.65 (both d, 1 H each, CH_2, J = 18.2 Hz); 6.47 (s, 1 H, H(11)); 6.79 (d, 1 H, H(4), J = 8.4 Hz); 7.01 (dd, 1 H, H(2), J = 7.5 Hz, J = 7.4 Hz); 7.08—7.27 (m, 5 H, Ar); 7.41 (dd, 1 H, H(3), J =7.4 Hz, J =8.2 Hz); 7.54 (s, 1 H, H(8)); 8.16 (d, 1 H, H(1), J = 7.8 Hz); 9.01 (s, 1 H, H(5′)).

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References

1. V. I. Minkin, L. P. Olekhnovich, and Yu. A. Zhdanov, *Acc. Chem. Res.*, 1981, **14**, 210.
2. L. P. Olekhnovich, N. G. Furmanova, V. I. Minkin, Yu. T. Struchkov, O. E. Kompan, Z. N. Budarina, I. A. Yudilevich, and O. V. Eryuzheva, *Zh. Org. Khim.*, 1982, **18**, 465, 474 [*J. Org. Chem. USSR*, 1982, **18**, 409, 416 (Engl. Transl.)].
3. N. G. Furmanova, A. V. Lesin, S. V. Kurbatov, N. I. Kirillova, A. I. Gusev, Z. N. Budarina, and L. P. Olekhnovich, *Zh. Org. Khim.*, 1991, **27**, 1151 [*J. Org. Chem. USSR*, 1991, **27**, 998 (Engl. Transl.)].
4. N. G. Furmanova, A. V. Lesin, S. V. Kurbatov, Z. N. Budarina, and L. P. Olekhnovich, *Zh. Strukt. Khim.,* 1989, **30**, 178 [*J. Struct. Chem.*, 1989, **30**, 325 (Engl. Transl.)].
5. L. P. Olekhnovich, S. V. Kurbatov, A. V. Lesin, Z. N. Budarina, Yu. A. Zhdanov, and V. I. Minkin, *Zh. Org. Khim.*, 1991, **27**, 6 [*J. Org. Chem. USSR*, 1991, **27**, 4 (Engl. Transl.)].
6. V. I. Minkin, L. P. Olekhnovich, and Yu. A. Zhdanov, *Molecular Design of Tautomeric Compounds*, Dordrecht, Boston, 1988, 280 pp.
7. L. P. Olekhnovich, Z. N. Budarina, A. V. Lesin, S. V. Kurbatov, G. S. Borodkin, and V. I. Minkin, *Mendeleev Commun.*, 1994, 162.
8. S. V. Kurbatov, Z. N. Budarina, G. S. Vaslyaeva, N. I. Borisenko, A. P. Knyazev, V. I. Minkin, Yu. A. Zhdanov, and L. P. Olekhnovich, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1509 [*Russ. Chem. Bull.*, 1997, **46**, 1445 (Engl. Transl.)].
9. L. P. Olekhnovich, Z. N. Budarina, G. S. Borodkin, G. S. Vaslyaeva, S. V. Kurbatov, and Yu. A. Zhdanov, *Zh. Org. Khim.*, 2002, **38**, 751 [*Russ. J. Org. Chem.*, 2002, **38**, 713 (Engl. Transl.)].
10. P. G. Morozov, S. V. Kurbatov, and L. P. Olekhnovich, *Khim. Geterotsikl. Soedin.*, 2002, 1611 [*Chem. Heterocycl. Compd.,* 2002, **38**, 1428 (Engl. Transl.)].
11. N. L. Khilkova, V. N. Knyazev, N. S. Patalakha, and V. N. Drozd, *Zh. Org. Khim.*, 1992, **28**, 1048 [*Russ. J. Org. Chem.*, 1992, **28** (Engl. Transl.)].
12. F. Terrier, E. Kizilian, J. C. Halle, and E. Buncel, *J. Am. Chem. Soc.*, 1992, **114**, 1740.
13. G. M. Sheldrick, *SHELXTL v. 5.10*, *Structure Determination Software Suite*, Bruker AXS, Madison, Wisconsin, USA, 1998.
14. I. S. Ioffe and D. N. Glebovskii, *Zh. Obshch. Khim.*, 1960, **30**, 1158 [*J. Gen. Chem. USSR*, 1960, **30** (Engl. Transl.)].
15. W. P. Norris, A. Chafin, R. J. Spear, and R. W. Read, *Heterocycles*, 1984, **22**, 271.

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