

# Synthesis and structure of azido- and amino-substituted dibenzoxazepinones

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1,3-Dinitro[*b,f*][1,4]dibenzoxazepin-11(10*H*)-one enters nucleophilic substitution reactions with N-nucleophiles, azide ion preferably replacing the nitro group in position 3, whereas amines the one in position 1. Structures of the substitution products were confirmed by X-ray diffraction and <sup>1</sup>H NMR NOE spectroscopy. The selectivity observed in the reaction with amines was caused by the stabilization of the intermediate  $\sigma$ -complex with the NH...O intramolecular hydrogen bond.

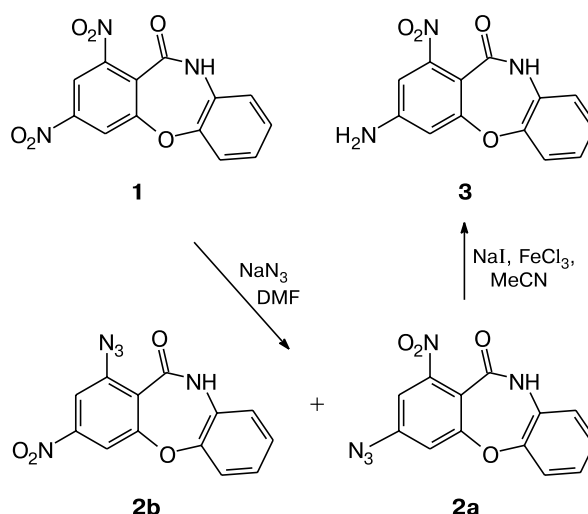
**Key words:** dibenz[*b,f*][1,4]oxazepinones, S<sub>N</sub>Ar substitution reaction, aromatic nitro compounds, arylazides, arylamines.

Earlier, during research on utilization of aromatic polynitro compounds,<sup>1–4</sup> we synthesized mono- and dinitro-substituted dibenz[*b,f*][1,4]oxazepin-11(10*H*)-ones and studied their reactions with O- and S-nucleophiles.<sup>5,6</sup> In particular, it was found that, depending on the conditions, the substitution products of one or both nitro groups can be obtained from 1,3-dinitrodibenz[*b,f*][1,4]oxazepin-11(10*H*)-one (**1**) (see Refs 2 and 5), and the nitro group in position 3, *i.e.*, the one remote from the point of the ring fusion, was substituted in the first place in all the cases.<sup>5</sup>

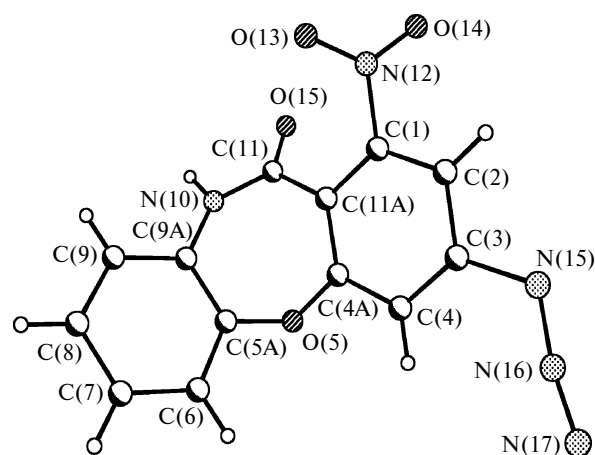
Benzo-fused oxazepines possess various biological activity<sup>7</sup> and are used as the medicines.<sup>8,9</sup> In this connection, the further quest for the methods of functionalization of these compounds is of undoubted interest.

In the present work, it was shown that N-nucleophiles (primary and secondary alkylamines and azide anion) can also react with dibenzoxazepinone **1** to replace a nitro group. The replacement by the azide ion proceeds in DMF under rather mild conditions (80 °C) and leads to a mixture of isomeric azides (Scheme 1) with considerable predominance of 3-azido derivative **2a** (ratio of isomers **2a** and **2b** is 90 : 10). Thus, similarly to the reactions of **1** with O- and S-nucleophiles,<sup>5</sup> the nitro group remote from the point of the rings fusion is mainly substituted, though the selectivity of the substitution in case of azide anion is lower. The reduction of the azido group in compound **2a** upon treatment with NaI and FeCl<sub>3</sub> in MeCN afforded 3-aminobenzoxazepinone **3** (leaving the nitro group intact).<sup>10</sup>

Scheme 1



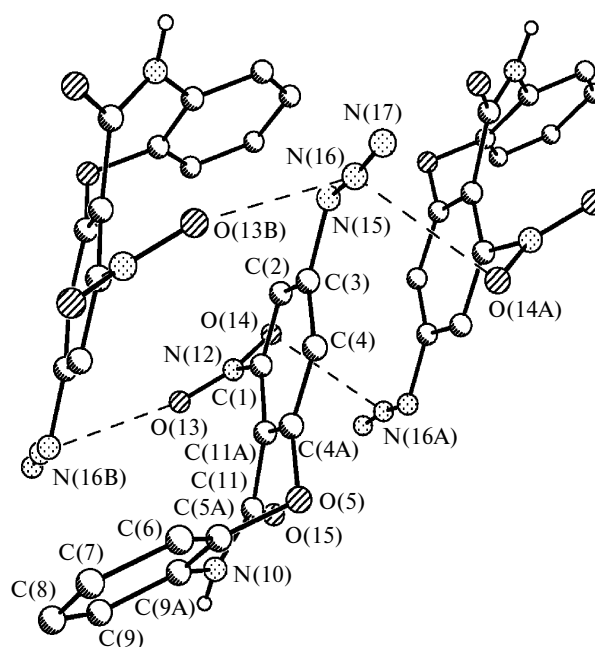
The structure of the predominant isomer **2a** was established by X-ray diffraction (Fig. 1). According to the analysis of the molecular geometry in a crystal of **2a**, the bond length and bond angle values in the heterocycle are typical of this class of compounds. The geometric parameters of the two benzene fragments differ insignificantly (Table 1). The similar tendency is also observed in case of the O(5)—C(4A) and O(5)—C(5A) bond lengths, which is caused by the influence of the electron-withdrawing substituents in one of the benzene rings. The central ring has the boat conformation with the deflection of the

Fig. 1. General view of molecule **2a**.Table 1. Most important geometric parameters of **2a** in a crystal

Bond	<i>d</i> /Å	Angle	$\omega$ /deg
O(5)—C(4A)	1.383(2)	C(4A)—O(5)—C(5A)	111.0(1)
O(5)—C(5A)	1.402(2)	O(5)—C(5A)—C(9A)	119.6(1)
C(4A)—C(11A)	1.395(2)	C(5A)—C(9A)—N(10)	121.2(1)
C(5A)—C(9A)	1.388(2)	C(9A)—N(10)—C(11)	127.5(1)
C(9A)—N(10)	1.415(2)	N(10)—C(11)—C(11A)	118.6(1)
N(10)—C(11)	1.346(2)	O(15)—C(11)—N(10)	122.0(1)
C(11)—C(11A)	1.499(2)	C(1)—C(11A)—C(11)	121.2(1)
C(11)—O(15)	1.237(2)	C(9)—C(9A)—N(10)	119.6(1)
C(1)—C(2)	1.379(2)	C(2)—C(1)—C(11A)	123.9(1)
C(2)—C(3)	1.403(2)	C(2)—C(3)—C(4)	120.9(1)
C(3)—C(4)	1.386(2)	C(8)—C(9)—C(9A)	119.6(1)
C(8)—C(9)	1.392(2)	C(6)—C(7)—C(8)	120.3(1)
C(7)—C(8)	1.386(2)	C(1)—N(12)—O(13)	117.4(1)
C(6)—C(7)	1.389(2)	O(13)—N(12)—O(14)	124.6(1)
C(3)—N(15)	1.415(2)	C(4)—C(3)—N(15)	124.9(1)
N(15)—N(16)	1.248(2)	C(3)—N(15)—N(16)	116.9(1)
N(16)—N(17)	1.129(2)	N(15)—N(16)—N(17)	170.9(1)

O(5) atom (0.65 Å) and the N(10)—C(11) bond (0.73 Å) from the plane of the C(4A), C(5A), C(9A), and C(11A) atoms. The dihedral angle between substituted and unsubstituted benzene rings is 62.6°. It should be noted that the nitro group is turned by 48.4° relatively to the plane of the benzene ring, whereas the N<sub>3</sub> group is coplanar with the plane of the aromatic ring.

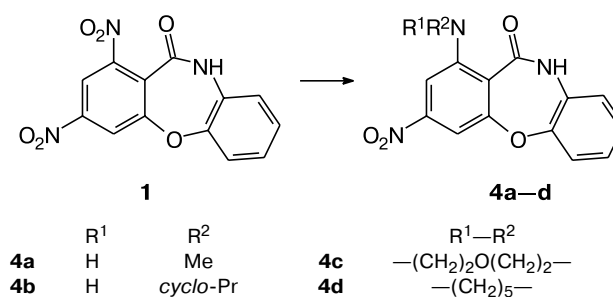
Analysis of the crystal packing of **2a** showed that the molecules in the crystal are associated to the center-symmetrical dimers by the N—H...O hydrogen bonds of medium strength (N...O 2.829(2) Å, H...O 1.99 Å, NHO 171°). In addition to the H-bonding, there are also rather unusual weak intermolecular contacts in the crystal, formed by the nitro and azido groups with the N...O distance equal to 2.874(2) and 2.886(2) Å (Fig. 2). It is worth to note that these interactions are characterized by specific direction: the N—O...N angle values are equal to 146.6 and 106.9° for N(16)...O(13) and N(16)...O(14),

Fig. 2. Fragment of the N...O-bonded chain in a crystal of **2a**.

respectively. These interactions associate molecules of **2a** to the endless chains, parallel to the crystallographic axis *a*.

The reactions of oxazepinone **1** with amines were carried out under heating in *n*-butanol (in case of methylamine, in ethanol) with excess reagent. In contrast to the similar reactions with O- and S-nucleophiles,<sup>5</sup> only one of two nitro groups was substituted in this case (despite of excess amine) (Scheme 2), apparently, the substitution of the second group is made difficult by the strong electron-donating properties of the alkylamino group.

Scheme 2

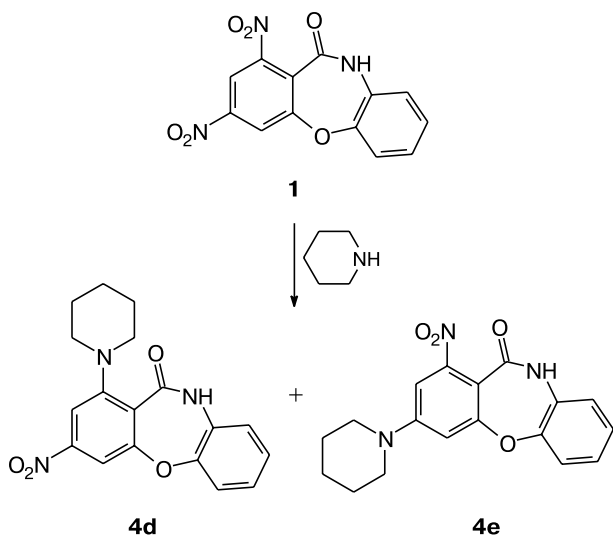


**Reagents and conditions:** 4–10 equiv. R<sup>1</sup>R<sup>2</sup>NH, Bu<sup>n</sup>OH/EtOH, reflux.

Dimethylformamide, which was successfully used for the nucleophilic substitution of a nitro group by O- and S-nucleophiles<sup>5</sup> and by azide ion, is not always suitable solvent in case of amines: while the reaction of compound **1** with piperidine proceeds smoothly to form a mixture of regioisomers (Scheme 3), the reactions with

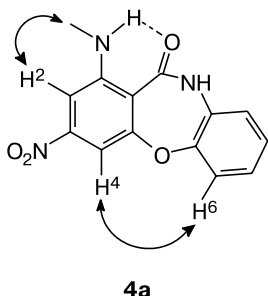
morpholine and cyclopropylamine are complicated by side reactions. The latter, apparently, result from the interaction of amines with DMF to form dimethylamine,<sup>11</sup> which, in its turn, also can substitute the nitro group in dibenzoxazepinone **1** as the nucleophile.

Scheme 3



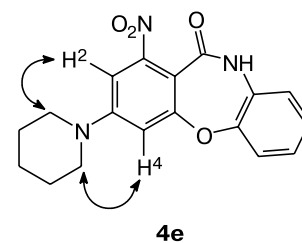
Conditions: DMF, 80 °C.

The selectivity of the nitro group replacement in compound **1** by amines sharply differs from the selectivity of replacement by O- and S-nucleophiles and depends on the nature of the solvent, in which the reaction proceeds (*cf.* Schemes 2 and 3). According to the <sup>1</sup>H NMR 2D NOESY spectral data, the substitution products of the nitro group in position 1 are selectively formed in butanol (ethanol), no matter which amine (secondary or primary) is used. At the same time, the reaction with piperidine in DMF proceeds with rather low selectivity (ratio of isomers is approximately 2 : 1). In the NOESY spectrum of the product of the reaction with methylamine (**4a**), a cross-peak between signals of the methyl protons of the NHMe group (a doublet at  $\delta$  2.87) and signal of the aromatic H(2) proton ( $\delta$  7.20) is observed, whereas there is no cross-peak between signals of the methyl protons of the NHMe group and signal of the aromatic H(4) proton (a doublet at  $\delta$  7.30). This proves that the NHMe substituent occupies the position 1. It should be particularly noted that there is no cross-peak between signal of the NH proton of the NHMe group (broad quartet at  $\delta$  7.50)

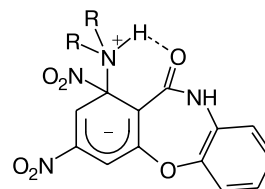


and signal of the aromatic H(2) proton ( $\delta$  7.20), apparently, due to the hydrogen bonding between this NH proton and the neighboring carbonyl group. It should be also pointed out the presence of a cross-peak between signals of the H(4) and H(6) protons (a doublet at  $\delta$  7.44), which additionally confirms the afore-mentioned assignments for the protons.

The <sup>1</sup>H NMR NOESY two-dimensional spectrum of a mixture of isomers **4d** and **4e** (the products of the reaction of oxazepinone **1** with piperidine in DMF) does not allow one to identify the structure of the main isomer, since signals of its H(2) and H(4) protons overlap (a singlet at  $\delta$  7.49) and, correspondingly, give the only cross-peak with signals of the protons of its NCH<sub>2</sub> group (a multiplet at  $\delta$  3.10). At the same time, in the NOESY spectrum of the mixture, it can be seen that signals of the protons of the NCH<sub>2</sub> group of the minor isomer (a multiplet at  $\delta$  3.41) form cross-peaks with two signals of the aromatic H(2) and H(4) protons ( $\delta$  6.98 and 7.20), *i.e.*, the minor isomer has the structure **4e** (the product of substitution of the nitro group in position 3), whereas the main one, correspondingly, **4d** (the product of substitution of the nitro group in position 1).



It can be supposed that "anomalous" direction of the reaction of 1,3-dinitrodibenzoxazepinone **1** with amines, leading, in contrast to the similar reactions with other nucleophiles, to the substitution of the nitro group in position 1, is caused by the formation of hydrogen bonding between the NH proton of the attacking amine and the carbonyl oxygen atom in the intermediate  $\sigma$ -complex:



Such a hydrogen bond, obviously, must stabilize this complex, whereas attack of an amine at position 3 does not provide such a stabilization. As the indirect proof of existence of the NH...O(C) bond in the intermediate  $\sigma$ -complexes can serve its presence in the products of the nucleophilic substitution reaction, which is attested by the <sup>1</sup>H NMR 2D NOESY spectrum of compound **4a** (see above).

A decrease in selectivity of the substitution in DMF (see Scheme 3) can be explained by an increase in activity of the nucleophile (piperidine) in dipolar aprotic solvent, which solvates the nucleophilic species less strongly than

alcohols (though the reaction of compound **1** with  $\text{NaN}_3$  in butanol gives the same ratio of isomers **2a** and **2b** as in DMF, merely it proceeds much slower). Another plausible explanation consists in the fact that dipolar aprotic solvent (DMF, DMSO) can itself form the strong bonds with NH proton, resulting in the weakening of the intramolecular NH...O bond (see Ref. 12).

### Experimental

$^1\text{H}$  NMR spectra were recorded on a Bruker AM300 and Bruker DRX500 spectrometers in  $\text{DMSO-d}_6$  (300.13 and 500.13 MHz, respectively). Mass spectra were recorded on a Kratos MS-30 instrument (EI, 70 eV). Conversions of the reactions were monitored by TLC (Silufol, eluent: hexane—ethyl acetate, 3 : 1).

X-ray diffraction experiments on the monocrystal of **2a** were carried out on a SMART APEX2 CCD diffractometer (Mo-K $\alpha$  radiation, graphite monochromator,  $\omega$ -scanning). The structures were solved by direct methods and refined by least squares method with anisotropic full-matrix approximation on  $F^2_{hkl}$ . Positions of the hydrogen atoms were calculated geometrically, excluding the hydrogen atom of the NH group, which was localized from the differential Fourier syntheses of the electron density. All the H atoms were refined by isotropic approximation using riding model. All the calculations performed using the SHELXTL PLUS program package. The main crystallographic data and refined parameters for compound **2a** are given in Table 2.

**3-Azido-1-nitrodibenz[*b,f*][1,4]oxazepin-11(10*H*)-one (2a) and 1-azido-3-nitrodibenz[*b,f*][1,4]oxazepin-11(10*H*)-one (2b).** A suspension of dinitrooxazepinone **1** (0.40 g, 1.33 mmol) and  $\text{NaN}_3$  (0.089 g, 1.37 mmol) in DMF (7 mL) was stirred for 2 h at 80 °C; DMF was half evaporated and the solution was kept for 16 h. The precipitate formed was filtered off and washed with MeOH (3×4 mL) to obtain crystals of 3-azido-1-nitro[*b,f*][1,4]oxazepin-11(10*H*)-one (**2a**). The yield was 0.14 g (36%), decomp.p. > 230 °C. Found (%): C, 52.82; H, 2.34; N, 23.39.  $\text{C}_{13}\text{H}_7\text{N}_5\text{O}_4$ . Calculated (%): C, 52.53; H, 2.37; N, 23.56. MS,  $m/z$  ( $I_{\text{rel}}$  (%)): 297 [ $\text{M}]^+$  (52), 241 (73), 223 (36), 195 (70), 140 (86).  $^1\text{H}$  NMR,  $\delta$ : 7.24 (m, 3 H); 7.43 (d, 1 H,  $J$  = 8.0 Hz); 7.51 (d, 1 H,  $J$  = 2.0 Hz); 7.56 (d, 1 H,  $J$  = 2.0 Hz); 10.92 (s, 1 H, NH). The filtrate was poured in water (100 mL), acidified to pH 3, the precipitate formed was filtered off and washed with water (3×20 mL). The yield of a mixture of isomers was 0.153 g (39%). Total ratio **2a/2b** was 9 : 1.

**3-Amino-1-nitrodibenz[*b,f*][1,4]oxazepin-11(10*H*)-one (3).** Sodium iodide (0.45 g, 3.00 mmol) and  $\text{FeCl}_3$  (0.08 g, 0.49 mmol) were added to a suspension of **2a** (0.10 g, 0.34 mmol) in MeCN (10 mL). The mixture was heated at 80 °C under stirring for 1 h and filtered while hot. The filtrate was concentrated, the residue was recrystallized from MeCN to obtain compound **3a** (0.074 g, 81%). Yellow crystals, decomp.p. > 300 °C. Found (%): C, 57.41; H, 3.43; N, 15.84.  $\text{C}_{13}\text{H}_9\text{N}_3\text{O}_4$ . Calculated (%): C, 57.57; H, 3.34; N, 15.49. MS,  $m/z$  ( $I_{\text{rel}}$  (%)): 271 [ $\text{M}]^+$  (33), 241 (100), 226 (40), 170 (28).  $^1\text{H}$  NMR,  $\delta$ : 6.58 (d, 1 H,  $J$  = 1.9 Hz); 6.61 (s, 2 H,  $\text{NH}_2$ ); 6.78 (d, 1 H,  $J$  = 1.9 Hz); 7.14–7.19 (m, 2 H); 7.23 (t, 1 H,  $J$  = 7.8 Hz); 7.30 (d, 1 H,  $J$  = 7.8 Hz); 10.42 (s, 1 H, NH).

**Table 2.** Main crystallographic data and refined parameters for compound **2a**

Parameter	Value
Molecular formula	$\text{C}_{13}\text{H}_7\text{N}_5\text{O}_4$
Molecular weight	297.24
$T/\text{K}$	100
Crystal system	Triclinic
Space group	$P\bar{1}$
$Z(Z')$	2(1)
$a/\text{\AA}$	7.0390(9)
$b/\text{\AA}$	9.2063(9)
$c/\text{\AA}$	10.801(1)
$\alpha/\text{deg}$	68.130(8)
$\beta/\text{deg}$	81.279(7)
$\gamma/\text{deg}$	71.796(7)
$V/\text{\AA}^3$	616.6(1)
$d_{\text{calc}}/\text{g cm}^{-3}$	1.601
$\mu/\text{cm}^{-1}$	1.24
$F(000)$	304
$2\theta_{\text{max}}/\text{deg}$	55
Total number of reflections	6037
Number of independent reflections	2813
Number of reflections with $I > 2\sigma(I)$	2393
Amount of refined parameters	199
$R_1$	0.0374
$wR_2$	0.1292
GOOF	1.033
Residual electron density/ $\text{e \AA}^{-3}$ ( $d_{\text{min}}/d_{\text{max}}$ )	0.333/−0.284

**RNH- and  $\text{R}_2\text{N}$ -Substituted 3-nitrodibenz[*b,f*][1,4]oxazepin-11(10*H*)-ones (4a–d) (general procedure).** A suspension of dinitrodibenzoxazepinone **1** (0.40 g, 1.33 mmol) and the corresponding amine (5.5 mmol) (in case of methylamine, 10-fold excess of 40% aqueous amine was used) in *n*-butanol (5 mL) (in case of methylamine, EtOH was used as the solvent) was refluxed for 4 h and kept for 16 h. The crystals formed were filtered off and washed with MeOH (2×3 mL).

**1-Methylamino-3-nitrodibenz[*b,f*][1,4]oxazepin-11(10*H*)-one (4a).** The yield was 77%, m.p. 260–262 °C. Found (%): C, 58.66; H, 3.99; N, 14.95.  $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_4$ . Calculated (%): C, 58.95; H, 3.89; N, 14.73. MS,  $m/z$  ( $I_{\text{rel}}$  (%)): 285 [ $\text{M}]^+$  (100), 268 (22), 238 (48), 211 (30).  $^1\text{H}$  NMR,  $\delta$ : 2.87 (d, 3 H,  $J$  = 6.0 Hz); 7.14–7.23 (m, 4 H); 7.30 (d, 1 H,  $J$  = 2.2 Hz); 7.44 (d, 1 H,  $J$  = 8.4 Hz); 7.50 (br.q, 1 H, NH,  $J$  = 6.0 Hz); 10.81 (br.s, 1 H, NH).

**1-Cyclopropylamino-3-nitrodibenz[*b,f*][1,4]oxazepin-11(10*H*)-one (4b).** The yield was 88%, m.p. 228–230 °C. Found (%): C, 61.94; H, 4.13; N, 13.44.  $\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_4$ . Calculated (%): C, 61.73; H, 4.21; N, 13.50. MS,  $m/z$  ( $I_{\text{rel}}$  (%)): 310 [ $\text{M}]^+$  (100), 294 (51), 282 (48), 264 (67), 256 (44), 236 (40), 210 (54), 154 (46).  $^1\text{H}$  NMR,  $\delta$ : 0.52 (m, 2 H); 0.84 (m, 2 H); 2.57 (m, 1 H); 7.14–7.24 (m, 3 H); 7.39 (d, 1 H,  $J$  = 2.0 Hz); 7.46 (d, 1 H,  $J$  = 8.4 Hz); 7.63 (d, 1 H,  $J$  = 2.0 Hz); 7.68 (br.s, 1 H, NH); 10.80 (br.s, 1 H, NH).

**1-(Morpholin-4-yl)-3-nitrodibenz[*b,f*][1,4]oxazepin-11(10*H*)-one (4c).** The yield was 74%, m.p. 209–211 °C. Found (%): C, 60.07; H, 4.47; N, 12.30.  $\text{C}_{17}\text{H}_{15}\text{N}_3\text{O}_5$ . Calculated (%): C, 60.07; H, 4.47; N, 12.30.

lated (%): C, 59.82; H, 4.40; N, 12.11. MS,  $m/z$  ( $I_{\text{rel}}$  (%)): 341  $[M]^+$  (15), 323 (100), 298 (53), 256 (51), 210 (93), 182 (64), 154 (36).  $^1\text{H}$  NMR,  $\delta$ : 3.13 (m, 4 H); 3.69 (m, 4 H); 7.17 (m, 2 H); 7.22 (t, 1 H,  $J = 8.2$  Hz); 7.43 (d, 1 H,  $J = 8.2$  Hz); 7.54 (d, 1 H,  $J = 2.0$  Hz); 7.59 (d, 1 H,  $J = 2.0$  Hz); 10.78 (s, 1 H, NH).

**3-Nitro-1-piperidinodibenz[*b,f*][1,4]oxazepin-11(10*H*)-one (4d) (procedure A).** The yield was 54%, m.p. 224–227 °C. Found (%): C, 63.48; H, 5.22; N, 12.55.  $\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_4$ . Calculated (%): C, 63.71; H, 5.05; N, 12.38. MS,  $m/z$  ( $I_{\text{rel}}$  (%)): 339  $[M]^+$  (100), 322 (35), 310 (52), 84 (32).  $^1\text{H}$  NMR,  $\delta$ : 1.58 (m, 6 H); 3.10 (m, 4 H); 7.18 (m, 3 H); 7.40 (d, 1 H,  $J = 8.0$  Hz); 7.49 (s, 2 H); 10.67 (br.s, 1 H, NH).

**Reaction of compound 1 with piperidine in DMF (procedure B).** **3-Nitro-1-piperidinodibenz[*b,f*][1,4]oxazepin-11(10*H*)-one (4d) and 1-nitro-3-piperidinodibenz[*b,f*][1,4]oxazepin-11(10*H*)-one (4e).** A suspension of dinitrooxazepinone **1** (0.20 g, 0.66 mmol) and piperidine (0.22 g, 2.58 mmol) in DMF (3 ml) was heated at 80 °C for 2 h. The reaction mixture was cooled, poured in water (50 mL), and neutralized with HCl. The precipitate was filtered off and washed with hot water (3×20 mL), then, with MeOH (3×2 mL). The yield of a mixture of isomers was 0.20 g (89%). 3-Nitro-1-piperidinodibenz[*b,f*][1,4]oxazepin-11(10*H*)-one (**4d**) was the main isomer. Ratio of isomers **4d** and **4e** was 2 : 1. Signals of the minor isomer **4e**, observed in the  $^1\text{H}$  NMR spectrum,  $\delta$ : 3.41 (m, 4 H); 6.98 (d, 1 H,  $J = 2.0$  Hz); 7.33 (d, 1 H,  $J = 8.2$  Hz); 10.42 (br.s, 1 H, NH).

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Received December 18, 2006;  
in revised form April 11, 2007