Tetrahedron 64 (2008) 11763–11767

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

A straightforward preparation of benzo[*f*]naphtho[*b*][1,4]oxazepines from TNT

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ARTICLE INFO

Article history:
Received 23 July 2008
Received in revised form 5 September 2008
Accepted 25 September 2008
Available online 8 October 2008

Keywords:
2,4,6-Trinitrotoluene
1-Nitroso-2-naphthol
Benzo[*f*]naphtho[*b*][1,4]oxazepines
S_NAr reactions

ABSTRACT

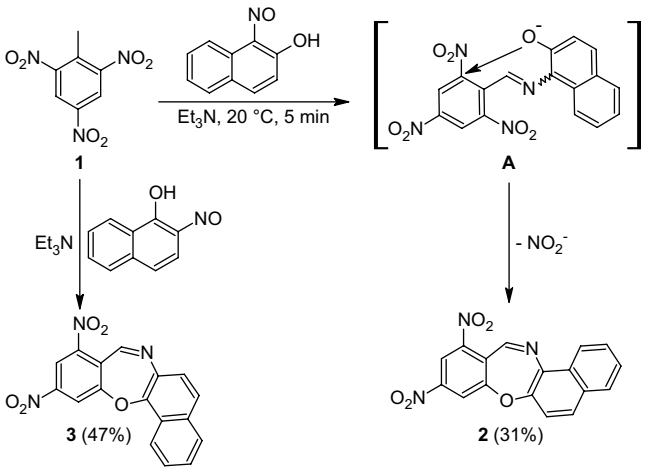
2,4,6-Trinitrotoluene readily reacts with 1-nitroso-2-naphthol to afford 9,11-dinitrobenzo[*f*]naphtho[2,1-*b*][1,4]oxazepine. The nitro groups of the latter undergo displacement by *O*- and *S*-nucleophiles with preferential substitution of the 11-NO_2 (*peri*-nitro group). The structures of the substitution products are confirmed by X-ray diffraction and ^{1}H NMR NOE experiments.

1. Introduction

Previously, during the course of work aimed at the utilization of aromatic polynitrocompounds, various benzoannulated five-, six- and seven-membered heterocycles were prepared; some of them possess promising biological activity.[1] In particular, derivatives of benz[*d*]isothiazole,[2,3] quinazoline[4,5] and dibenz[*b*,*f*][1,4]oxazepine[6,7] were synthesized starting from 2,4,6-trinitrobenzoic acid. The latter, in turn, was prepared by oxidation of 2,4,6-trinitrotoluene (TNT).[8] In the present work, we demonstrate that TNT itself could be used directly for a surprisingly simple and straightforward synthesis of benzoannulated seven-membered heterocycles, which are difficult to prepare by other methods.[9]

2. Results and discussion

We found that TNT **1** readily reacted with 1-nitroso-2-naphthol under mild conditions in the presence of a base to yield dinitrosubstituted benzonaphthooxazepine **2**.[10] The reaction of TNT with 2-nitroso-1-naphthol under the same conditions affords an isomeric benzonaphthooxazepine **3**. Unfortunately, the yields are only moderate at the best (significant amounts of tarry products are formed), and our attempts to improve the yields by varying the solvents (DMF, EtOH) and bases (K_2CO_3, NH_3) failed. On the other hand, the pure products are isolated by a simple filtration in 5 min. The reactions evidently proceed via intermediate imines of type **A** with subsequent intramolecular displacement of a nitro group by the phenolate anion (Scheme 1).



Scheme 1.

The following facts provide evidence for the proposed mechanistic sequence: displacement of the nitro groups in TNT by *O*-nucleophiles was never reported,[11] whereas the reaction of TNT

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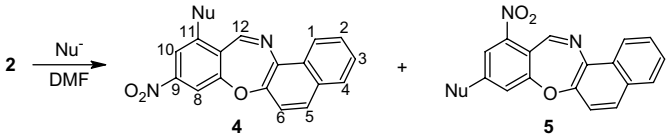
0040-4020/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.09.090

with aromatic nitroso compounds is known to occur readily, affording the corresponding imines.[12] To the best of our knowledge, this approach to 1,4-oxazepine synthesis has not been described previously: usually, the oxazepine ring is constructed from 1,4-*N*,*O*-dinucleophilic (N^-–C–C–O^-) and 1,3-*C*,*C*-dielectrophilic (C^+–C–C^+) fragments,[13] while in the present case quite another synthetic scheme is realized: (N^+–C–C–O^-)+(C^-–C–C^+).[14]

Nitro groups in compound **2** undergo smooth displacement by *S*- and *O*-nucleophiles under mild conditions (20 °C for the *S*-nucleophiles and 80 °C for their *O*-counterparts), yielding both possible isomeric substitution products **4** and **5** (Scheme 2).



4a, 5a: Nu = MeO (total yield 86%, isomeric ratio **4a/5a** 3:1)

4b, 5b: Nu = 4-MeC_6H_4O (81%, **4b/5b** 2:1)

4c, 5c: Nu = BuS (89%, **4c/5c** 6:1)

4d, 5d: Nu = $PhCH_2S$ (85%, **4d/5d** 4:1)

Scheme 2.

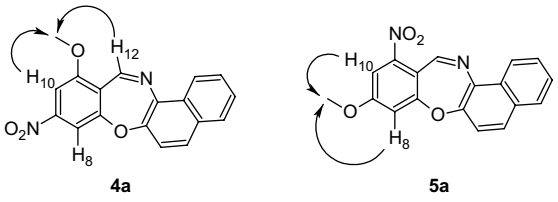


Figure 1. Key cross-peaks in 2D ^{1}H NMR NOESY spectrum of **4a**+**5a** mixture.

In all cases, compounds **4** (where an 11-NO_2 group is displaced) are predominant, and this is confirmed by NOE experiments. In the 2D ^{1}H NMR NOESY spectrum of a mixture (**4a**+**5a**), the major isomer features a cross-peak between the OCH_3 protons (δ 4.02) and the aromatic proton H(10) (δ 7.74), whereas a cross-peak between the OCH_3 protons and the aromatic proton H(8) (δ 7.81) is absent. In addition, a cross-peak between the OCH_3 protons and the H(12) proton (δ 9.00) is observed. A minor isomer features a cross-peak between the OCH_3 protons (δ 3.91) and the two aromatic protons H(8) and H(10) (δ 7.42 and 7.54), whereas a cross-peak between the signals of OCH_3 protons and the H(12) proton (δ 8.95) is not observed. Accordingly, a structure of **4a** is assigned to the major isomer and a structure of **5a** to the minor one (Fig. 1).

Similarly, 2D ^{1}H NMR NOESY spectrum of a mixture (**4d**+**5d**) shows **4d** to be a major isomer and **5d** to be a minor one (Fig. 2).

The structure of compound **4b** (a major product in the reaction of **2** with 4-methylphenol) was confirmed by X-ray diffraction (Fig. 3).

Noteworthy, some substitution of both nitro groups is usually observed in the reaction—even if 1 equiv of nucleophile is used. Probably, this is due to a very low solubility of the starting compound **2**, resulting in a local excess of the nucleophile in the reaction mixture. To minimize bis-substitution, the nucleophile is added in small portions under vigorous stirring. When a twofold excess of the nucleophile is used, the bis-substitution products **6** turn to be the sole products of the reaction and are isolated in high yields (Scheme 3).

It is interesting to compare the selectivity observed for the nitro group displacement in the oxazepine **2** with reactivity of the other similar compounds. Thus, dinitrosubstituted benzoannulated five-membered heterocycles are known to undergo selective nucleophilic displacement of a nitro group adjacent to a ring fusion point (*peri*-nitro group),[3,15–19] while in 1,3-dinitrodibenz[*b*,*f*][1,4]oxazepine-11(10*H*)-one **7** the non-adjacent nitro group (*para*-nitro group) is displaced with *O*- and *S*-nucleophiles (Fig. 4).[6]

In order to explain these facts, it was assumed[6] that steric hindrance of the nucleophilic attack at the *peri*-position, created by an *ortho*-substituent, was more significant in the seven-membered benzoannulated heterocycle than in five-membered heterocycles (due to different geometry of the molecule) (Fig. 5).

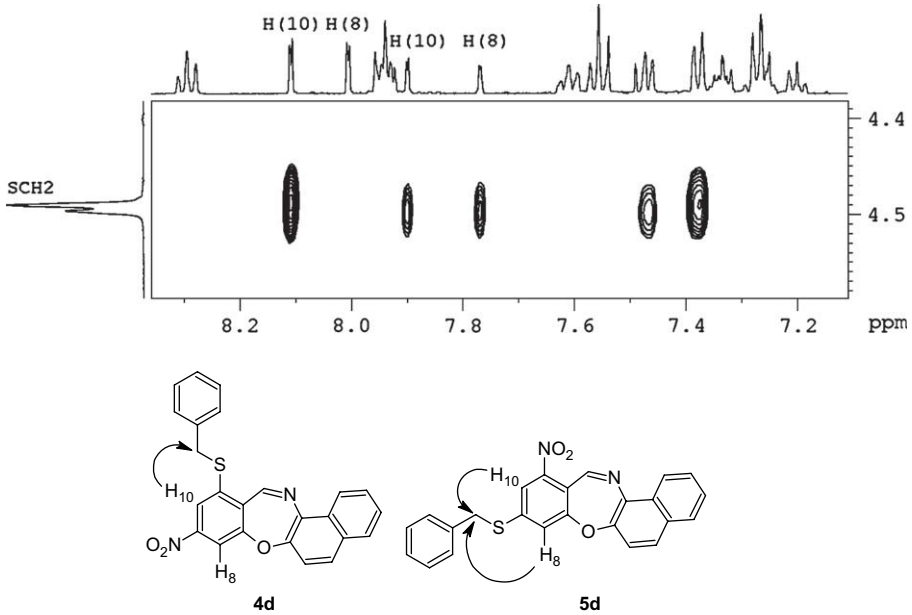


Figure 2. Fragment of the 2D ^{1}H NMR NOESY spectrum of **4d**+**5d** mixture and key cross-peaks.

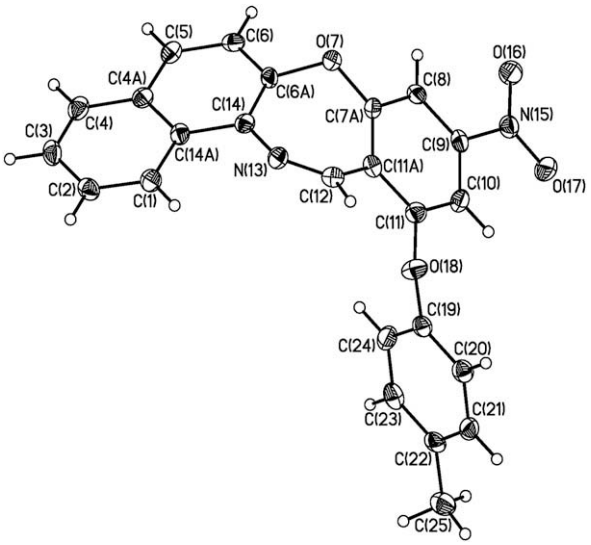


Figure 3. The general view of compound **4b** in representation of atoms via thermal ellipsoids (p=50%).

In this case, replacement of a C=O *ortho*-substituent (which is present in compound **7**) with a less bulky C–H in compound **2** should favour *peri*-substitution—which is exactly what is observed in the present work. Thus, the results obtained provide additional evidence in favour of a crucial role of steric effects in nucleophilic nitro group displacement.

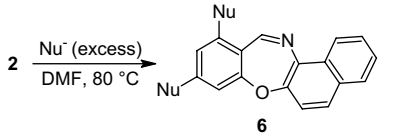
3. Experimental

3.1. General

^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 on a Bruker DRX500 spectrometer (500.13 MHz and 125.75 MHz, respectively); mass-spectra were measured on a Kratos MS-30 instrument (EI, 70 eV). IR spectra were obtained on a 'Specord M-80-1' spectrometer.

3.2. Crystallographic data

Crystals of **4b** ($C_{24}H_{16}N_2O_4$, M=369.39) are orthorhombic, space group *Pbca*, at 100 K: a=7.2939(9), b=13.9611(14), c=35.094(5) Å, V=3573.7(8) Å^3, Z=8 (Z'=1), d_{calcd}=1.473 g cm^{-3}, μ(Mo Kα)=1.02 cm^{-1}, F(000)=1648. Intensities of 10,950 reflections were measured with a Bruker SMART APEX2 CCD diffractometer [λ(Mo Kα)=0.71072*E*, ω-scans, $2\theta<54°$] and 3844 independent reflections [R_{int}=0.0736] were used in further refinements. The structure was solved by direct methods and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. The H(C) hydrogen atom positions were calculated. All hydrogen atoms were refined in the isotropic approximation in the riding model. For **4b** the refinement converged to $wR2$=0.1103 and GOF=1.003 for all independent reflections ($R1$=0.0490 was calculated against F for 2333 observed reflections with $I>2\sigma(I)$). All calculations were performed using SHELXTL PLUS 5.0. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 615151 for **4b**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).



6

6a: Nu = MeO (81%)

6b: Nu = EtO (70%)

6c: Nu = PhO (73%)

6d: Nu = 4-MeC$_6$H$_4$O (78%)

Scheme 3.

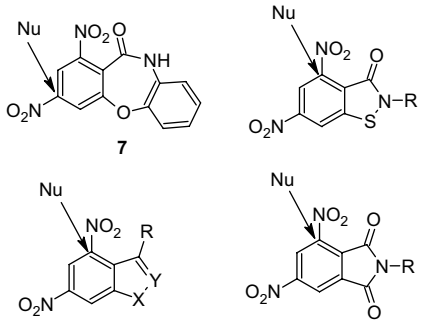


Figure 4. Selectivity of aromatic nitro group displacement in some benzoannulated systems.

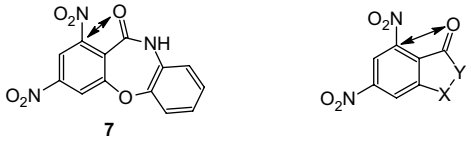


Figure 5. Relative steric hindrance in some benzoannulated structures.

3.3. Synthetic procedures

*3.3.1. 9,11-Dinitrodibenzo[f]naphtho[2,1-b][1,4]oxazepine (**2**)*

To a solution of 1-nitroso-2-naphthol (3.46 g, 20 mmol) and trinitrotoluene **1** (4.54 g, 20 mmol) in CH_3CN (30 ml), Et_3N (2.0 g, 20 mmol) was added dropwise with stirring. In 5 min, the resulting precipitate was filtered off and washed with MeOH (3×10 ml). Yield 2.08 g (31%), deep-orange needles, mp 276–278 °C. Found, %: C, 60.65; H, 2.58; N, 12.73. $C_{17}H_9N_3O_5$ calculated, %: C, 60.90; H, 2.71; N, 12.53. MS, m/z (I (%)): 335 [M]$^+$ (100), 243 (68), 231 (43), 214 (41). ^{1}H NMR (δ, J/Hz): 7.55–7.65 (m, 3H), 7.92 (m, 2H), 8.32 (d, J=8.4, 1H), 8.60 (s, 1H), 8.68 (s, 1H) (both H-8 and H-10), 9.19 (s, 1H, H-12). IR (ν_{max}, KBr): 1600, 1520, 1505, 1345, 1210, 1045.

*3.3.2. 9,11-Dinitrodibenzo[f]naphtho[1,2-b][1,4]oxazepine (**3**)*

Compound **3** was prepared by the same procedure starting from 2-nitroso-1-naphthol and trinitrotoluene **1**. Yield 47%, deep-orange needles, mp 263–266 °C. Found, %: C, 61.26; H, 2.88; N, 12.83. $C_{17}H_9N_3O_5$ calculated, %: C, 60.90; H, 2.71; N, 12.53. MS, m/z (I (%)): 335 [M]$^+$ (100), 243 (48), 231 (32), 214 (26). ^{1}H NMR (δ, J/Hz): 7.53 (d, J=8.5, 1H), 7.60 (t, J=8.2, 1H), 7.70 (t, J=8.2, 1H), 7.87 (d, J=8.0, 1H), 7.97 (d, J=8.0, 1H), 8.17 (m, 2H), 8.26 (s, 1H), 9.03 (s, 1H, H-8). IR (ν_{max}, KBr): 1600, 1525, 1500, 1340, 1205, 1045.

*3.3.3. 11-Methoxy-9-nitrobenzo[f]naphtho[2,1-b][1,4]oxazepine (**4a**) and 9-methoxy-11-nitrobenzo[f]naphtho[2,1-b][1,4]-oxazepine (**5a**)*

A suspension of the oxazepine **2** (0.20 g, 0.60 mmol) in dry DMF (7 ml) was stirred at 80 °C. To the mixture, a solution of Na (0.014 g,

0.62 mmol) in MeOH (5 ml) was added dropwise over 4 h. The mixture was cooled, poured into water (50 ml) and acidified to pH 6 with HCl. The resulting precipitate was filtered off, washed with MeOH (3×0.5 ml) and hot water (5×10 ml) and dried. Yield of the isomeric mixture 0.165 g (86%), ratio **4a**/**5a** 3:1. The major isomer **4a** was isolated by crystallization from CH_3CN (yield 51%). Yellowish-brown prisms. Mp 184–187 °C. Found, %: C, 67.92; H, 3.64; N, 8.33. $C_{18}H_{12}N_2O_4$ calculated, %: C, 67.50; H, 3.78; N, 8.75. MS, *m*/*z* (*I* (%)): 320 $[M]^+$ (100), 290 (63), 247 (61), 231 (69), 219 (72), 203 (61). ^{1}H NMR (*δ*, *J*/Hz): 4.02 (s, 3H, OMe), 7.57 (m, 3H), 7.74 (d, *J*=1.9, 1H, H-10), 7.81 (d, *J*=1.9, 1H, H-8), 7.94 (m, 2H), 8.33 (d, *J*=8.2, 1H), 9.00 (s, 1H, H-12). ^{13}C NMR (*δ*): 57.3 (OCH_3), 104.0 (CH), 108.1 (CH), 120.8, 120.9 (CH), 123.4 (CH), 126.3 (CH), 127.3 (CH), 127.9 (CH), 129.8 (CH), 130.0, 131.6, 134.3, 147.6, 151.3, 156.7 (CH), 159.0, 162.0. IR (ν_{max}, KBr): 1595, 1525, 1340, 1215, 1095.

3.3.4. *Preparation of monosubstitution products **4** and **5** (general procedure)*

To a stirred suspension of **2** (0.40 g, 1.19 mmol) and dried K_2CO_3 (0.25 g, 1.80 mmol) in dry DMF (5 ml), a solution of the corresponding phenol or thiol (1.25 mmol) in DMF (2 ml) was added dropwise over 4 h. Reaction with thiols was carried out at rt, while *p*-cresol required heating at 80 °C. The mixture was cooled, poured into water (50 ml) and acidified to pH 6 with HCl. The resulting precipitate was filtered off, washed with MeOH (3×1 ml) and hot water (5×20 ml) and dried.

*3.3.4.1. 11-(4-Methylphenoxy)-9-nitrobenzo[f]naphtho[2,1-b][1,4]oxazepine (**4b**) and 9-(4-methylphenoxy)-11-nitrobenzo[f]naphtho[2,1-b][1,4]oxazepine (**5b**).* Yield of the isomeric mixture 81%, ratio **4b**/**5b** 2:1. The major isomer **4b** was isolated by crystallization from CH_3CN (yield 42%). Orange plates, mp 156–159 °C. Found, %: C, 73.01; H, 4.21; N, 7.31. $C_{24}H_{16}N_2O_4$ calculated, %: C, 72.72; H, 4.07; N, 7.07. MS, *m*/*z* (*I* (%)): 396 $[M]^+$ (18), 379 (47), 366 (49), 349 (100). ^{1}H NMR (*δ*, *J*/Hz): 2.36 (s, 3H, Me), 7.19 (d, *J*=8.1, 2H), 7.22 (d, *J*=2.0, 1H, H-10), 7.32 (d, *J*=8.1, 2H), 7.56–7.65 (m, 3H), 7.92 (d, *J*=2.0, 1H, H-8), 7.97 (d, *J*=8.0, 1H), 8.00 (d, *J*=8.2, 1H), 8.36 (d, *J*=8.0, 1H), 9.19 (s, 1H, H-12). ^{13}C NMR (*δ*): 19.2 (CH_3), 105.9 (CH), 108.4 (CH), 119.3 (2CH), 119.6 (CH), 120.8, 122.3 (CH), 125.1 (CH), 126.1 (CH), 126.6 (CH), 128.8 (CH), 128.9, 129.8 (2CH), 130.4, 133.0, 134.2, 146.4, 149.5, 150.6, 154.9 (CH), 156.4, 161.3. IR (ν_{max}, KBr): 1600, 1530, 1500, 1345, 1215, 1045, 820.

*3.3.4.2. 11-Butylsulfanyl-9-nitrobenzo[f]naphtho[2,1-b][1,4]oxazepine (**4c**) and 9-butylsulfanyl-11-nitrobenzo[f]naphtho[2,1-b][1,4]oxazepine (**5c**).* Yield of the isomeric mixture 89%, ratio **4c**/**5c** 6:1. The major isomer **4c** was isolated by crystallization from CH_3CN (yield 62%). Orange plates, mp 104–106 °C. Found, %: C, 66.34; H, 4.93; N, 7.12; S, 8.73. $C_{21}H_{18}N_2O_3S$ calculated, %: C, 66.65; H, 4.79; N, 7.40; S, 8.47. MS, *m*/*z* (*I* (%)): 378 $[M]^+$ (100), 348 (64), 322 (39), 292 (62), 231 (42). ^{1}H NMR (*δ*, *J*/Hz): 0.89 (t, *J*=7.5, 3H, Me), 1.43 (m, 2H, CH_2), 1.63 (m, 2H, CH_2), 3.21 (t, *J*=7.5, 2H, CH_2), 7.57 (m, 2H), 7.62 (t, *J*=8.2, 1H), 7.96 (m, 2H), 8.01 (d, *J*=2.0, 1H), 8.03 (d, *J*=2.0, 1H) (both H-8 and H-10), 8.31 (d, *J*=8.0, 1H), 9.06 (s, 1H, H-12). ^{13}C NMR (*δ*): 13.3 (CH_3), 21.2 (CH_2), 29.8 (CH_2), 32.0 (CH_2), 112.2 (CH), 118.4 (CH), 120.6 (CH), 123.2 (CH), 126.2 (CH), 127.2 (CH), 127.7 (CH), 129.4, 129.7 (CH), 131.4, 134.1, 141.4, 147.6, 150.2, 157.1 (CH), 162.1. IR (ν_{max}, KBr): 2985, 1520, 1345, 1235, 810, 750.

*3.3.4.3. 11-Benzylsulfanyl-9-nitrobenzo[f]naphtho[2,1-b][1,4]oxazepine (**4d**) and 9-benzylsulfanyl-11-nitrobenzo[f]naphtho[2,1-b][1,4]-oxazepine (**5d**).* Pure **4d** isomer precipitates from the reaction mixture (yield 58%), and the filtrate was worked up as specified above. Total yield of the isomeric mixture 85%, ratio **4d**/**5d** 4:1. Major isomer **4d**: orange plates, mp 178–181 °C. Found, %: C, 70.29; H, 3.82; N, 6.97; S, 7.26. $C_{24}H_{16}N_2O_3S$ calculated, %: C, 69.89; H, 3.91; N, 6.79; S, 7.77. MS, *m*/*z* (*I* (%)): 412 $[M]^+$ (16), 382 (100), 291 (10), 91 (67). ^{1}H NMR (*δ*, *J*/Hz): 4.49 (s, 2H, CH_2), 7.23 (m, 3H), 7.38 (d, *J*=8.2, 2H), 7.58 (m, 3H), 7.95 (m, 2H), 8.01 (d, *J*=2.0, 1H, H-8), 8.11 (d, *J*=2.0, 1H, H-10), 8.30 (d, *J*=8.2, 1H), 9.01 (s, 1H, H-12). ^{13}C NMR (*δ*): 37.3 (CH_2), 113.1 (CH), 120.1 (CH), 120.7 (CH), 123.4 (CH), 126.4 (CH), 127.3 (CH), 127.7 (CH), 127.9 (CH), 128.7 (2CH), 129.1 (2CH), 129.9 (CH), 130.2, 131.6, 134.2, 135.8, 140.7, 147.7, 150.1, 157.4 (CH), 162.1. IR (ν_{max}, KBr): 1605, 1520, 1500, 1350, 1235, 995, 875, 690.

3.3.5. *9,11-Bis(RO)-benzo[f]naphtho[2,1-b][1,4]oxazepines (**6a–d**) (general procedure)*

A suspension of **2** (1.50 g, 4.48 mmol), the corresponding ArOH or AlkOH (9.09 mmol or 44.8 mmol, respectively) and dried K_2CO_3 (1.88 g, 13.63 mmol) in dry DMF (5 ml) was stirred at 80 °C for 4 h. The mixture was cooled, poured into water (50 ml) and acidified to pH 6 with HCl. The resulting precipitate was filtered off, washed with MeOH (3×2 ml) and hot water (5×50 ml) and dried.

*3.3.5.1. 9,11-Dimethoxybenzo[f]naphtho[2,1-b][1,4]oxazepine (**6a**).* Yield 81%, brownish-yellow scales, mp 117–119 °C (MeCN). Found, %: C, 74.62; H, 4.81; N, 4.30. $C_{19}H_{15}NO_3$ calculated, %: C, 74.74; H, 4.95; N, 4.59. MS, *m*/*z* (*I* (%)): 305 $[M]^+$ (100), 262 (23). ^{1}H NMR (*δ*, *J*/Hz): 3.84 (s, 3H, OMe), 3.87 (s, 3H, OMe), 6.44 (s, 2H, H-8 and H-10), 7.31 (d, *J*=8.2, 1H), 7.50 (m, 2H), 7.80 (d, *J*=8.0, 1H), 7.86 (d, *J*=8.2, 1H), 8.39 (d, *J*=8.2, 1H), 8.78 (s, 1H, H-12). ^{13}C NMR (*δ*): 55.9 (OCH_3), 56.3 (OCH_3), 95.5 (CH), 97.8 (CH), 109.3, 121.0 (CH), 123.5 (CH), 125.7 (CH), 126.6 (CH), 127.6 (CH), 128.4 (CH), 130.3, 131.4, 134.8, 148.0, 157.3 (CH), 159.9, 163.8, 165.0. IR (ν_{max}, KBr): 1600, 1220, 1145, 1100.

*3.3.5.2. 9,11-Diethoxybenzo[f]naphtho[2,1-b][1,4]oxazepine (**6b**).* Yield 70%, brown scales, mp 102–104 °C (MeCN). Found, %: C, 75.97; H, 5.96; N, 4.58. $C_{21}H_{19}NO_3$ calculated, %: C, 75.66; H, 5.74; N, 4.20. MS, *m*/*z* (*I* (%)): 333 $[M]^+$ (100), 276 (20), 248 (30). ^{1}H NMR (*δ*, *J*/Hz): 1.39 (m, 6H, 2Me), 4.11 (m, 4H, $2CH_2$); 6.39 (s, 2H, H-8 and H-10), 7.30 (d, *J*=8.2, 1H), 7.50 (m, 2H), 7.78 (d, *J*=8.0, 1H), 7.84 (d, *J*=8.0, 1H), 8.40 (d, *J*=8.0, 1H), 8.77 (s, 1H, H-12). ^{13}C NMR (*δ*): 14.4 (CH_3), 14.5 (CH_3), 64.0 (OCH_2), 64.5 (OCH_2), 96.4 (CH), 98.1 (CH), 109.3, 121.1 (CH), 123.6 (CH), 125.9 (CH), 126.7 (CH), 127.7 (CH), 128.5 (CH), 130.3, 131.4, 134.9, 148.0, 157.5 (CH), 159.2, 163.9, 164.3. IR (ν_{max}, KBr): 2990, 1600, 1325, 1220, 1150, 1090, 815.

*3.3.5.3. 9,11-Diphenoxybenzo[f]naphtho[2,1-b][1,4]oxazepine (**6c**).* Yield 73%, yellowish plates, mp 124–126 °C (benzene). Found, %: C, 81.38; H, 4.39; N, 3.56. $C_{29}H_{19}NO_3$ calculated, %: C, 81.10; H, 4.46; N, 3.26. MS, *m*/*z* (*I* (%)): 429 $[M]^+$ (100), 412 (48), 77 (78). ^{1}H NMR (*δ*, *J*/Hz): 6.17 (s, 1H), 6.52 (s, 1H) (both H-8 and H-10), 7.06 (d, *J*=8.0, 2H), 7.12 (d, *J*=8.2, 2H), 7.21 (m, 2H), 7.32 (d, *J*=8.2, 1H), 7.40 (m, 4H), 7.53 (m, 2H), 7.83 (d, *J*=7.8, 1H), 7.88 (d, *J*=8.0, 1H), 8.38 (d, *J*=8.0, 1H), 8.93 (s, 1H, H-12). ^{13}C NMR (*δ*): 102.4 (CH), 103.3 (CH), 112.6, 119.8 (2CH), 120.0 (2CH), 120.9 (CH), 123.4 (CH), 125.0 (CH), 125.1 (CH), 125.9 (CH), 126.8 (CH), 127.6 (CH), 129.0 (CH), 130.2 (4CH), 131.4, 134.4, 147.8, 154.2, 154.7, 156.5 (CH), 158.0, 162.4, 163.9. IR (ν_{max}, KBr): 1585, 1490, 1215, 1125, 1050, 765, 695.

*3.3.5.4. 9,11-Bis(4-methylphenoxy)benzo[f]naphtho[2,1-b][1,4]oxazepine (**6d**).* Yield 78%, yellowish prisms, mp 83–85 °C (benzene). Found, %: C, 81.12; H, 5.15; N, 3.36. $C_{31}H_{23}NO_3$ calculated, %: C, 81.38; H, 5.07; N, 3.06. MS, *m*/*z* (*I* (%)): 457 $[M]^+$ (100), 440 (78), 306 (30). ^{1}H NMR (*δ*, *J*/Hz): 2.31 (s, 6H, 2Me), 6.11 (s, 1H), 6.41 (s, 1H) (both H-8 and H-10), 6.94 (d, *J*=8.2, 2H), 7.02 (d, *J*=8.2, 2H), 7.20 (m, 4H), 7.30 (d, *J*=8.0, 1H), 7.53 (m, 2H), 7.82 (d, *J*=7.9, 1H), 7.88 (d, *J*=7.9, 1H), 8.38 (d, *J*=8.0, 1H), 8.92 (s, 1H, H-12). ^{13}C NMR (*δ*): 20.4 ($2CH_3$), 102.0 (CH), 102.7 (CH), 112.3, 119.9 (2CH), 120.1 (2CH), 121.0 (CH), 123.6 (CH), 126.1 (CH), 126.9 (CH), 127.8 (CH), 129.1 (CH), 130.3, 130.7 (4CH), 131.5, 134.5, 134.6, 148.0, 152.0,

152.5, 156.7 (CH), 158.5, 162.9, 164.0. IR (ν_{max}, KBr): 1600, 1510, 1215, 1125, 1050, 815.

Acknowledgements

This research was supported by grant from Chemical Block Ltd (www.chemblock.com).

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