Synthesis and amination of 5- and 8-amino derivatives of 2-phenylnaphtho[2,3-*d*]-1,3-thiazole-4,9-dione

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5- and 8-Amino-2-phenylnaphtho[2,3-*d*]-1,3-thiazole-4,9-diones were obtained by treatment of 3,5-diamino-2-chloro- and 2,5-diamino-3-chloro-1,4-naphthoquinones with sodium sulfide followed by condensation with benzaldehyde. Thermal and photochemical butylamination and $CoCl_2$-promoted arylamination of 5-amino-2-phenylnaphthothiazole-4,9-dione in position 8 was carried out.

Key words: 1,4-naphthoquinone; 5- and 8-amino-2-phenyl-naphtho[2,3-*d*]-1,3-thiazole-4,9-dione; heteroannelation; direct amination; photoamination.

Certain 5,8-diamino derivatives of 1,4-naphthoquinone that absorb in the near infrared region of the spectrum may be used in optical disks for laser recording of information.[1] On going from 1,4-naphthoquinones to the corresponding derivatives of anthraquinone, a hypsochromic shift of the long-wavelength absorption maximum occurs, but the resulting dyes possess higher chemical and photochemical stabilities. Linearly heteroannelated 1,4-naphthoquinones combine the long-wavelength absorption of the naphthoquinone system with the stability typical of anthraquinone dyes,[2,3] which has been shown, in particular, for 5,8-diamino derivatives of 1,4-naphthoquinones fused with an imidazole[2,4] or thiophene[3,5] ring at positions 2 and 3. Of naphthoquinones having amino substituents in the benzene ring and fused with a 5-membered heterocycle containing both nitrogen and sulfur atoms, 5- and 8-monoamino derivatives of naphtho[2,3-*d*]-1,3-thiazole-4,9-dione (NTD) are known. These compounds differ little from one another in the absorption spectrum (λ_{max} 510 and 508 nm), but have a deeper color than 5-aminonaphtho[2,3-*d*]imidazole-4,9-dione (λ_{max} 487 nm). This has been explained by the fact that conjugation between the lone electron pair of the S atom in the fused thiazole ring and the π-electrons of the quinone is more pronounced than in the case of the N atom of the imidazole ring.[6]

In the present work we report the synthesis of 5- and 8-amino-2-phenylnaphtho[2,3-*d*]-1,3-thiazole-4,9-diones (**1a,b**) and an attempt to prepare 5,8-diamino derivatives of 2-phenyl-NTD based on them. We considered that the synthetic pathway to 2-phenyl-NTD, which has an amino group in the benzene ring, similar to that reported for NTD[6] and involving nitration of 2-phenyl-NTD followed by reduction, was unsuitable owing to the presence of an additional phenyl ring, which would result in the formation of an even more complex mixture of products on nitration than that obtained previously,[6] when a mixture of three isomers with similar R_f values was formed, and the yields of 5- and 8-nitro derivatives were as low as 3 and 19 %, respectively. We prepared 5- and 8-amino-2-phenyl-NTD **1a,b** from 3,5-diamino-2-chloro- and 2,5-diamino-3-chloro-1,4-naphthoquinones (**2a,b**) by the known reaction with sodium sulfide and subsequent condensation *in situ* of the corresponding thiol derivatives (**3a,b**) with benzaldehyde in acetic acid (*cf.* Ref. 7) (Scheme 1).

In turn, 3,5- and 2,5-diaminonaphthoquinones **2a,b** were prepared by amination of 5-amino-2,3-dichloro-1,4-naphthoquinone by aqueous ammonia in DMSO; isomers **2a** and **2b** were formed in a ratio of ~10 : 1, which is in agreement with the known data on the orientation of nucleophilic reagents in reactions with 1,4-naphthoquinones having an electron-donating substituent in position 5.[8,9] The structure of isomer **2b** is indicated by the fact that it is identical with the specimen prepared by reduction of 2-amino-3-chloro-5-nitro-1,4-naphthoquinone[10] with $SnCl_2$ in AcOH.

It should be noted that condensation of diamines **3a,b** with benzaldehyde yields, along with 5- and 8-amino-2-phenyl-NTD **1a,b**, deeply colored products of their subsequent transformations. For example, in the case of the 2,5-diamino derivative, 8-benzylamino-2-phenyl-NTD (**4**) was isolated in 7 % yield, which may be explained by the condensation of the primary aromatic amine **1b** with benzaldehyde and subsequent reduction of the resulting Schiff's base with aldehyde and/or sodium sulfide, which are present in excess in the reaction mixture.

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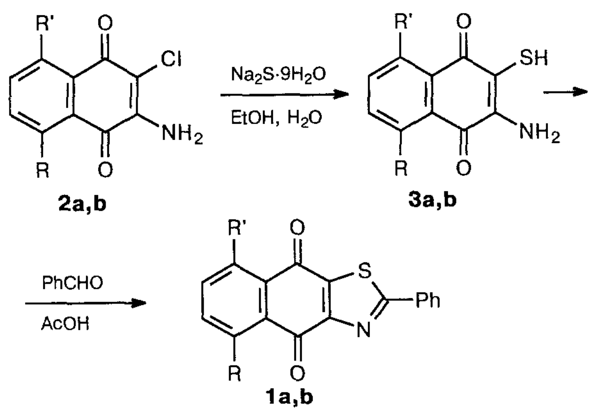
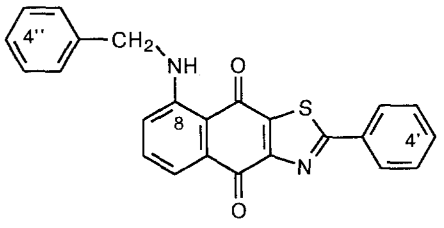
Scheme 1

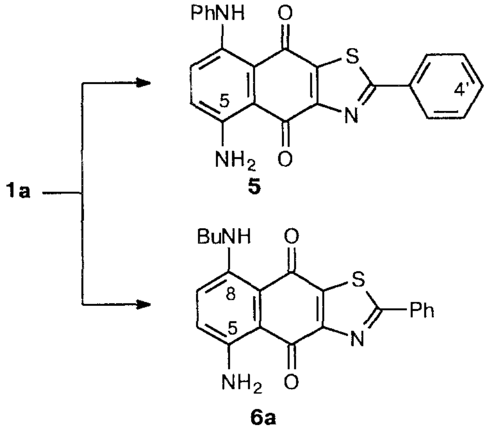


a: R = NH_2, R' = H
b: R = H, R' = NH_2



4

Scheme 2



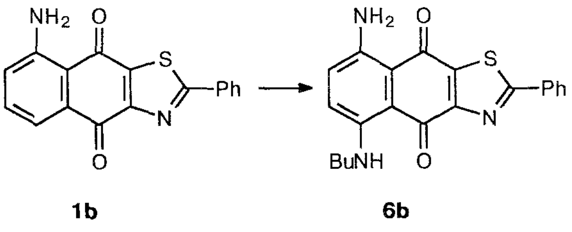
In order to synthesize 5,8-diamino derivatives of naphthothiazoledione we studied the possibility of nucleophilic replacement of the hydrogen atom in 5- and 8-amino-2-phenyl-NTD **1a,b**, which is attractive from the practical point of view. No examples of the direct introduction of an alkyl- or arylamino group into the benzene ring of 1,4-naphthoquinones annelated with a heterocycle have been reported. The arylamination of an activated compound, 5-amino-2,3-dicyano-1,4-naphthoquinone, described in the literature, is made possible by quinone-quinonimine tautomerism (the second tautomer is 2,3-dicyano-4-hydroxy-5-imino-1,5-naphthoquinone).[11] Photochemical[12] and $CoCl_2$-promoted (see Ref. 13) alkylamination of 5-amino-2-butylamino-3-cyano-1,4-naphthoquinone in position 8 is also known.

We found that 5-amino-2-phenyl-NTD **1a** does not react with aniline when boiled in ethanol or in a mixture of EtOH and AcOH (under the previously described conditions[11]), and reacts only in the presence of $Cu(OAc)_2$ or $CoCl_2$ to give 5-amino-8-anilino-2-phenyl-NTD (**5**, 28 %). The reaction of compound **1a** with the more basic butylamine (in the amine itself or in Bu^nOH) occurs at room temperature without metal ions and affords the 8-butylamino derivative (**6a**, 13 %). In benzene, the reaction occurs only under irradiation, and the yield of product **6a** is 17 % (Scheme 2).

The fact that the second amino group is introduced into the *para*-position with respect to the amino group present in 5-amino-2-phenyl-NTD **1a** is confirmed by spectroscopic data. For example, the ^1H NMR spectrum of 8-anilino derivative **5** in DMSO-d_6 exhibits a sharp singlet at 12.42 ppm, in addition to the signals for the aromatic protons and a broadened singlet for one of the H atoms of the NH_2 group at 8.25 ppm, and the spectrum of 8-butylamino derivative **6a** contains a broadened singlet at 10.87 ppm. These signals correspond to the NH group bound to the carbonyl group located in the *peri*-position by an intramolecular hydrogen bond. Structure **6a** is also confirmed by the fact that the H-6 and H-7 protons of the benzene ring of the NTD are manifested as doublets at 7.01 and 7.14 ppm with J_{ortho} = 9.5 Hz.

8-Amino-2-phenyl-NTD **1b** is less reactive than **1a**: it does not react with aniline, and the reaction with butylamine occurs only in the presence of $CoCl_2$ to yield only traces of the corresponding 5-butylamino derivative (**6b**) (Scheme 3).

Scheme 3



The electronic absorption spectrum of the latter, like the spectra of compounds **5** and **6a**, exhibits two maxima in the long-wavelength region, at 602 and 650 nm, which is typical of 5,8-diamino substituted 1,4-naphthoquinones.[12,13] In the photochemical amination of compound **1b** with butylamine (an inert atmosphere, radiation wavelength ≥400 nm), we also obtained no more than 3 % diamine **6b**. This difference in the reactivities of 5- and 8-amino isomers **1a** and **1b** is difficult to explain without the calculation data. It is possible that the activation of the benzene ring in **1a** is somewhat greater than in **1b** owing to the formation of a stronger intramolecular hydrogen bond, which is indicated by the spectroscopic data. For example, the signal for NH in the ^{1}H NMR spectrum of **1a** is shifted downfield with respect to the corresponding signal for compound **1b** by 0.08 ppm.

In contrast to 2-phenylnaphtho-1,3-thiazole-4,9-dione, which has no amino group in the naphthoquinone benzene ring, 5- and 8-amino-2-phenyl-NTD **1a,b** undergo thermal and photochemical amination in positions 8 and 5, respectively. The direct alkylamination observed for 5-amino-2-phenyl-NTD **1a** is probably made possible by the formation of the quinonimine structure, as has been described for 5-amino-2,3-dicyano-1,4-naphthoquinone.[11] Arylamination of compound **1a** and butylamination of 8-amino-2-phenyl-NTD **1b**, which occurs only in the presence of $CoCl_2$, attests to the relatively low reactivity of these compounds and probably occurs according to the mechanism suggested for amination of 1-aminoanthraquinone.[14] First, a six-membered complex is formed in which a metal atom is bonded with the carbonyl oxygen atom and with the nitrogen atom of the *peri*-located amino group. The subsequent nucleophilic attack on position 5 or 8 (the *para*-position with respect to the amino group already present in the ring) by the amine and oxidative abstraction of a hydride anion give the direct amination product.

Experimental

The electronic absorption spectra (UV/VIS) were recorded on Specord UV-VIS and Beckman DU-8 spectrophotometers; IR spectra were obtained on a Specord M-80 instrument in $CHCl_3$ and in KBr pellets. ^{1}H NMR spectra were run on Bruker WP-200 SY and Bruker AC-200 spectrometers. The molecular weights and elemental compositions of compounds were determined from the precise mass numbers of molecular ions obtained on Finnigan MAT 8200 and AEI MS-902 mass spectrometers (EI, 70 eV). The course of the reactions was monitored by TLC using Silufol UV 254 plates and a C_6H_6—Me_2CO (9 : 1) mixture as the eluent. Preparative chromatography was carried out on columns with KSK silica gel (0.140—0.315 μm) and Al_2O_3 (activity II) and on plates with an unfixed sorbent layer (SiO_2, PKN-200, 100—200 μm) in C_6H_6 and $CHCl_3$.

2,5-Diamino-3-chloro-1,4-naphthoquinone (2b) was prepared by the reduction of 2-amino-3-chloro-5-nitro-1,4-naphthoquinone[10] with $SnCl_2 \cdot 2H_2O$ according to the known procedure.[15] Yield 83 %, m.p. 197 °C (from benzene). R_f 0.35. Found (%): Cl, 15,44. *m/z*: 222.0168 $[M]^+$. $C_{10}H_7ClN_2O_2$. Calculated (%): Cl, 15.76. Mol. weight 222.0196. IR, ν/cm^{-1}: 3455, 3430, 3370, 3325 (NH_2); 1620 (C=O). UV/VIS (EtOH), λ_{max}/nm (ε): 270 (16000), 300 sh (11300), 461 (3830), 518 (4500). ^{1}H NMR (DMSO-d$_6$), δ: 7.01 (br.s, 2 H, NH_2); 7.09 (dd, J_o = 9 Hz, J_m = 1.5 Hz, 1 H, H-6); 7.22 (dd, J_o = 7 Hz, 1 H, H-8); 7.33 (t, 1 H, H-7); 7.58 (br.s, 2 H, 5-NH_2).

3,5-Diamino-2-chloro-1,4-naphthoquinone (2a). 40 mL of 25 % ammonia was added at 50 °C to a solution of 2.42 g of 5-amino-2,3-dichloro-1,4-naphthoquinone in 80 mL of DMSO. The mixture was stirred for 1 h and poured into 100 mL of water. The precipitate was filtered off, dried, and chromatographed on a column with SiO_2. Elution with C_6H_6 gave 0.11 g (5 %) of **2b** and elution with a 1 : 1 C_6H_6—$CHCl_3$ mixture gave 1.06 g (48 %) of **2a**, m.p. 291—292 °C (from EtOH). R_f 0.21. Found (%): C, 54.39; H, 2.93; Cl, 15.15; N, 12.17. *m/z*: 222 $[M]^+$. $C_{10}H_7ClN_2O_2$. Calculated (%): C, 54.05; H, 3.18; Cl, 15.76; N, 12.62. IR, ν/cm^{-1}: 3465, 3430, 3350, 3320 (NH_2); 1665 (C=O). UV/VIS (EtOH), λ_{max}/nm (ε): 250 (17500), 266 sh (12700), 295 sh (7990), 460 (5300), 492 (5070). ^{1}H NMR (DMSO-d$_6$), δ: 7.04 (d, *J* = 9 Hz, 1 H, H-6); 7.20 (d, *J* = 7 Hz, 1 H, H-8); 7.37—7.45 (m, 3 H, H-7 and NH_2); 7.89 (br.s, 2 H, NH_2).

3,5-Diamino-2-mercapto-1,4-naphthoquinone (3a) was prepared by a procedure similar to that described previously.[2] Yield 77 %, m.p. 243—245 °C (precipitated from DMF by water). Found (%): S, 14.80. *m/z*: 220 $[M]^+$. $C_{10}H_8N_2O_2S$. Calculated (%): S, 14.53. ^{1}H NMR (DMSO-d$_6$), δ: 7.00—7.51 (m, 5 H arom. and NH_2); 7.95 (br.s, 2 H, 5-NH_2); 8.46 (br.s, 1 H, SH).

5-Amino-2-phenylnaphtho[2,3-*d*]-1,3-thiazole-4,9-dione (1a). 4.8 g (0.02 mol) of $Na_2S \cdot 9H_2O$ was added with stirring to a suspension of 2.2 g (0.01 mol) of 3,5-diaminoquinone **2a** in 15 mL of water and 8 mL of EtOH heated to 70 °C. The mixture was stirred for 30 min, and 2 mL (0.02 mol) of PhCHO, 4 mL of AcOH, and 4 mL of H_2O were added. The mixture was stirred for an additional 30 min and cooled to room temperature. 12 mL of EtOH was added, and the mixture was cooled to 5—10 °C and held at this temperature for 1 h. The black resin was filtered off and washed with water until the washings became colorless. The dry residue was dissolved in C_6H_6 and chromatographed on a column with Al_2O_3. The main dark-red fraction* was eluted with $CHCl_3$ and concentrated under reduced pressure to give 0.86 g (28 %) of **1a**, m.p. 294—295 °C (from benzene). R_f 0.51. Found (%): C, 66.65; H, 3.41; N, 8.84; S, 10.30. *m/ z*: 306.0450 $[M]^+$. $C_{17}H_{10}N_2O_2S$. Calculated (%): C, 66.65; H, 3.29; N, 9.15; S, 10.47. Mol. weight 306.0463. IR, ν/cm^{-1}: 3425, 3320 (NH_2); 1652, 1610 (C=O). UV/VIS ($CHCl_3$), λ_{max}/nm (ε): 276 (22500), 384 (6450), 502 (6600); UV/VIS (DMF), λ_{max}/nm (ε): 277 (6960), 384 (1480), 516 (1560). ^{1}H NMR (DMSO-d$_6$), δ: 7.22 (d, *J* = 9 Hz, 1 H, H-6); 7.33 (d, *J* = 7 Hz, 1 H, H-8); 7.45 (t, 1 H, H-7); 7.58 (m, 3 H, H-3'—H-5'); 8.09 (m, 3 H, H-2', H-6', 1 H from NH_2**).

8-Amino-2-phenylnaphtho[2,3-*d*]-1,3-thiazole-4,9-dione (1b) and 8-benzylamino-2-phenylnaphtho[2,3-*d*]-1,3-thiazole-4,9-dione (4) were prepared from 2,5-diamino-3-chloronaphthoquinone **2b** according to the above-described procedure. Elution with C_6H_6 afforded 8-benzylamino-2-phenyl-NTD **4**, yield 7 %, m.p. 255—256 °C (from benzene). R_f 0.83. Found, *m/z*: 396.0912 $[M]^+$. $C_{24}H_{16}N_2O_2S$. Calculated, mol. weight: 396.0933. IR, ν/cm^{-1}: 3420 (NH); 1660, 1615 (C=O). UV/VIS ($CHCl_3$), λ_{max}/nm (ε): 370 (1200), 546 (9640). ^{1}H NMR ($CDCl_3$), δ: 4.59 (d, ^3J = 5.5 Hz, 2 H, CH_2); 7.03 (dd, J_o = 9, J_m = 1.5 Hz, 1 H, H-7); 7.35—7.51 (m, 9 H, H-3'—H-5', H-2"—H-6", H-6); 7.65 (dd, J_o = 7, J_m = 1.5 Hz, 1 H, H-5); 8.11 (m, 2 H, H-2', H-6'); 9.89 (br.s, 1 H, NH). The second fraction was eluted with $CHCl_3$, and 8-amino-2-phenyl-NTD **1b** (36 %) was isolated, m.p. 343—

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* The first fraction contained trace amounts of a violet compound with R_f 0.85, similar to **4**.

** One of the H atoms of the NH_2 group exchanges with deuterium from the solvent.

345 °C (from chloroform). R_f 0.60. Found, *m/z*: 306.0468 $[M]^+$. $C_{17}H_{10}N_2O_2S$. Calculated, mol. weight: 306.0463. IR, ν/cm^{-1}: 3440, 3325 (NH_2); 1665, 1605—1620 br (C=O). UV/VIS ($CHCl_3$), λ_{max}/nm (ε): 278 (4620), 385 (1020), 501 (4220); UV/VIS (DMF), λ_{max}/nm (ε): 282 (14600), 516 (4260). ^1H NMR (DMSO-d_6), δ: 7.22 (dd, J_o = 9 Hz, J_m = 1.5 Hz, 1 H, H-7); 7.43 (dd, J_o = 7 Hz, 1 H, H-5); 7.54 (t, 1 H, H-6); 7.61 (m, 3 H, H-3'—H-5'); 8.01 (br.s, 1 H from NH_2*); 8.13 (m, 2 H, H-2', H-6').

5-Amino-8-anilino-2-phenylnaphtho[2,3-*d*]-1,3-thiazole-4,9-dione (5). A suspension of 0.092 g (0.3 mmol) of **1a**, 5 mL of aniline, and 0.040 g (0.3 mmol) of $CoCl_2$ in 10 mL of AcOH was boiled for 24 h. The reaction mixture was repeatedly treated with 1 % HCl and hot water, and the hardened residue was filtered off, dried, dissolved in $CHCl_3$, and chromatographed on plates with Al_2O_3 using $CHCl_3$ as the eluent. 0.022 g (24 %) of the starting **1a** was recovered and 0.034 g (28 %) of compound **5** was obtained, m.p. 285—287 °C (from a C_6H_6—EtOH mixture (1 : 1)). R_f 0.20. Found, *m/z*: 397.0871 $[M]^+$. $C_{24}H_{17}N_3O_2S$. Calculated, mol. weight 397.0890. IR ($CHCl_3$), ν/cm^{-1}: 3485, 3280, 3265 (NH, NH_2); 1645 (C=O). UV/VIS ($CHCl_3$), λ_{max}/nm (ε): 300 (36000), 382—407 sh (4200), 616 (14800), 661 (16000). ^1H NMR (DMSO-d_6), δ: 7.22—7.61 (m, 10 H arom.); 8.12 (m, 3 H, H-2', H-6', and 1 H from NH_2); 8.25 (br.s, 1 H, NH_2); 12.42 (s, 1 H, NH).

5-Amino-8-butylamino-2-phenylnaphtho[2,3-*d*]-1,3-thiazole-4,9-dione (6a). A solution of 0.030 g (0.1 mmol) of **1a** and 3 mL of $BuNH_2$ in 3 mL of Bu^nOH was kept for 3 days at room temperature, the solvent was removed as an azeotrope with water under reduced pressure, and the residue was treated with 1 % HCl. The precipitate was filtered off, washed with water, dried, and chromatographed on plates with SiO_2 using $CHCl_3$ as the eluent to give 0.010 g of **1a** and 0.005 g (13 %) of **6a**, m.p. 115—117 °C. R_f 0.15. Found, *m/z*: 377.1200 $[M]^+$. $C_{21}H_{19}N_3O_2S$. Calculated, mol. weight 377.1198. IR, ν/cm^{-1}: 3470, 3420, 3400 (NH, NH_2); 2925, 2860 (CH_2); 1645, 1635 (C=O). UV/VIS ($CHCl_3$), λ_{max}/nm (ε): 380 (2000), 601 (6460), 650 (7460). ^1H NMR ($CDCl_3$), δ: 0.98 (t, 3 H, CH_3); 1.28 (m, 2 H, CH_2); 1.69 (m, 2 H, CH_2); 3.43 (q, 2 H, CH_2—N); 7.01 (d, J = 9.5 Hz, 1 H, H-7(6)); 7.14 (d, J = 9.5 Hz, 1 H, H-6(7)); 7.48 (m, 5 H, Ph); 8.15 (m, 2 H, NH_2); 10.87 (br.s, 1 H, NH).

Photochemical reaction of 5- and 8-amino-2-phenyl-NTD (1a,b) with butylamine. A flow of argon was passed for 45 min through a solution of 10 mg (0.03 mmol) of **1a,b** and 1 mL of Bu^nNH_2 in 30 mL of dry C_6H_6 in a Pyrex tube, then the tube was evacuated and sealed. Photolysis was carried out at 21 °C for 60 h by the light of a DRSh-500 lamp passed through a water light filter and a ZhS-11 light filter. The solvent was removed under reduced pressure and the residue was treated with 1 % HCl, washed with water, filtered, dried, and chromatographed on plates with SiO_2 ($CHCl_3$). In the experiment with **1a**, 4 mg (40 %) of the starting compound was recovered and 2 mg (17 %) of **6a** was obtained. In the case of **1b**, the yield of **6b** was 2—3 %, the rest was a mixture of a great number of compounds that were difficult to separate.

8-Amino-5-butylamino-2-phenyl-NTD (6b), m.p. ~190 °C (dec.), R_f 0.31. Found, *m/z*: 377.1200 $[M]^+$. $C_{21}H_{19}N_3O_2S$. Calculated, mol. weight 377.1198. UV/VIS ($CHCl_3$), λ_{max}/nm (ε): 383 (2500), 602 (6760), 650 (7700). ^1H NMR ($CDCl_3$) δ: 0.97 (t, 3 H, CH_3); 1.29 (m, 2 H, CH_2); 1.65 (m, 2 H, CH_2); 3.44 (q, 2 H, CH_2—N); 6.97 (d, J = 9.5 Hz, 1 H, H-6(7)); 7.16 (d, J = 9.5 Hz, 1 H, H-7(6)); 7.47 (m, 5 H, Ph); 8.17 (m, 2 H, NH_2); 11.23 (br.s, 1 H, NH).

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* One of the H atoms of the NH_2 group exchanges with deuterium from the solvent.