POLYANNULATED TROPYLIUM COMPOUNDS HAVING BENZOTHIAZINE AND RELATED HETEROCYCLIC RINGS. FORMATION OF o- AND p-BENZOQUINONOID PRODUCTS BY REARRANGEMENT[1]

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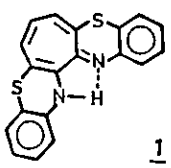
Abstract - Tropylium compounds having tri-annulated heterocycles (11 and 15) are obtained by the reaction of 2,4-dibromo-7-methoxy- and 3,5,7-tribromo-2-methoxytropone with o-aminophenol and o-aminobenzenethiol, via di-annulated compounds. Rearrangements to di- and tri-annulated o- and p-benzoquinonoid compounds (13, 16 and 20) take place during the attempted synthesis of some tri-annulated tropylium systems. Possible pathways for these reactions are discussed.

One of the authors (T.N.) and his coworkers obtained 14H-cyclohepta[1,2-b:4,3-b']-benzothiazine (1)[2] by the reaction of 3,7-dibromotropolone with o-aminobenzenethiol (3a). Later, present authors obtained[3] O-analogue 2 of 1 as one of the products of the reaction of 3-bromo-2-methoxytropone (4a) with o-aminophenol (3b). Compound 2 has later been obtained in a better yield by the condensation of 6-bromocyclohepta[b][1,4]benzoxazine (5a) with 3b in refluxing acetic acid followed



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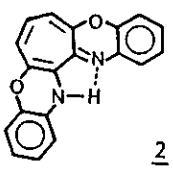

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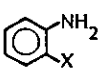
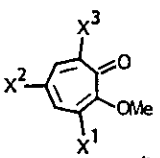
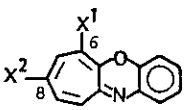


3a: X=SH
3b: X=OH
3c: X=NHMe

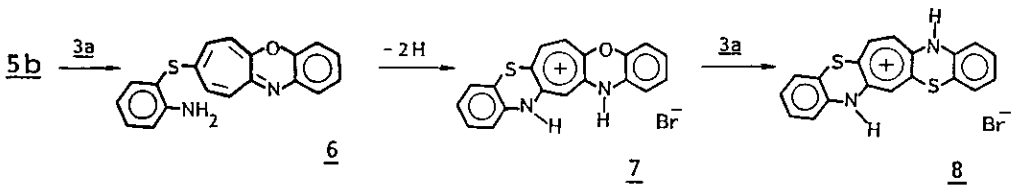


4a: X^1=Br, X^2=X^3=H
4b: X^1=X^2=X^3=Br
4c: X^1=X^3=H, X^2=Br



5a: X^1=Br, X^2=H
5b: X^1=H, X^2=Br
5c: X^1=X^2=Br

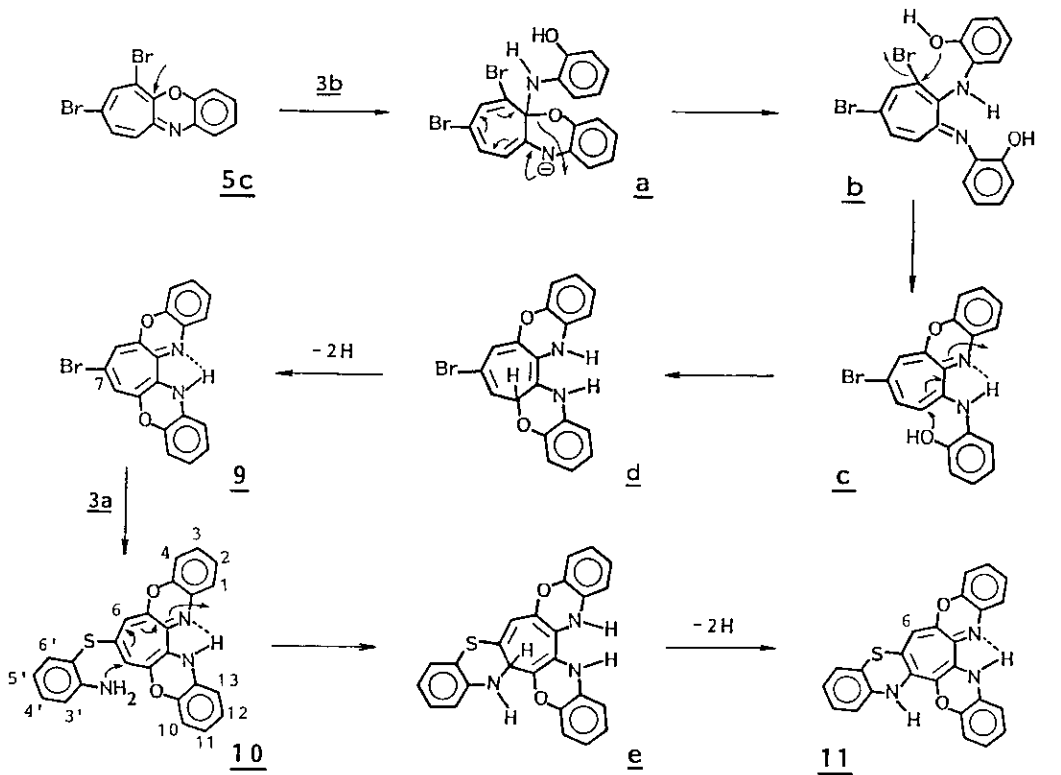
by autoxidation[4]. Very recently we have reported synthesis of the tropylium ion 7 from 8-bromo compound 5b and 3a in methanol at room temperature via S-substituted compound 6, and 7 has been led to the cation 8 having di-annulated benzothiazine rings by the intermolecular heterocycle-exchange reaction between 7 and 3a[5]. (Scheme 1)



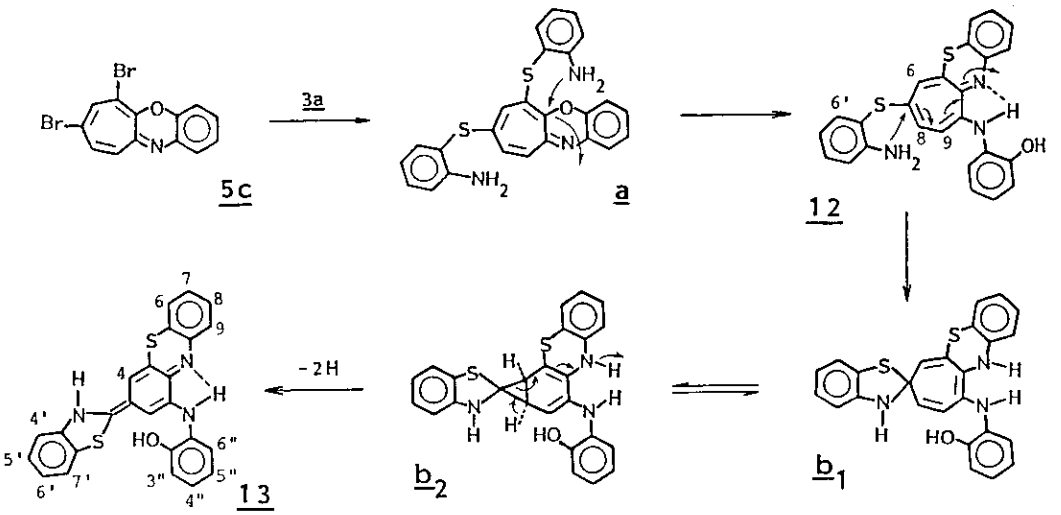
Scheme 1.

In this communication we wish to describe the synthesis of some tropylium compounds having tri-annulated heterocycles and interesting aspects of intramolecular transposition of heterocyclic ring on the seven-membered nucleus as well as some rearrangement reactions to o- and p-benzoquinonoid compounds during the attempted synthesis of these poly-annulated tropylium compounds.

7-Bromo-14H-cyclohepta[1,2-b:4,3-b']bis[1,4]benzoxazine (9) was prepared from 6,8-dibromo compound 5c and 3b by an intramolecular hetero-ring transposition via a - c, followed by dehydrogenation as shown in Scheme 2[6]. When 9 and 3a were allowed

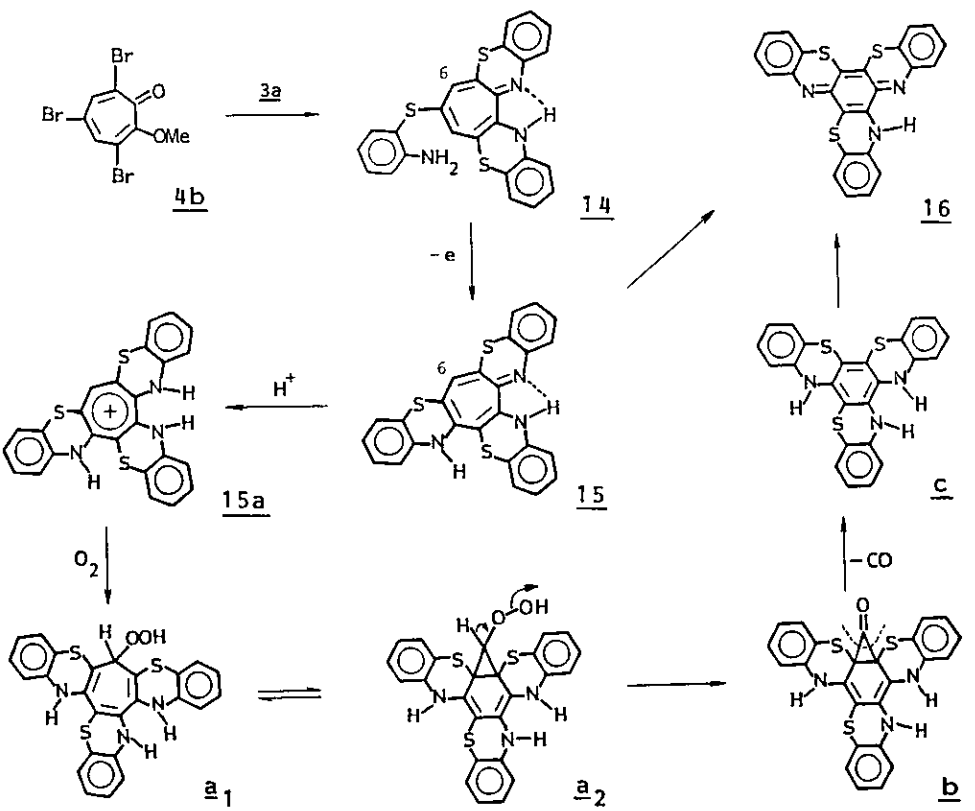


Scheme 2.



Scheme 3.

to stand at room temperature S-substituted compound 10[7] was obtained (85% yield). 10 was dehydrocyclized in acetic acid by anodic oxidation, giving 11[8].

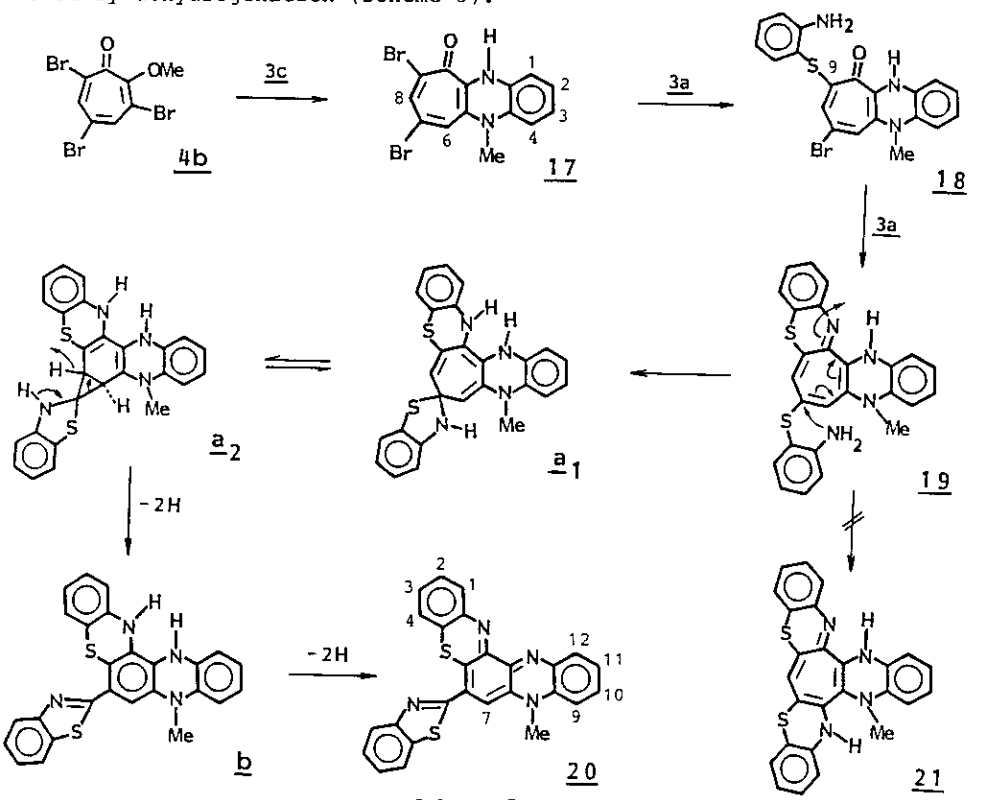


Scheme 4.

Reaction of 5c with an excess of 3a in methanol-chloroform at room temperature for 1 day gave, via intermediate a followed by the ring conversion, di-S-substituted compound 12[9], which afforded p-benzoquinonoid derivative 13[10] on attempted ring-closure by anodic oxidation. This rearrangement is considered to proceed via spiro intermediate b_1 and its norcaradiene form b_2, followed by the oxidative H-abstraction as shown in Scheme 3.

We next synthesized tropylium compound 15 having tri-annulated benzothiazine ring. Namely, treatment of 3,5,7-tribromo-2-methoxytropone (4b) with an excess of 3a at room temperature gave compounds 14[11] which by anodic oxidation gave the ring-closed compound 15[12]. The deep green-colored cation 15a was easily converted in air or with DDQ in acetic acid into the one-carbon-less p-benzoquinone-diimide derivative 16[13], presumably via hydroperoxide a_1 and its norcaradiene form a_2 and decarbonylation as shown in Scheme 4.

Treatment of 4b with N-methyl-o-phenylenediamine (3c) gave dibromo compound 17[14] (68%), which in turn condensed with 3a in chloroform to give the mono-S-substituted compound 18[15] (86%). When a mixture of 18 and 3a was heated at 100 °C in a sealed tube (or further kept standing at room temperature for a day), a rearranged product having o-benzoquinone-diimide structure 20[16] was obtained, instead of the expected tri-annulated tropylium compound 21. Compound 20 is presumed to be produced from 19 via spiro intermediate a_1 and its norcaradiene form a_2 and then b, followed by dehydrogenation (Scheme 5).



Scheme 5.

It should especially be noted that interesting p- and o-benzoquinonoid compounds 13, 16, and 20, which are otherwise very difficult to prepare, are produced very easily by the present reaction schemes.

We are grateful to Professor Hiroshi Yamamoto (Okayama Univ.) for his helpful discussion.

REFERENCES AND NOTES

1. T. Nozoe, K. Shindo, H. Okai, H. Wakabayashi, and S. Ishikawa, partly presented at (a) 5th International Symposium on the Chemistry of Novel Aromatic Compounds, St. Andrews, U. K., 1985; (b) 18th National Symposium on the Chemistry of Nonbebzenoid Aromatic Compounds, Toyama, 1985, Abstr. A2-03.
2. T. Nozoe, T. Asao, and K. Takahashi, Bull. Chem. Soc. Jpn., 1966, **36**, 1980.
3. T. Someya, H. Okai, H. Wakabayashi, and T. Nozoe, Bull. Chem. Soc. Jpn., 1983, **56**, 2756.
4. T. Nozoe, H. Okai, H. Wakabayashi, and S. Ishikawa, Bull. Chem. Soc. Jpn., accepted.
5. T. Nozoe, K. Shindo, and S. Ishikawa, Chem. Lett., **1988**, 1593.
6. 9: T. Nozoe, H. Wakabayashi, and S. Ishikawa, Heterocycles, accepted.
7. 10: Reddish violet needles, mp 263-264 °C; Uv (MeOH) 277, 300(sh), 360, 518, 600(sh), and 690(sh) nm, (MeOH + HCl) 279, 332, 405, and 550 nm; ^{1}H nmr (270 MHz in $CDCl_3$) δ=4.31 (2H, br, NH_2), 5.56 (2H, s, H-6,8), 6.44 (2H, dd, J=8.0 and 2.0 Hz, H-4,10), 6.63 (2H, dd, J=8.0 and 2.0 Hz, H-1,13), 6.66 (2H, td, J=8.0 and 2.0 Hz, H-3,11), 6.72 (2H, td, dd, J=8.0 and 2.0 Hz, H-2,12), 6.77 (1H, td, J=8.0 and 2.0 Hz, H-4'), 6.80 (1H, dd, J=8.0 and 2.0 Hz, H-6'), 7.15 (1H, br, NH), 7.26 (1H, m, H-5'), and 7.37 (1H, dd, J=8.0 and 2.0 Hz, H-3'); ms m/z 423 (M^+).
8. 11: Dark violet needles, mp >300 °C; Uv (MeOH) 264, 315(sh), 480, and 610(sh) nm, (MeOH + HCl) 280(sh), 350, 555, 595(sh), and 700 nm; ^{1}H nmr (270 MHz in $CDCl_3$) δ=6.54 (1H, s, H-6), 6.84-7.66 (12H, m, other H); ^{13}C nmr (67.2 MHz in $CDCl_3$) δ =112.6, 114.6, 114.8, 117.3, 122.7, 124.2, 124.4, 124.6, 127.2, 128.3, 129.3, 129.8, 129.9, 130.5, 130.9, 131.8, 133.6, 133.7, 136.8, 140.3, 146.4, 146.6, 147.4, 147.6, and 148.4; ms m/z 437 (M^+).
9. 12: Red oil; Uv (MeOH) 286 and 480 nm, (MeOH + HCl) 280, 358, and 510 nm; ^{1}H nmr (270 MHz in C_6D_6) δ =3.64 (2H, br, NH_2), 6.04 (1H, dd, J=11.7 and 1.8 Hz, H-8), 6.22 (1H, d, J=11.7 Hz, H-9), 6.58 (1H, d, J=1.8 Hz, H-6), 6.50-6.70 (7H, m, other H), 7.04-7.44 (4H, m, other H), and 7.52 (1H, dd, J=7.7 and 1.5 Hz, H-6'); ms m/z 441 (M^+).
10. 13: Yellow crystal, mp >300 °C; Uv (MeOH) 262, 302, and 400 nm; ^{1}H nmr (270 MHz in DMSO-d_6) δ =6.76-7.06 (8H, m, H-6,7,8,9,4',5',6',7'), 7.20 (1H, d, J=1.5 Hz, H-4), 7.30 (1H, d, J=1.5 Hz, H-2), 7.37 (1H, td, J=8 and 1.5 Hz, H-4" or 5"), 7.47 (1H, td, J=8 and 1.5 Hz, H-5" or 4"), 7.92 (1H, dd, J=8 and 1.5 Hz, H-3" or 6"), 8.04 (1H, dd, J=8 and 1.5 Hz, H-6" or 3"), 8.24 (1H, s, NH), 8.33 (1H, s, NH), and 9.65 (1H, s, OH); ms m/z 439 (M^+).

11. 14: Reddish violet needles (from benzene), mp 171 °C; Uv (MeOH) 248, 296, and 508 nm (log ε 4.45, 4.42, and 3.94); ^{1}H nmr (270 MHz in $CDCl_3$) δ =4.26 (2H, br, NH_2), 5.99 (2H, s, H-6,8), 6.76 (1H, td, J=8 and 2 Hz, H-5'), 6.75-6.86 (5H, m, H-1,4,10,13,3'), 6.89 (2H, td, J=8 and 2 Hz, H-3,11 or 2,12), 7.00 (2H, td, J=8 and 2 Hz, H-2,12 or 3,11), 7.23 (1H, td, J=8 and 2 Hz, H-4'), 7.34 (1H, dd, J=8 and 2 Hz, H-6'), 8.88 (1H, br, NH); ^{13}C nmr (67.8 MHz, in $CDCl_3$) δ =76.5, 77.0, 77.5, 113.8, 115.5, 118.9, 121.2, 122.5, 125.4, 125.5, 127.6, 127.7, 128.3, 131.6, 136.3, 136.9, 140.9, 143.2, and 148.6; ms m/z 455 (20), 348 (19), 320 (37), 287 (27), 255 (12), and 125 (100). Found: m/z 455.0591. Calcd for $C_{25}H_{17}N_3S_3$: M, 455.0597.
12. 15: Red needles, mp 215 °C; Uv (MeOH) 270, 312, 355, and 480 nm, (MeOH + HCl) 265, 310, 395, and 572 nm; ^{1}H nmr (270 MHz in $CDCl_3$) δ =7.04 (1H, s, H-6) and 7.20-7.68 (12H, m, other H); ^{13}C nmr (67.8 MHz in $CDCl_3$) δ =96.2, 117.2 124.2, 124.3, 124.7, 124.9, 125.7, 126.2, 127.1, 127.2, 127.5, 128.3, 128.5, 128.6, 129.4, 130.1, 130.2, 131.0, 131.1, 140.2, 141.7, 141.9, 150.3, 150.6, and 153.1. Found: m/z 453.0422. Calcd for $C_{25}H_{15}N_3S_3$: M, 453.0431.
13. 16: Blue violet needles ($CHCl_3$), mp >300 °C; Uv (MeOH) 250, 322, 530(sh), and 570 nm, (MeOH + HCl) 258, 324, 424, 572(sh), 643, and 700(sh) nm; ^{1}H nmr (270 MHz in $CDCl_3$) δ =6.49 (1H, d, J=7.7 Hz), 6.74 (1H, t, J=7.3 Hz), 6.87 (1H, d, J=7.3 Hz), 6.88 (1H, t, J=7.7 Hz), 7.1-7.4 (6H, m), 7.55 (1H, d, J=8 Hz), 7.59 (1H, s, NH), and 7.70 (1H, d, J=8 Hz). Found: m/z 439.0257. Calcd. for $C_{24}H_{13}N_3S_3$: M, 439.0274.
14. 17: Violet crystal (MeOH), mp >300 °C; Uv (MeOH) 254, 290, 484, and 583 nm; ^{1}H nmr (270 MHz in $CDCl_3$) δ =2.94 (3H, s, N-CH_3), 6.24 (1H, dd, J=8.0 and 1.5 Hz, H-4), 6.37 (1H, dd, J=8.0 and 1.5 Hz, H-1), 6.49 (1H, d, J=1.8 Hz, H-6), 6.62 (1H, td, J=8.0 and 1.5 Hz, H-2), 6.74 (1H, td, J=8.0 and 1.5 Hz, H-3), 7.35 (1H, br, NH), and 7.69 (1H, d, J=1.8 Hz, H-8); ms m/z 382 (M^+).
15. 18: Reddish violet solid; Uv (MeOH) 238, 288, 362, 489, and 544(sh) nm; ^{1}H nmr (270 MHz in $CDCl_3$) δ =2.95 (3H, s, Me), 4.28 (2H, br, NH_2), 6.24 (1H, dd, J=7.5 and 1.3 Hz, H-4), 6.33 (1H, d, J=1.5 Hz, H-8), 6.34 (1H, dd, J=5.6 and 1.3 Hz, H-1), 6.42 (1H, d, J=1.5 Hz, H-6), 6.62 (1H, td, J=6.9 and 1.3 Hz, H-2), 6.69 (1H, td, J=6.9 and 1.3 Hz, H-3) 6.80 (1H, td, J=6.9 and 1.3 Hz, H-5'), 6.83 (1H, dd, J=6.9 and 1.3 Hz, H-3'), 7.29 (1H, td, J=6.9 and 1.3 Hz, H-4'), 7.38 (1H, dd, J=6.9 and 1.3 Hz, H-6'), and 8.14 (1H, br, NH). Found: m/z 425.0216. Calcd for $C_{20}H_{16}ON_3SBr$: M, 425.0199.
16. 20: Blue violet crystal ($CHCl_3$-MeOH), mp 195-200 °C; Uv (MeOH) 273, 323(sh), 357, 447, and 544 nm; ^{1}H nmr (270 MHz in $CDCl_3$) δ =3.43 (3H, s, CH_3), 6.11 (1H, s, H-7), 7.04 (1H, dd, J=8 and 1.5 Hz, H-9), 7.09 (1H, td, J=8 and 1.5 Hz), 7.11 (1H, dd, J=7 and 1.5 Hz), 7.18-7.30 (4H, m), 7.33-7.42 (3H, m), 7.70 (1H, dd, J=8 and 1.5 Hz), and 7.73 (1H, dd, J=8 and 1.5 Hz); ms m/z 448 (100), 434 (60), 433 (60), 402 (30), 401 (28), and 124 (20). Found: m/z 448.0817. Calcd for $C_{26}H_{16}N_4S_2$: M, 448.0817.

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