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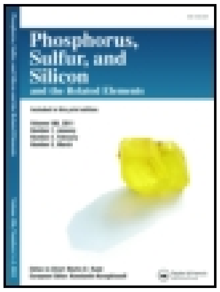

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2-(2-ARYL-2-OXOETHYL)-4H-BENZO-1,4-THIAZIN-3-ONES AS PRODUCTS OF THE REACTION OF 2-AMINOTHIOPHENOL WITH β-AROYLACRYLIC ACIDS

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2-(2-ARYL-2-OXOETHYL)-4H-BENZO-1,4-THIAZIN-3-ONES AS PRODUCTS OF THE REACTION OF 2-AMINOTHIOPHENOL WITH β-AROYLACRYLIC ACIDS

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Interaction of 2-aminothiophenol with β-aroylacrylic acids and their dibromo derivatives led to 2-(2-aryl-2-oxoethyl)-4H-benzo-1,4-thiazin-3-ones. The structure of synthesized compounds was confirmed by IR, ^{1}H, and ^{13}C NMR spectra and X-ray analysis.

Keywords: 2-Aminothiophenol; β-aroylacrylic acids; Thiazinones; NMR spectra

INTRODUCTION

The interaction of 2-aminothiophenol with α,β-unsaturated acids[1,2] and α,β-unsaturated carbonyl compounds[3,4] led to the formation of 1,5-benzothiazepines. In similar studies several authors[5–9] proposed, on the basis of spectroscopic data and elemental analyses, 1,5-benzothiazepine structure for the products of the reaction of 2-aminothiophenol with β-aroylacrylic acids. However, the formation of 1,4-benzothiazin-3-ones in this reaction has been reported earlier.[10]

We studied the reactions of β-aroylacrylic acids with substituted *o*-phenylenediamines and with diamines of the pyrimidine series and found that the products of the interaction are 3-phenacylquinoxalin-2-one[11] and pteridinone[12] derivatives, correspondingly. The alternative direction of the heterocyclization with the formation of a

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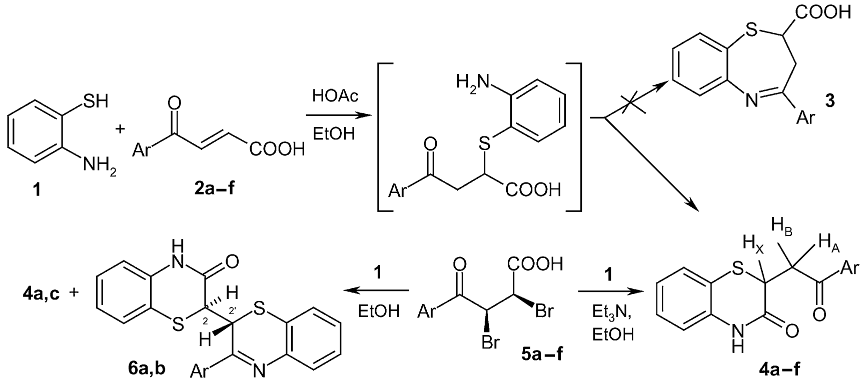
seven-membered ring did not occur. In the present study we reproduced the conditions of the interaction of 2-aminothiophenol (**1**) with β-aroylacrylic acids **2a–f**, which have been reported earlier,[5–9] and additionally studied the structure of the reaction products.

RESULTS AND DISCUSSION

Refluxing of 2-aminothiophenol (**1**) with acids **2a–f** in ethanol in the presence of glacial acetic acid resulted in the formation of compounds **4a–f** in the form of colorless crystals with good yields. Melting points of compounds **4a–f** as well as positions and intensity of signals in the ^{1}H NMR spectra of the product **4a** ($CDCl_3$) were similar to those reported earlier.[7,8]



2, 4, 5 a Ar = Ph, b Ar = 4-CH_3-C_6H_4, c Ar = 4-Cl-C_6H_4, d Ar = 4-Br-C_6H_4, e Ar = 4-F-C_6H_4, f Ar = 3,4-$(F)_2$-C_6H_3; **6** a Ar = Ph, b Ar = 4-Cl-C_6H_4

SCHEME 1

The structures of compounds **4a–f** were confirmed by IR, ^{1}H, and ^{13}C NMR spectroscopic data, and X-ray and elemental analyses (see Experimental section below). Thus, in the IR spectra sharp absorptions were observed due to the stretching vibration of the carbonyl groups in the region of 1668–1688 cm^{-1} and also the bands at 3182–3206 cm^{-1}. The latter we assign to the vibrations of the associated NH–CO group, while others[5–9] erroneously treated it as absorption bands of OH group. The ^{1}H NMR (DMSO-d_6 + CCl_4) spectra of compounds **4a–f** exhibited clear signals due to protons of the aromatic ring at 6.92–7.99 ppm, a singlet due to proton of the NH group at 10.63–10.66 ppm (disappearing after exchange with deuterium), and

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a group of signals due to protons of the CH_2–CH unit with a typical ABX structure: two doublets of doublets for the methylene group protons at $\delta = 3.10-3.72$ ppm ($J_{AB} = 17.2-17.6$ Hz, $J_{AX} = 6.4-7.0$ Hz, $J_{BX} = 6.4-6.8$ Hz) and doublet of doublets for the methine proton at $\delta = 4.05-4.07$ ppm ($J_{AX} = 6.4-7.0$ Hz, $J_{BX} = 6.4-6.8$ Hz). Similar ABX structure can be expected for the structure **3**. The ^{13}C NMR spectral data agree with both structures **4** and **3**. Thus, the spectroscopic data and the results of elemental analysis cannot give an unambiguous answer about the true structure of the compounds synthesized. Ultimately, the structures of the products **4a–f** were confirmed by X-ray structural analysis for compound **4d**, which is 2-[2-(4-bromophenyl)-2-oxoethyl]-4H-benzo-1,4-thiazin-3-one (Tables I–III).

The heterocycle in the product **4d** is found to exist in intermediate conformation between twisted boat and chair type (Figure 1). Atoms $C_{(7)}$ and $C_{(8)}$ deviate from the plane of the remaining ring atoms by 0.335(4) Å and 1.024(4) Å, respectively. The substituent at atom $C_{(8)}$ is equatorially oriented (torsion angle $O_{(2)}$–$C_{(7)}$–$C_{(8)}$–$C_{(9)}$–172.9(2)°). The carbonyl group is slightly turned relative to the bromophenyl substituent (torsion angle $O_{(2)}$–$C_{(10)}$–$C_{(11)}$–$C_{(12)}$ 11.5(4)°) in consequence of sterical difficulties (the short intramolecular contact $C_{(9)}$–$H_{(16)}$ 2.36 Å, sum of Van der Waals radii 2.87 Å).[13] In the crystalline state, molecules **4d** form centrosymmetrical dimers due to intermolecular hydrogen bonds $N_{(1)}$–$H_{(1N)} \cdots O_{(1)}$ (3-x, 2-y, 1-z) ($H \cdots O$ distance 2.02 Å, $N–H \cdots O$ angle 177°). Their formation results in the lengthening of the bond $C_{(7)}$–$O_{(1)}$ up to 1.236(3) Å in comparison with the mean value 1.210 Å.[14]

The conclusion that can be made from the above is that 2-aminothiophenol (**1**) reacts with β-aroylacrylic acids **2a–f** similar to

TABLE I Bond Lengths (d) in the Structure of Compound **4d**

Bond	d(Å)	Bond	d(Å)
$Br_{(1)}$—$C_{(14)}$	1.896 (3)	$C_{(5)}$—$C_{(6)}$	1.381 (4)
$S_{(1)}$—$C_{(1)}$	1.758 (3)	$C_{(7)}$—$C_{(8)}$	1.495 (4)
$S_{(1)}$—$C_{(8)}$	1.822 (3)	$C_{(8)}$—$C_{(9)}$	1.516 (4)
$O_{(1)}$—$C_{(7)}$	1.236 (3)	$C_{(9)}$—$C_{(10)}$	1.517 (4)
$O_{(2)}$—$C_{(10)}$	1.204 (3)	$C_{(10)}$—$C_{(11)}$	1.502 (4)
$N_{(1)}$—$C_{(7)}$	1.354 (3)	$C_{(11)}$—$C_{(16)}$	1.386 (4)
$N_{(1)}$—$C_{(6)}$	1.414 (3)	$C_{(11)}$—$C_{(12)}$	1.390 (4)
$C_{(1)}$—$C_{(6)}$	1.378 (4)	$C_{(12)}$—$C_{(13)}$	1.385 (4)
$C_{(1)}$—$C_{(2)}$	1.387 (4)	$C_{(13)}$—$C_{(14)}$	1.380 (5)
$C_{(2)}$—$C_{(3)}$	1.376 (5)	$C_{(14)}$—$C_{(15)}$	1.367 (4)
$C_{(3)}$—$C_{(4)}$	1.372 (5)	$C_{(15)}$—$C_{(16)}$	1.371 (4)
$C_{(4)}$—$C_{(5)}$	1.392 (4)		

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TABLE II Bond Angles (ω) in the Structure of Compound **4d**

Angle	ω (deg.)	Angle	ω (deg.)
$C_{(1)}$—$S_{(1)}$—$C_{(8)}$	97.2 (1)	$C_{(7)}$—$C_{(8)}$—$S_{(1)}$	107.8 (2)
$C_{(7)}$—$N_{(1)}$—$C_{(6)}$	126.1 (3)	$C_{(9)}$—$C_{(8)}$—$S_{(1)}$	108.5 (2)
$C_{(6)}$—$C_{(1)}$—$C_{(2)}$	119.1 (3)	$C_{(8)}$—$C_{(9)}$—$C_{(10)}$	113.3 (2)
$C_{(6)}$—$C_{(1)}$—$S_{(1)}$	119.8 (2)	$O_{(2)}$—$C_{(10)}$—$C_{(11)}$	120.7 (3)
$C_{(2)}$—$C_{(1)}$—$S_{(1)}$	121.1 (3)	$O_{(2)}$—$C_{(10)}$—$C_{(9)}$	122.3 (2)
$C_{(3)}$—$C_{(2)}$—$C_{(1)}$	120.8 (3)	$C_{(11)}$—$C_{(10)}$—$C_{(9)}$	116.9 (2)
$C_{(4)}$—$C_{(3)}$—$C_{(2)}$	120.4 (3)	$C_{(16)}$—$C_{(11)}$—$C_{(12)}$	118.8 (3)
$C_{(3)}$—$C_{(4)}$—$C_{(5)}$	119.1 (3)	$C_{(16)}$—$C_{(11)}$—$C_{(10)}$	123.1 (3)
$C_{(6)}$—$C_{(5)}$—$C_{(4)}$	120.5 (3)	$C_{(12)}$—$C_{(11)}$—$C_{(10)}$	118.1 (3)
$C_{(1)}$—$C_{(6)}$—$C_{(5)}$	120.2 (3)	$C_{(13)}$—$C_{(12)}$—$C_{(11)}$	120.4 (3)
$C_{(1)}$—$C_{(6)}$—$N_{(1)}$	121.2 (2)	$C_{(14)}$—$C_{(13)}$—$C_{(12)}$	118.9 (3)
$C_{(5)}$—$C_{(6)}$—$N_{(1)}$	118.6 (3)	$C_{(15)}$—$C_{(14)}$—$C_{(13)}$	121.4 (3)
$O_{(1)}$—$C_{(7)}$—$N_{(1)}$	120.6 (3)	$C_{(15)}$—$C_{(14)}$—$Br_{(1)}$	118.7 (2)
$O_{(1)}$—$C_{(7)}$—$C_{(8)}$	122.9 (2)	$C_{(13)}$—$C_{(14)}$—$Br_{(1)}$	120.0 (2)
$N_{(1)}$—$C_{(7)}$—$C_{(8)}$	116.4 (2)	$C_{(14)}$—$C_{(15)}$—$C_{(16)}$	119.5 (3)
$C_{(7)}$—$C_{(8)}$—$C_{(9)}$	112.8 (2)	$C_{(15)}$—$C_{(16)}$—$C_{(11)}$	121.0 (3)

TABLE III Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters for the Nonhydrogen Atmos in the Structure of Compound **4d**

Atom	x	y	z	U(eq)
$Br_{(1)}$	3797 (1)	6222 (1)	8727 (1)	65 (1)
$S_{(1)}$	13144 (1)	8425 (1)	2306 (1)	42 (1)
$O_{(1)}$	13010 (3)	9280 (2)	5194 (2)	33 (1)
$O_{(2)}$	12887 (3)	5769 (3)	5773 (2)	45 (1)
$N_{(1)}$	15487 (3)	9032 (3)	3646 (2)	29 (1)
$C_{(1)}$	15517 (4)	8399 (3)	1780 (2)	32 (1)
$C_{(2)}$	16458 (5)	8180 (4)	640 (3)	48 (1)
$C_{(3)}$	18287 (5)	8232 (4)	225 (3)	57 (1)
$C_{(4)}$	19216 (5)	8491 (4)	936 (3)	50 (1)
$C_{(5)}$	18277 (4)	8718 (4)	2080 (3)	39 (1)
$C_{(6)}$	16432 (4)	8686 (3)	2494 (2)	27 (1)
$C_{(7)}$	13889 (3)	8698 (3)	4249 (2)	25 (1)
$C_{(8)}$	13300 (4)	7576 (3)	3720 (2)	27 (1)
$C_{(9)}$	11376 (4)	7442 (3)	4382 (2)	27 (1)
$C_{(10)}$	11422 (4)	6470 (3)	5499 (2)	28 (1)
$C_{(11)}$	9543 (4)	6410 (3)	6261 (2)	29 (1)
$C_{(12)}$	9488 (4)	5791 (4)	7365 (3)	41 (1)
$C_{(13)}$	7791 (4)	5710 (4)	8103 (3)	43 (1)
$C_{(14)}$	6162 (4)	6239 (4)	7722 (3)	37 (1)
$C_{(15)}$	6207 (4)	6797 (3)	6627 (3)	37 (1)
$C_{(16)}$	7887 (4)	6883 (3)	5902 (3)	33 (1)

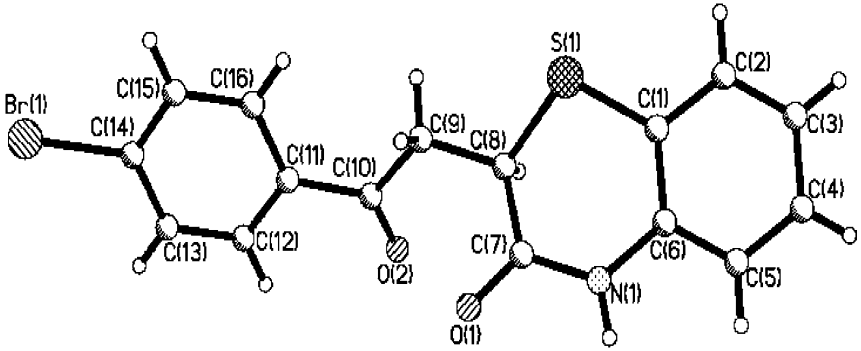

FIGURE 1 Molecular structure of compound **4d**.

o-phenylenediamine[11] and forms, a thermodynamically more stable six-membered ring.

It is necessary to note that compounds **4a–f** were isolated with low yields also in the reaction of 2-aminothiophenol (**1**) with 3-aroyl-2,3-dibromopropionic acids **5a–f** in boiling ethanol in the presence of triethylamine. We explain this unexpected result by the reduction of intermediate α-bromoolefines into β-aroylacrylic acids with triethylamine.[15] 2-Aminothiophenol (**1**) can also play the role of the reductant. Thus, thiazinones **4a**,**c** were obtained with 30% yields when triethylamine was missing in the reaction mixture.

3′-Aryl-4H,2′H[2,2′]di-(benzo-1,4-thiazinyl)-3-ones (**6a**,**b**) were isolated as the by-products of that reaction. The formation of compounds **6a**,**b** proceeds via the stage of nucleophylic substitution of bromine atoms with consequent cyclization by the carbonyl and carboxyl groups. The structures of products **6a**,**b** were confirmed by the ^{1}H NMR and mass spectroscopic data. Thus, the ^{1}H NMR spectrum of **6a** $(CD_3)_2CO$ exhibited doublets due to CH protons on the positions 2 and 2′ with $\delta = 3.33$ and 4.57 ppm ($J = 11.0$ Hz), a singlet due to the amino group with $\delta = 10.78$ ppm (disappearing after exchange with deuterium), and multiplets due to the protons of the aromatic nuclei at 6.86–7.91 ppm. In the mass spectrum of **6a** the molecular ion signal was absent, but the peaks of both benzothiazine fragments with m/z 224 (100%) and 164 (7%) were present.

EXPERIMENTAL

All melting points were taken on a Kofler melting point apparatus and are uncorrected. IR spectra were recorded on Impact-400

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spectrophotometer in KBr tablets. ^1H and ^{13}C NMR spectra were taken on Varian Mercury 400 (400 MHz) spectrometer using DMSO-d_6 + CCl_4, $CDCl_3$ and $(CD_3)_2O$ as solvents at 25°C and tetramethyl silane (TMS) as internal standard. Mass spectra were recorded on FINNIGAN MAT. INCOS 50 instrument at 70 eV. Microanalyses were carried out on LECO CHNS-900 elemental analyzer.

General Procedure for the Preparation of the 2-(2-Aryl-2-oxoethyl)-4H-benzo-1,4-thiazin-3-ones (4a–f)

Method A

A solution of **1** (0.38 g, 3.00 mmol), corresponding acid **2a–f** (3.00 mmol), and glacial acetic acid (0.7 ml) in ethanol (15 ml) was refluxed for 1 h. After cooling, the precipitate was filtered off and crystallized from benzene twice. Duration of the reaction is 1.5 h for **4b** and 15 min for **4c–f**.

Method B

A solution of corresponding acid **5a–f** (1.00 mmol) and triethylamine (0.1 g, 1.00 mmol) in ethanol (6 ml) was refluxed for 10 min. 2-Aminobenzenethiole (0.13 g, 1 mmol) was then added and the reaction mixture was refluxed for 10 min. After cooling, the precipitate was filtered off and crystallized from benzene twice.

2-(2-Oxoethyl-2-phenyl)-4H-benzo-1,4-thiazin-3-one (4a)

Yield: **Method A**, 0.68 g (80%), **Method B**, 0.09 g (30%); m.p. 163°C (173–175°C,[7] 178°C[8]). IR (KBr), ν (cm^{-1}): 1688 (C=O), 3185 (NH). ^1H NMR ($CDCl_3$), δ (ppm): 3.22 (dd, 1H, CH_A, $J_{AB} = 16.0$ Hz, $J_{AX} = 8.0$ Hz), 3.88 (dd, 1H, CH_B, $J_{AB} = 17.4$ Hz, $J_{AX} = 6.4$ Hz), 4.33 (dd, 1H, CH_X, $J_{AX} = 7.0$ Hz, $J_{BX} = 6.4$ Hz), 6.80–7.99 (m, 9H, $H_{arom.}$), 8.70 (s, 1H, NH). ^1H NMR (DMSO-d_6 + CCl_4), δ (ppm): 3.11 (dd, 1H, CH_A, $J_{AB} = 17.4$ Hz, $J_{AX} = 7.0$ Hz), 3.70 (dd, 1H, CH_B, $J_{AB} = 17.4$ Hz, $J_{BX} = 6.4$ Hz), 4.05 (dd, 1H, CH_X, $J_{AX} = 7.0$ Hz, $J_{BX} = 6.4$ Hz), 6.92 (t, 1H, $H_{arom.}$), 7.01 (d, 1H, $H_{arom.}$), 7.14 (t, 1H, $H_{arom.}$), 7.21 (d, 1H, $H_{arom.}$), 7.46–7.60 (m, 3H, $H_{arom.}$), 7.96 (d, 2H, $H_{arom.}$), 10.63 (s, 1H, NH). Analysis: Calcd. For $C_{16}H_{13}NO_2S$ (283.35): C, 67.82%; H, 4.62%; N, 4.94%. Found: C, 67.81%; H, 4.60%; N, 4.94.

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2-[2-(4-Methylphenyl)-2-oxoethyl]-4H-benzo-1,4-thiazin-3-one (4b)

Yield: **Method A**, 0.63 g (71%), **Method B**, 0.08 g (26%); m.p. 203°C (205–206°C,[7] 196°C[8]). IR (KBr), ν (cm^{-1}): 1678 (C=O), 3206 (NH). ^{1}H NMR (DMSO-d$_6$ + CCl$_4$), δ (ppm): 2.42 (s, 3H, CH$_3$), 3.10 (dd, 1H, CH$_A$, $J_{AB} = 17.2$ Hz, $J_{AX} = 6.8$ Hz), 3.67 (dd, 1H, CH$_B$, $J_{AB} = 17.2$ Hz, $J_{BX} = 6.6$ Hz), 4.06 (dd, 1H, CH$_X$, $J_{AX} = 6.8$ Hz, $J_{BX} = 6.6$ Hz), 6.94 (t, 1H, H$_{arom.}$), 7.03 (d, 1H, H$_{Ar}$), 7.15 (t, 1H, H$_{arom.}$), 7.23 (d, 1H, H$_{arom.}$), 7.29 (d, 2H, H$_{arom.}$), 7.87 (d, 2H, H$_{arom.}$), 10.64 (s, 1H, NH). Analysis: Calcd. For $C_{17}H_{15}NO_2S$ (297.37): C, 68.66%; H, 5.08%; N, 4.71%. Found: C, 68.63%; H, 5.07%; N, 4.72.

2-[2-(4-Chlorophenyl)-2-oxoethyl]-4H-benzo-1,4-thiazin-3-one (4c)

Yield: **Method A**, 0.71 g (75%), **Method B**, 0.10 g (32%); m.p. 193°C (188°C,[8] 193–195°C[9]). IR (KBr), ν (cm^{-1}): 1673 (C=O), 3190 (NH). ^{1}H NMR (DMSO-d$_6$ + CCl$_4$), δ (ppm): 3.12 (dd, 1H, CH$_A$, $J_{AB} = 17.6$ Hz, $J_{AX} = 6.4$ Hz), 3.72 (dd, 1H, CH$_B$, $J_{AB} = 17.6$ Hz, $J_{BX} = 6.8$ Hz), 4.07 (dd, 1H, CH$_X$, $J_{AX} = 6.4$ Hz, $J_{BX} = 6.8$ Hz), 6.94 (t, 1H, H$_{arom.}$), 7.03 (d, 1H, H$_{arom.}$), 7.16 (t, 1H, H$_{arom.}$), 7.23 (d, 1H, H$_{arom.}$), 7.50 (d, 2H, H$_{arom.}$), 7.99 (d, 2H, H$_{arom.}$), 10.66 (s, 1H, NH). ^{13}C NMR (DMSO-d$_6$), δ (ppm): 37.2, 37.7, 117.8, 119.4, 123.6, 127.8, 128.1, 129.4, 130.6, 135.3, 137.5, 139.0, 166.5, 195.7. Analysis: Calcd. For $C_{16}H_{12}ClNO_2S$ (317.79): C, 60.47%; H, 3.81%; N, 4.41%. Found: C, 60.44%; H, 3.80%; N, 4.42.

2-[2-(4-Bromophenyl)-2-oxoethyl]-4H-benzo-1,4-thiazin-3-one (4d)

Yield: **Method A**, 0.99 g (91%), **Method B**, 0.09 g (26%); m.p. 192°C. IR (KBr), ν (cm^{-1}): 1673 (C=O), 3190 (NH). ^{1}H NMR (DMSO-d$_6$ + CCl$_4$), δ (ppm): 3.09 (dd, 1H, CH$_A$, $J_{AB} = 17.8$ Hz, $J_{AX} = 7.0$ Hz), 3.69 (dd, 1H, CH$_B$, $J_{AB} = 17.8$ Hz, $J_{BX} = 6.6$ Hz), 4.04 (dd, 1H, CH$_X$, $J_{AX} = 7.0$ Hz, $J_{BX} = 6.6$ Hz), 6.92 (t, 1H, H$_{arom.}$), 7.01 (d, 1H, H$_{arom.}$), 7.14 (t, 1H, H$_{arom.}$), 7.21 (d, 1H, H$_{arom.}$), 7.64 (d, 2H, H$_{arom.}$), 7.90 (d, 2H, H$_{arom.}$), 10.65 (s, 1H, NH). Analysis: Calcd. For $C_{16}H_{12}BrNO_2S$ (362.24): C, 53.05%; H, 3.34%; N, 3.87%. Found: C, 53.05%; H, 3.33%; N, 3.89.

2-[2-(4-Fluorophenyl)-2-oxoethyl]-4H-benzo-1,4-thiazin-3-one (4e)

Yield: **Method A**, 0.58 g (61%), **Method B**, 0.08 g (25%); m.p. 172°C (171–173°C).[7] IR (KBr), ν (cm^{-1}): 1668 (C=O), 3196 (NH). ^{1}H NMR (DMSO-d$_6$ + CCl$_4$), δ (ppm): 3.12 (dd, 1H, CH$_A$, J_{AB} = 17.6 Hz, J_{AX} = 6.8 Hz), 3.71 (dd, 1H, CH$_B$, J_{AB} = 17.6 Hz, J_{BX} = 6.8 Hz), 4.07 (dd, 1H, CH$_X$, J_{AX} = 6.8 Hz, J_{BX} = 6.8 Hz), 6.94 (t, 1H, H$_{arom.}$), 7.03 (d, 1H, H$_{arom.}$), 7.15 (t, 1H, H$_{arom.}$), 7.20–7.25 (m, 3H, H$_{arom.}$), 8.05 (t, 2H, H$_{arom.}$), 10.65 (s, 1H, NH). Analysis: Calcd. For $C_{16}H_{12}FNO_2S$ (317.79): C, 60.47%; H, 3.81%; N, 4.41%. Found: C, 60.44%; H, 3.80%; N, 4.42.

2-[2-(3,4-Difluorophenyl)-2-oxoethyl]-4H-benzo-1,4-thiazin-3-one (4f)

Yield: **Method A**, 0.72 g (75%), **Method B**, 0.1 g (31%); m.p. 192°C. IR (KBr), ν (cm^{-1}): 1683 (C=O), 3190 (NH). ^{1}H NMR (DMSO-d$_6$ + CCl$_4$), δ (ppm): 3.12 (dd, 1H, CH$_A$, J_{AB} = 17.6 Hz, J_{AX} = 6.4 Hz), 3.72 (dd, 1H, CH$_B$, J_{AB} = 17.6 Hz, J_{BX} = 6.8 Hz), 4.06 (dd, 1H, CH$_X$, J_{AX} = 6.4 Hz, J_{BX} = 6.8 Hz), 6.95 (t, 1H, H$_{arom.}$), 7.03 (d, 1H, H$_{arom.}$), 7.16 (t, 1H, H$_{arom.}$), 7.23 (d, 1H, H$_{arom.}$), 7.40–7.47 (k, 1H, H$_{arom.}$), 7.88–7.97 (m, 2H, H$_{arom.}$), 10.66 (s, 1H, NH). ^{13}C NMR (DMSO-d$_6$), δ (ppm): 37.2, 37.7, 117.8, 118.1, 118.3, 119.4, 123.6, 126.5, 127.8, 128.1, 134.2, 137.5, 166.5, 194.7. Analysis: Calcd. For $C_{16}H_{11}F_2NO_2S$ (319.33): C, 60.18%; H, 3.47%; N, 4.39%. Found: C, 60.20%; H, 3.48%; N, 4.36.

General Procedure for the Preparation of the 3′-Aryl-4H,2′H[2,2′]di-(benzo-1,4-thiazinyl)-3-ones (6a,b)

A solution of corresponding acid **5a,c** (1.00 mmol) and **1** (0.13 g, 1.00 mmol) in methanol (5 ml) was refluxed for 15 min. After cooling, the precipitate was filtered off to give thiazinyl-3-ones **4a,c** (30%). The precipitate formed from mother liquor was filtered off and crystallized from ethanol to give the products **6a,b**.

3′-Phenyl-4H,2′H[2,2′]di-(benzo-1,4-thiazinyl)-3-one (6a)

Yield: 0.039 g (10%); m.p. 232°C. ^{1}H NMR ((CD$_3$)$_2$CO), δ (ppm): 3.13 (d, 1H, CH, J = 11.2 Hz), 4.57 (d, 1H, CH, J = 11.2 Hz), 6.86 (d, 1H, H$_{arom.}$), 6.94–7.03 (m, 2H, H$_{arom.}$), 7.13–7.58 (m, 10H, H$_{arom.}$), 7.91 (d, 2H, H$_{arom.}$), 10.78 (s, 1H, NH). MS, m/z (%): 226 (5), 225 (28), 224 (100), 165 (7), 121 (6), 77 (6), 58 (49). Analysis: Calcd. For $C_{22}H_{16}N_2OS_2$ (388.51): C, 68.01%; H, 4.15%; N, 7.21%. Found: C, 60.00%; H, 4.18%; N, 7.24.

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3′-(4-Chlorophenyl)-4H,2′H[2,2′]di-(benzo-1,4-thiazinyl)-3-one (6b)

Yield: 0.042 g (10%); m.p. 209°C. ^1H NMR ($CDCl_3$), δ (ppm): 3.40 (d, 1H, CH, $J = 11.0$ Hz), 4.20 (d, 1H, CH, $J = 11.0$ Hz), 6.86 (d, 1H, $H_{arom.}$), 6.92–7.74 (m, 12H, $H_{arom.}$), 8.40 (s, 1H, NH). Analysis: Calcd. For $C_{22}H_{15}ClN_2OS_2$ (422.95): C, 62.47%; H, 3.57%; N, 6.62%. Found: C, 62.50%; H, 3.58%; N, 6.61.

X-Ray Structural Investigation of Compound 4d

Crystals of the compound **4d** ($C_{16}H_{12}BrNO_2S$) are triclinic. At 20°C $a = 7.762(3), b = 8.616(3), c = 12.357(4)$ Å; $\alpha = 82.22(3)^\circ$, $\beta = 72.99(3)^\circ$, $\gamma = 68.96(2)^\circ$, $V = 737.2(4)$ Å^3; $d_{calc} = 1.632$ g/cm^3; space group P1; Z = 2. The unit cell parameters and intensities of 2479 independent reflections ($R_{int} = 0.039$) were measured using a Siemens P3/PC automatic four-circle diffractometer (λMoKα, graphite monochromator, $\theta/2\theta$ scanning, $2\theta_{max} = 50^\circ$).

The structure was solved by a direct method using the SHELXTL PLUS[16] computer package. The positions of hydrogen atoms were located from the difference maps of electron density and refined using "riding" model with fixed $U_{iso} = 1.2U_{eq}$ of nonhydrogen atom bonded to the given hydrogen atom. Refinement of F^2 by the full-matrix, least-squares analysis in the anisotropic approximation for nonhydrogen atoms gave $\omega R_2 = 0.111$ for 2478 reflections ($R_1 = 0.045$ for 1463 reflections with $F > 4\sigma(F)$, $S = 0.997$). Adsorption correction was made semiempirically using ψ-scan data ($T_{max} = 0.844$, $T_{min} = 0.604$). Bond lengths, bond angles, and coordinates of nonhydrogen atoms are given in Tables I–III.

REFERENCES

[1] W. H. Mills and J. B. Whitworth, *J. Chem. Soc.*, **130,** 2738 (1927).

[2] H. Duddeck, M. Kaiser, and A. Levai, *Leibig's Ann.*, **869** (1985).

[3] A. Levai and R. Bognar, *Acta Chim. Acad. Sci. Hung.*, **88,** 293 (1976).

[4] A. Levai and R. Bognar, *Acta Chim. Acad. Sci. Hung.*, **92,** 415 (1977).

[5] U. C. Pant, B. C. Gaur, and M. Chugn, *Indian J. Chem.*, **26B,** 947 (1987).

[6] U. C. Pant and M. Chugn, *Indian J. Chem.*, **28B,** 435 (1989).

[7] U. C. Pant and M. Chugn, *Indian J. Chem.*, **28B,** 437 (1989).

[8] M. Upreti, S. Pant, A. Dandia, and U. C. Pant, *Phosphorus Sulfur Silicon*, **113,** 165 (1996).

[9] U. C. Pant, M. Upreti, S. Pant, A. Dandia, G. K. Patnaik, and A. K. Goel, *Phosphorus Sulfur Silicon*, **126,** 193 (1997).

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[10] F. K. Kirchner and E. J. Alexander, *J. Am. Chem. Soc.*, **81,** 1721 (1959).

[11] N. N. Kolos, A. A. Tishchenko, V. D. Orlov, T. V. Beryozkina, S. V. Shishkina, and O. V. Shishkin, *Khim. Geterotsikl. Soedin.*, **10,** 1407 (2001). English translation in *Chem. Heterocycl. Comp.*, **10,** 1407 (2001).

[12] N. Kolos, T. Beryozkina, and V. Orlov, *Heterocycles*, **60,** 2115 (2003).

[13] Yu. V. Zefirov and P. M. Zorkii, *Usp. Khim.*, **58,** 713 (1989).

[14] H.-B. Burgi and J. D. Dunitz, *Structure Correlation* (Weinheim, VCH, 1994).

[15] G. S. Kajtmazova, N. P. Gambaryan, and E. M. Rokhlin, *Usp. Khim.*, **58,** 2011 (1989).

[16] G. M. Sheldrick, *SHELXTL PLUS. PC Version. A system of computer programs for the determination of crystal structure from X-ray diffraction data. Revision 5.1* (1998).

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