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Heterocyclic Thiones and Their Analogs in 1,3-Dipolar Cycloaddition Reactions: IV.* Reactions of 4-Aryl-2-phenyl-1,2-dihydrophthalazine-1-thiones with Nitrile Imides

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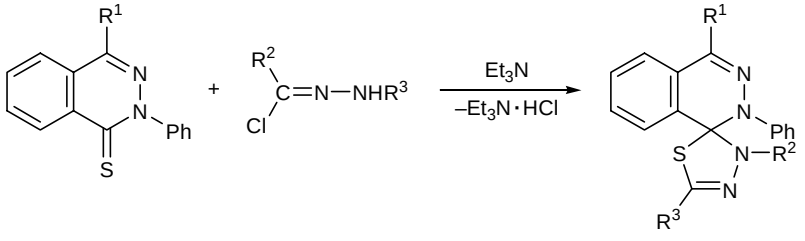
Abstract—4-Aryl-2-phenyl-1,2-dihydrophthalazine-1-thiones react with nitrile imides according to the [3+2]-cycloaddition pattern to give phthalazinespirothiadiazoles. The reaction occurs regioselectively at the exocyclic C=S bond.

Compounds possessing a C=S bond are highly reactive as dipolarophiles in 1,3-dipolar cycloadditions [2]. Reactions of various thiocarbonyl compounds with nitrile imides are known to give substituted thiadiazoles [3]. There are only fragmentary published data on reactions of cyclic thioxo derivatives with nitrile imides. For example, pyrimidinethiones were reported to react with nitrile imides to afford pyrimidinespirothiadiazoles [4]. We previously showed that substituted 3*H*-2-benzothiophene-1-thiones exhibit a high reactivity as dipolarophiles toward C,N-disubstituted nitrile imides [5, 6]. We also reported on the behavior of substituted phthalazinethiones in 1,3-dipolar cycloaddition reactions [7].

The present work continues our studies on 1,3-dipolar cycloaddition reactions of heterocyclic thiones. Here, we report the results of our more detailed study on the reaction of 2,4-disubstituted 1,2-dihydrophthalazines **Ia**–**Ic** with C,N-disubstituted nitrile imides which were generated *in situ* by the action of triethylamine on the corresponding benzohydrazonoyl chlorides. 1,3-Dipolar cycloaddition reactions were carried out in boiling benzene with equimolar amounts of dihydrophthalazinethione **Ia**–**Ic** and benzohydrazonoyl chloride **IIa**–**IIg**. The progress of the reactions was monitored by TLC. The reactions occurred in a regioselective fashion at the exocyclic C=S bond and resulted in formation of previously unknown 2,4,3',5'-

Scheme 1.



Ia–Ic **IIa–IIg** **IIIa–IIIk**

I, R^1 = Ph (**a**), *p*-MeC_6H_4 (**b**), *p*-ClC_6H_4 (**c**); **II**, $R^2 = R^3$ = Ph (**a**), R^2 = Ph, R^3 = MeCO (**b**), R^2 = Ph, R^3 = PhCO (**c**), R^2 = Ph, R^3 = *p*-$O_2NC_6H_4$ (**d**), R^2 = Ph, R^3 = EtOCO (**e**), R^2 = p-$O_2NC_6H_4$, R^3 = EtOCO (**f**), R^2 = *p*-$MeOC_6H_4$, R^3 = EtOCO (**g**); **III**, $R^1 = R^2 = R^3$ = Ph (**a**), R^1 = *p*-MeC_6H_4, $R^2 = R^3$ = Ph (**b**), R^1 = *p*-ClC_6H_4, $R^2 = R^3$ = Ph (**c**), $R^1 = R^2$ = Ph, R^3 = MeCO (**d**), R^1 = *p*-MeC_6H_4, R^2 = Ph, R^3 = MeCO (**e**), R^1 = *p*-ClC_6H_4, R^2 = Ph, R^3 = MeCO (**f**), $R^1 = R^2$ = Ph, R^3 = PhCO (**g**), $R^1 = R^2$ = Ph, R^3 = *p*-$O_2NC_6H_4$ (**h**), $R^1 = R^2$ = Ph, R^3 = EtOCO (**i**), R^1 = Ph, R^2 = *p*-$O_2NC_6H_4$, R^3 = EtOCO (**j**), R^1 = Ph, R^2 = *p*-$MeOC_6H_4$, R^3 = EtOCO (**k**).

* For communication III, see [1].

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tetrasubstituted 1,2,2',3'-tetrahydrophthalazine-1-spiro-2'-[1,3,4]thiadiazoles **IIIa**–**IIIk** (Scheme 1). Compounds **IIIa**–**IIIk** are crystalline substances which can be stored in air for a long time. The IR spectra of adducts **IIIa**–**IIIk** lack absorption bands in the region 1260–1270 cm^{-1} (which is typical of C=S stretching vibrations) but contain those at 1590–1595 and 1329–1366 cm^{-1} due to stretching vibrations of the C=N and C–N bonds in the thiadiazole ring. Vibrations of the carbonyl group in the 5'-substituent in compounds **IIId**–**IIIg** and **IIIi**–**IIIk** appear at 1635–1708 cm^{-1}, and the aromatic nitro groups in **IIIh** and **IIIj** give rise to absorption at 1340–1342, 1549, and 1558 cm^{-1}.

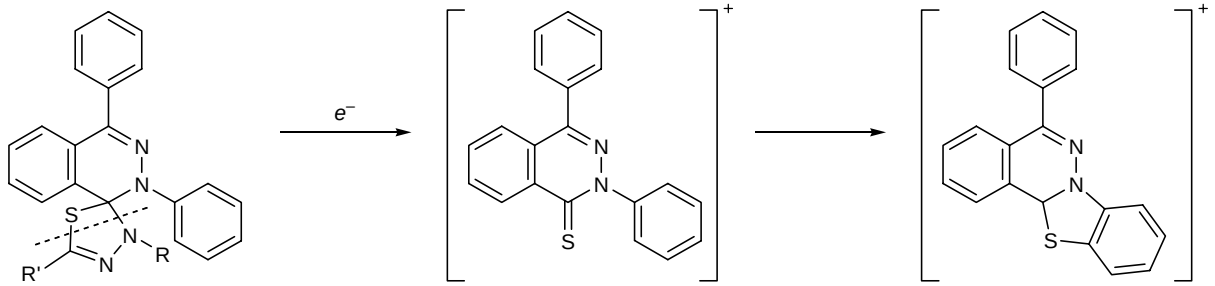
Compounds **IIIa**–**IIIk** displayed in the ultraviolet region of the electron absorption spectra two maxima with approximately equal intensities at λ 220–230 and 240–250 nm, and a less intense band was present in the visible region (λ_{max} 339–389 nm; log ε 4.04–4.29). The position of the latter almost does not depend on the nature of the substituent in position *4* of the phthalazine ring and is determined mainly by the nature of substituents in the thiadiazole fragment. Characteristically, the red shift of the long-wave maximum increases in the series **IIIa**–**IIIc** ≈ **IIIj** < **IIId**–**IIIf** < **IIIg** < **IIIh**. Substituent in position *5* of the thiadiazole ring exerts a stronger effect on the position of the long-wave absorption maximum than does that attached to N^3. For example, the red shift of the long-wave absorption maximum Δλ, induced by introduction of a nitro group into the benzene ring at $C^{5'}$ (compound **IIIh**), is equal to 84 nm (relative to **IIIa**), while the effect of a nitro group introduced into the benzene ring on N^3 is almost twice as low (cf. compounds **IIIj** and **IIIi**, Δλ = 49 nm). Electron-donor substituents (e.g., methoxy group) in the *para* position of the aromatic ring in position *3*' insignificantly affect the position of the long-wave absorption maximum (cf. **IIIk** and **IIIi**, Δλ = 5 nm).

The ^{1}H NMR spectra of spiro heterocycles **IIIa**, **IIId**, **IIIg**, **IIIh**, **IIIj**, and **IIIk** contained signals from aromatic protons and those corresponding to substituents in position *5* of the thiadiazole ring. Compound **IIId** showed in the spectrum a singlet at δ 1.57 ppm due to protons of the acetyl group, and in the spectra of **IIIj** and **IIIk** signals from the ethoxycarbonyl group were present at δ 1.31 (t) and 4.28 ppm (q) and 1.27 (t) and 4.24 ppm (q), J = 7 Hz. In the ^{13}C NMR spectra of **IIIa**, **IIId**, **IIIg**, **IIIh**, **IIIj**, and **IIIk**, the spiro carbon atom linked to three heteroatoms appeared at δ_C 113–119 ppm, and the $C^{5'}$ signal was located at δ_C 141–144 ppm; the other ^{13}C NMR parameters were consistent with the assumed structures.

The structure of the cycloaddition products was also confirmed by mass spectrometry. Compounds **IIIg**–**IIIk** showed in the mass spectra low-intense molecular ion peaks (M^+). Only the molecular ion peak of **IIIg** had a relative intensity of 44% due to strong stabilization via delocalization of the positive charge over the benzoyl substituent. A specific feature of the mass spectra of these compounds is the absence of fragment ions resulting from elimination of any substituent from the spirobicyclic framework, which is typical of other complex molecules. The mass spectra of **IIIj** and **IIIk** contained an ion peak with *m*/*z* 395; however, it was difficult to rationalize the origin of that ion. The most abundant ion in the spectra of **IIIg**–**IIIj** (100%; 60% for **IIIk**) was that with *m*/*z* 313. Its formation may be illustrated by Scheme 2. Cleavage of the five-membered ring gives ion $\mathbf{F}_1$ with *m*/*z* 314, in which the positive charge may be localized with a high probability on the sulfur atom. The subsequent ring closure with participation of the *ortho*-position of the nearby phenyl group (S_{Earom}) leads to formation of cation $\mathbf{F}_2$ which is stabilized due to charge delocalization over both benzene rings and heteroatoms.

The product structure was also proved by the X-ray diffraction data obtained from a single crystal of

Scheme 2.



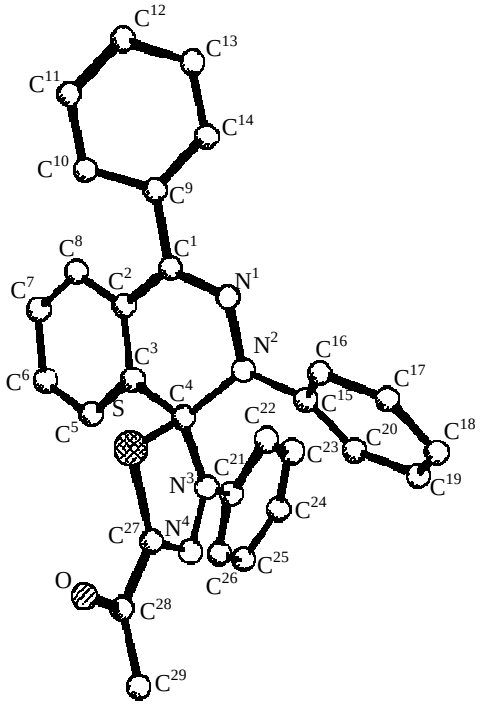
$\mathbf{F}_1$, *m*/*z* 314 $\mathbf{F}_2$, *m*/*z* 313

5'-acetyl-2,4,3'-triphenyl-1,2,2',3'-tetrahydrophthalazine-1-spiro-2'-[1,3,4]thiadiazole (**IIId**). The structure of molecule **IIId** is shown in figure, and the bond lengths and bond angles therein (except for those in the aromatic substituents) are given in table. The benzene ring in the phthalazine fragment is almost planar; the average deviation of atoms from the mean-square plane is 0.0065 Å. However, the corresponding value for the dihydropyridazine ring is 0.1388 Å; here, the N^2 atom deviates from the mean-square plane by 0.2395 Å, and the C^4 atom, by –0.2514 Å. As a result, the dihedral angle between the mean-square planes of the benzene and pyridazine rings is 10.0° (hereinafter the atom numbering corresponds to that shown in figure). The C^9–C^{14} and C^{15}–C^{20} benzene rings are turned through dihedral angles of 54.6 and 45.4°, respectively, relative the $C^1C^2C^3C^4N^1N^2$ plane; therefore, no conjugation exists between the heteroring and aromatic substituents therein. The average deviation of atoms in the five-membered thiadiazole ring ($SC^4C^{27}N^3N^4$) is 0.0059 Å, while the sulfur atom deviates from the mean-square plane by 0.0072 Å. This means that conjugation within the thiadiazole ring is possible. The $SC^4C^{27}N^3N^4$ plane is almost orthogonal to the pyridazine ring plane: the corresponding dihedral angle is 87.4°. The dihedral angle between the C^{21}–C^{26} benzene and thiadiazole ring planes is 26.8°, which is likely to rule out the possibility for effective conjugation between these fragments, but the acetyl group is almost coplanar to the thiadiazole ring (the dihedral angle is as small as 3.4°). The average deviation of atoms from the $OC^{27}C^{28}C^{29}$ plane is 0.0037 Å.

Thus we have found that 2,4-disubstituted 1,2-dihydrophthalazine-1-thiones regioselectively react with C,N-disubstituted nitrile imides at the exocyclic C=S bond to give phthalazinespirothiadiazoles.

EXPERIMENTAL

The IR spectra of solutions of compounds **IIIa**–**IIIk** in chloroform were recorded on a Specord 75IR spectrometer (layer thickness 0.97 mm). The electron absorption spectra of solutions in acetonitrile were measured on a Specord UV-Vis spectrophotometer using 1-cm cells. The ^1H and ^{13}C NMR spectra were obtained on a Bruker AM-500 instrument at 500 and 125 MHz, respectively, from 20% solutions in chloroform-*d* using HMDS as internal reference. The mass spectra (electron impact, 70 eV) were run on an MKh-1321 mass spectrometer; direct inlet probe temperature 120°C, ion source temperature 200°C.



Structure of the molecule of 5'-acetyl-2,4,3'-triphenyl-1,2,2',3'-tetrahydrophthalazine-1-spiro-2'-[1,3,4]thiadiazole (**IIId**) according to the X-ray diffraction data (hydrogen atoms are not shown).

X-Ray analysis of a single crystal of 5'-acetyl-2,4,3'-triphenyl-1,2,2',3'-tetrahydrophthalazine-1-spiro-2'-[1,3,4]-thiadiazole (**IIId**) was performed on a Syntex P1 automatic diffractometer (MoK_α irradiation, Nb filter, $\theta/2\theta$-scanning, $2\theta \leq 45°$). Monoclinic crystals, $C_{29}H_{22}N_4OS$, with the following unit cell parameters: a = 8.787(1), b = 17.959(3), c = 15.343(1) Å; β = 99.39(1)°; V = 2388.8(1.1) Å^3; space group $P2_1/c$; Z = 4; d_{calc} = 1.320 g/cm^3. The structure was solved by the direct method from 2434 reflections with $I > 3\sigma(I)$ in the full-matrix anisotropic approximation for C, N, O, and S atoms and isotropic approximation for hydrogen atoms; the final divergence factors were R = 0.030, R_w = 0.035 (no correction for absorption was introduced). All calculations were performed on a NOVA-3 minicomputer using SHELXTL program. The coordinates of non-hydrogen and hydrogen atoms and their equivalent temperature factors are available from the authors.

Initial dihydrophthalazine-1-thiones **Ia** and **Ic** were synthesized by the procedure described in [7].

2-Phenyl-4-*p*-tolyl-1,2-dihydrophthalazine-1-thione (Ib). A mixture of 3.1 g of 2-phenyl-4-*p*-tolyl-1,2-dihydrophthalazine-1-one and 2.2 g of P_2S_5 in 20 ml of anhydrous *o*-xylene was heated for 30 min

Bond lengths *d* (Å) and bond angles ω (deg) in the molecule of 5'-acetyl-2,4,3'-triphenyl-1,2,2',3'-tetrahydrophthalazine-1-spiro-2'-[1,3,4]thiadiazole (**IIId**)

Bond	*d*	Bond	*d*
$S–C^4$	1.889(2)	$S–C^{27}$	1.740(2)
$O–C^{28}$	1.216(3)	$N^1–N^2$	1.396(2)
$N^1–C^1$	1.292(3)	$N^2–C^4$	1.468(3)
$N^2–C^{15}$	1.454(3)	$N^3–N^4$	1.358(2)
$N^3–C^4$	1.473(3)	$N^3–C^{21}$	1.428(3)
$N^4–C^{27}$	1.291(2)	$C^1–C^2$	1.463(3)
$C^1–C^9$	1.490(3)	$C^2–C^3$	1.384(3)
$C^2–C^8$	1.396(3)	$C^3–C^4$	1.508(3)
$C^3–C^5$	1.391(3)	$C^5–C^6$	1.375(3)
$C^6–C^7$	1.385(3)	$C^7–C^8$	1.379(3)
$C^{27}–C^{28}$	1.471(3)	$C^{28}–C^{29}$	1.485(3)
Angle	ω	Angle	ω
C^4SC^{27}	89.5(1)	$N^2N^1C^1$	119.0(2)
$N^1N^2C^4$	117.0(2)	$N^1N^2C^{15}$	110.2(2)
$C^4N^2C^{15}$	118.2(15)	$N^4N^3C^4$	118.1(1)
$N^4N^3C^{21}$	116.6(2)	$C^4N^3C^{21}$	123.9(2)
$N^3N^4C^{27}$	112.9(2)	$N^1C^1C^2$	122.6(2)
$N^1C^1C^9$	116.6(2)	$C^2C^1C^9$	120.8(2)
$C^1C^2C^3$	117.6(2)	$C^1C^2C^8$	122.9(2)
$C^3C^2C^8$	119.5(2)	$C^2C^3C^4$	117.9(2)
$C^2C^3C^5$	120.1(2)	$C^4C^3C^5$	121.7(2)
SC^4N^2	111.1(1)	SC^4N^3	102.3(1)
$N^2C^4N^3$	112.1(2)	SC^4C^3	108.6(1)
$N^2C^4C^3$	109.4(2)	$N^3C^4C^3$	113.2(2)
$C^3C^5C^6$	120.1(2)	$C^5C^6C^7$	120.2(2)
$C^6C^7C^8$	120.1(2)	$C^2C^8C^7$	120.1(2)
$C^1C^9C^{10}$	119.6(2)	$C^1C^9C^{14}$	121.7(2)
$N^2C^{15}C^{16}$	120.3(2)	$N^2C^{15}C^{20}$	119.9(2)
$N^3C^{21}C^{22}$	121.0(2)	$N^3C^{21}C^{26}$	119.1(2)
$SC^{27}N^4$	117.2(2)	$SC^{27}C^{28}$	120.9(1)
$N^4C^{27}C^{28}$	121.8(2)	$OC^{28}C^{27}$	118.7(2)
$OC^{28}C^{29}$	122.4(2)	$C^{27}C^{28}C^{29}$	118.9(2)

under reflux. After cooling, the precipitate was filtered off, the solvent was removed from the filtrate under reduced pressure, and the residue was recrystallized from glacial acetic acid. Yield 2.7 g (82%). Yellow needles, mp 158–160°C. IR spectrum, ν, cm^{-1}: 1590 (C=N), 1348 (C–N), 1282 (C=S). UV spectrum, λ_{max}, nm (logε): 286 (3.98), 297 (4.02), 369 (4.06). Found, %: C 76.55; H 5.03; S 9.48. $C_{21}H_{16}N_2S$. Calculated, %: C 76.79; H 4.92; S 9.76.

Nitrile imides were generated *in situ* by the action of triethylamine on benzohydrazonoyl chlorides **IIa**–**IIg**, following the procedure reported in [8].

Reactions of 1,2-dihydrophthalazine-1-thiones Ia–Ic with nitrile imides generated from compounds IIa–IIg (*general procedure***).** A solution of 1 mmol of triethylamine in 2 ml of anhydrous benzene was added to a solution of 0.5 mmol of 1,2-dihydrophthalazine-1-thione **Ia**–**Ic** and 0.5 mmol of benzohydrazonoyl chloride **IIa**–**IIg** in 7 ml of dry benzene. The mixture was heated for 0.5 h under reflux, cooled, and filtered, the precipitate was washed with benzene, the filtrate was evaporated under reduced pressure, and the residue was made crystalline by grinding with pentane and was recrystallized from acetonitrile.

2,4,3',5'-Tetraphenyl-1,2,2',3'-dihydrophthalazine-1-spiro-2'-[1,3,4]thiadiazole (IIIa). Yield 75%, mp 184–186°C. IR spectrum, ν, cm^{-1}: 1590 (C=N), 1329 (C–N). UV spectrum: λ_{max} 339 nm (logε 4.27). ^1H NMR spectrum, δ, ppm: 6.91–7.72 m (24H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 117.91 ($C^{1(2')}$); 120.74, 124.76, 125.20, 126.23, 126.75, 127.35, 128.04, 128.41, 128.52, 128.70, 129.14, 129.22, 131.15, 132.89, 135.79 (C_{arom}); 142.85 ($C^{5'}$); 144.83 (C^4). Found, %: C 77.53; H 4.88; S 6.01. $C_{33}H_{24}N_4S$. Calculated, %: C 77.91; H 4.76; S 6.30.

2,3',5'-Triphenyl-4-*p*-tolyl-1,2,2',3'-tetrahydrophthalazine-1-spiro-2'-[1,3,4]thiadiazole (IIIb). Yield 80%, mp 192–194°C. IR spectrum, ν, cm^{-1}: 1591 (C=N), 1329 (C–N). UV spectrum: λ_{max} 340 nm (logε 4.25). Found, %: C 77.83; H 5.43; S 5.98. $C_{34}H_{26}N_4S$. Calculated, %: C 78.12; H 5.02; S 6.13.

4-*p*-Chlorophenyl-2,3',5'-triphenyl-1,2,2',3'-tetrahydrophthalazine-1-spiro-2'-[1,3,4]thiadiazole (IIIc). Yield 89%, mp 197–199°C. IR spectrum, ν, cm^{-1}: 1595 (C=N), 1332 (C–N). UV spectrum: λ_{max} 339 nm (logε 4.27). Found, %: C 72.55; H 4.36; Cl 6.32; S 5.77. $C_{33}H_{23}ClN_4S$. Calculated, %: C 72.97; H 4.28; Cl 6.53; S 5.90.

5'-Acetyl-2,4,3'-triphenyl-1,2,2',3'-tetrahydrophthalazine-1-spiro-2'-[1,3,4]thiadiazole (IIId). Yield 92%, mp 196–198°C. IR spectrum, ν, cm^{-1}: 1592 (C=N), 1345 (C–N), 1670 (C=O). UV spectrum: λ_{max} 367 nm (logε 4.12). ^1H NMR spectrum, δ, ppm:

1.57 s (3H, CH_3CO), 7.03–7.66 m (19H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 25.17 (CH_3); 118.94 ($C^{1(2')}$); 122.93, 124.40, 125.30, 127.06, 127.19, 127.84, 128.20, 128.42, 128.79, 129.06, 129.13, 131.14 (C_{arom}); 135.46 ($C^{5'}$); 141.80 (C^4); 178.50 (C=O). Found, %: C 73.09; H 4.81; S 6.47. $C_{29}H_{22}N_4OS$. Calculated, %: C 73.38; H 4.68; S 6.75.

5'-Acetyl-2,3'-diphenyl-4-*p*-tolyl-1,2,2',3'-tetrahydrophthalazine-1-spiro-2'-[1,3,4]thiadiazole (IIIe). Yield 75%, mp 224–226°C. IR spectrum, ν, cm^{-1}: 1591 (C=N), 1343 (C–N), 1670 (C=O). UV spectrum: λ_{max} 368 nm (logε 4.09). Found, %: C 73.44; H 5.11; S 6.39. $C_{30}H_{24}N_4OS$. Calculated, %: C 73.73; H 4.96; S 6.56.

5'-Acetyl-4-*p*-chlorophenyl-2,3'-diphenyl-1,2,-2',3'-tetrahydrophthalazine-1-spiro-2'-[1,3,4]thiadiazole (IIIf). Yield 72%, mp 205–207°C. IR spectrum, ν, cm^{-1}: 1592 (C=N), 1344 (C–N), 1670 (C=O). UV spectrum: λ_{max} 364 nm (logε 4.11). Found, %: C 68.26; H 4.28; Cl 6.49; S 5.98. $C_{29}H_{21}ClN_4OS$. Calculated, %: C 68.42; H 4.17; Cl 6.96; S 6.30.

5'-Benzoyl-2,4,3'-triphenyl-1,2,2',3'-tetrahydrophthalazine-1-spiro-2'-[1,3,4]thiadiazole (IIIg). Yield 74%, mp 205–207°C. IR spectrum, ν, cm^{-1}: 1594 (C=N), 1348 (C–N), 1635 (C=O). UV spectrum: λ_{max} 380 nm (logε 4.01). ^1H NMR spectrum, δ, ppm: 7.02–7.83 m (24H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 119.07 ($C^{1(2')}$); 122.88, 125.31, 126.85, 127.19, 127.37, 127.95, 128.13, 128.26, 128.44, 128.66, 128.83, 129.03, 129.15, 129.58, 130.12, 131.16, 132.00, 132.73 (C_{arom}); 141.94 ($C^{5'}$), 147.03 (C^4), 182.73 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 536 (44) $[C_{34}H_{24}N_4OS]^+$, 314 (28) $[C_{20}H_{14}N_2S]^+$, 313 (100) $[C_{20}H_{13}N_2S]^+$, 222 (2) $[C_{14}H_{10}N_2O]^+$, 91 (2) $[C_6H_5N]^+$, 77 (73) $[C_6H_5]^+$. Found, %: C 75.78; H 4.66; S 5.77. $C_{34}H_{24}N_4OS$. Calculated, %: C 79.06; H 4.59; S 5.97.

5'-*p*-Nitrophenyl-2,4,3'-triphenyl-1,2,2',3'-tetrahydrophthalazine-1-spiro-2'-[1,3,4]thiadiazole (IIIh). Yield 88%, mp 206–208°C. IR spectrum, ν, cm^{-1}: 1593 (C=N), 1330 (C–N), 1549, 1342 (NO_2). UV spectrum: λ_{max} 423 nm (logε 4.04). ^1H NMR spectrum, δ, ppm: 6.98–9.17 m (23H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 118.38 ($C^{1(2')}$); 121.78, 123.78, 124.79, 125.46, 126.54, 126.85, 127.13, 127.60, 128.10, 128.47, 128.71, 128.88, 129.14, 129.24, 129.60, 131.27, 132.00, 132.85, 137.49 (C_{arom}); 142.38 ($C^{5'}$); 144.62 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 553 (5) $[M]^+$, 314 (33) $[C_{20}H_{14}N_2S]^+$, 313 (100) $[C_{20}H_{13}N_2S]^+$, 239 (6) $[C_{13}H_9N_3O_2]^+$, 91 (70) $[C_6H_5N]^+$, 77 (85) $[C_6H_5]^+$. Found, %: C 71.34; H 4.36; S 5.68. $C_{33}H_{23}N_5O_2S$. Calculated, %: C 71.58; H 4.20; S 5.79.

Ethyl 2,4,3'-triphenyl-1,2,2',3'-tetrahydrophthalazine-1-spiro-2'-[1,3,4]thiadiazole-5'-carboxylate (IIIi). Yield 90%, mp 193–195°C. IR spectrum, ν, cm^{-1}: 1594 (C=N); 1346 (C–N); 1704 (C=O); 1140, 1084 (C–O). UV spectrum: λ_{max} 340 nm (logε 4.09). Mass spectrum, *m*/*z* (I_{rel}, %): 504 (5) $[M]^+$, 314 (24) $[C_{20}H_{14}N_2S]^+$, 313 (100) $[C_{20}H_{13}N_2S]^+$, 190 (10) $[C_{10}H_{10}N_2O_2]^+$, 91 (19) $[C_6H_5N]^+$, 77 (86) $[C_6H_5]^+$. Found, %: C 71.25; H 4.88; S 6.11. $C_{30}H_{24}N_4O_2S$. Calculated, %: C 71.40; H 4.80; S 6.35.

Ethyl 3'-*p*-nitrophenyl-2,4-diphenyl-1,2,2',3'-tetrahydrophthalazine-1-spiro-2'-[1,3,4]thiadiazole-5'-carboxylate (IIIj). Yield 87%, mp 225–227°C. IR spectrum, ν, cm^{-1}: 1588 (C=N); 1332 (C–N); 1708 (C=O); 1139, 1087 (C–O); 1558, 1340 (NO_2). UV spectrum: λ_{max} 389 nm (logε 4.29). ^1H NMR spectrum, δ, ppm: 1.31 t (3H, CH_3CH_2, J = 7 Hz), 4.28 q (2H, CH_3CH_2, J = 7 Hz), 7.22–8.09 m (18H, C_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 14.05 (CH_3); 62.56 (CH_2); 117.90 ($C^{1(2')}$); 124.73, 125.86, 126.38, 127.13, 127.59, 128.55, 128.60, 129.10, 129.69, 131.78 (C_{arom}); 142.24 ($C^{5'}$); 147.00 (C^4); 159.38 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 549 (4) $[M]^+$, 314 (30) $[C_{20}H_{14}N_2S]^+$, 313 (100) $[C_{20}H_{13}N_2S]^+$, 235 (5) $[C_{10}H_{10}N_2O_2]^+$, 91 (4) $[C_6H_5N]^+$, 77 (39) $[C_6H_5]^+$. Found, %: C 65.33; H 4.42; S 5.64. $C_{30}H_{23}N_5O_4S$. Calculated, %: C 65.55; H 4.23; S 5.83.

Ethyl 3'-*p*-methoxyphenyl-2,4-diphenyl-1,2,2',3'-tetrahydrophthalazine-1-spiro-2'-[1,3,4]thiadiazole-5'-carboxylate (IIIk). Yield 78%, mp 172–173°C. IR spectrum, ν, cm^{-1}: 1590 (C=N); 1347 (C–N); 1703 (C=O); 1142, 1087 (C–O); 2828 (OCH_3). UV spectrum: λ_{max} 345 nm (logε 4.07). ^1H NMR spectrum, δ, ppm: 1.27 t (3H, CH_3CH_2, J = 7 Hz), 3.74 s (3H, OCH_3), 4.24 q (2H, CH_3CH_2, J = 7 Hz), 6.74–7.64 m (18H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 14.13 (CH_3); 55.36 (OCH_3); 61.90 (CH_2); 113.99 ($C^{1(2')}$); 120.42, 124.36, 125.10, 127.04, 127.32, 127.42, 128.32, 128.41, 128.76, 128.98, 129.11, 131.12 (C_{arom}); 144.66 ($C^{5'}$); 155.44 (C^4); 160.09 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 534 (10) $[M]^+$, 314 (15) $[C_{20}H_{14}N_2S]^+$, 313 (100) $[C_{20}H_{13}N_2S]^+$, 220 (5) $[C_{11}H_{12}N_2O_3]^+$, 91 (8) $[C_6H_5N]^+$, 77 (78) $[C_6H_5]^+$. Found, %: C 69.47; H 5.05; S 5.86. $C_{31}H_{26}N_4O_3S$. Calculated, %: C 69.63; H 4.91; S 6.00.

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