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REACTION OF ACETYLENEDICARBOXYLIC ACIDS ESTERS WITH 4,5-DIHYDRO-1*H*-PYRAZOLE-1-CARBOTHIOAMIDES AND 3,4,5,6-TETRAHYDRO-2*H*-1,2,4-TRIAZEPINE-3-THIONES

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The reactions of dimethyl acetylenecarboxylate with 3,4,5,6-tetrahydro-2H-1,2,4-triazepine-3-thiones and 4,5-dihydro-1H-pyrazole-1-carbothioamides are convenient methods for the synthesis of 7,8-dihydrothiazolo[3,2-b][1,2,4]triazepin-3-ones derivatives and methyl esters of (2Z)-[2-(4,5-dihydro-1H-pyrazol-1-yl)-4-oxo-1,3-thiazol-5(4H)-ylidene]acetic acids, respectively. The reaction of methyl propynoates with 4,5-dihydro-1H-pyrazole-1-carbothioamides or with 5,5,7-trimethyl-2,4,5,6-tetrahydro-3H-1,2,4-triazepine-3-thione gives 2-(4,5-dihydro-1H-pyrazol-1-yl)-4H-1,3-thiazin-4-ones.

Keywords: 4,5-dihydro-1*H*-pyrazole-1-carbothioamides, 2,4,5,6-tetrahydro-3*H*-1,2,4-triazepine-3-thiones, 1,3-thiazin-4-ones, 1,3-thiazol-4-ones, thiazolo[3,2-*b*][1,2,4]triazepin-3-ones, acetylenecarboxylic acids esters, C–H coupling constants.

The reaction of thioamides with acetylenecarboxylic acids esters is a convenient method for the synthesis of thiazoles and thiazines [1]. There have been no reports concerning reactions of pyrazolecarbothioamides and triazepinethione with alkyl propynoates although such reactions should open a convenient approach to the preparation of new derivatives of pyrazoline and triazepine containing thiazole and thiazine rings. Recently, pyrazolinecarbothioamides have been attracting increasing attention since some of these compounds display hypotensive [2], antidepressant [3], and anti-inflammatory activity [4], serve as inhibitors of cholinesterase [6-8], monoamine oxidase A [3], and monoamine oxidase B [3, 5], and have antiamebic action [6-8]. Interest in bicyclic compounds containing azepine rings has arisen upon finding immunosuppressant and antitumor activity for such natural products as coformicine [12–15] and pentostatin [12–15] and their synthetic analogs [16–19]. Thus, there is current interest in the synthesis of new derivatives of pyrazoline and azepines.

In the present work, we studied the reactions of pyrazolecarbothioamides and triazepinethiones with acetylenecarboxylic acid esters and developed methods for the synthesis of new derivatives of pyrazoline and triazepine containing thiazole and thiazine rings.

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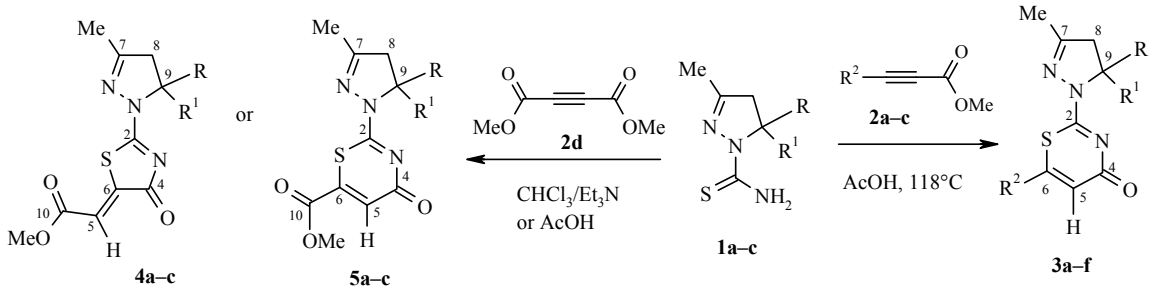
2-(4,5-Dihydro-1*H*-pyrazol-1-yl)-4*H*-1,3-thiazin-4-ones **3a–f*** were isolated in the reaction of 4,5-dihydro-1*H*-pyrazole-1-carbothioamides **1a–c** with acetylenecarboxylic acid esters **2a–c**.



1a, **3a–c**, **4a** R = R^1 = Me; **1b**, **3d,e**, **4b** R = Ph, R^1 = H; **1c**, **3f**, **4c** R = 4-$MeOC_6H_4$, R^1 = H;
2a, **3c**,**e**,**f** R^2 = H; **2b**, **3a**,**d** R^2 = Ph; **2c**, **3b** R^2 = 4-$MeOC_6H_4$

The structure of these compounds was supported by spectral methods (Tables 1–4) and by X-ray diffraction crystallographic analysis for compound **3d** (Tables 5–7, Fig. 1).

Since a second ester group exists in dimethyl acetylenedicarboxylate (DMAD) (**2d**), we might have expected that the reaction of this diester with thioamides **1a–c** would lead not only to methyl esters of 2-(3-methyl-4,5-dihydro-1*H*-pyrazol-1-yl)-4-oxo-4*H*-1,3-thiazine-6-carboxylic acids **5a–c** but also derivatives of 2-[2-(3-methyl-4,5-dihydro-1*H*-pyrazol-1-yl)-4-oxo-1,3-thiazol-5(4*H*)-ylidene]acetic acid **4a–c**.

The method of Vögeli [20], based on analysis of the $^nJ_{C–H}$ coupling constants between H-5 and exocyclic C(10) and endocyclic C(4) carbonyl carbon atoms, was used to establish the size of the ring formed. The ^{13}C NMR spectra of the compounds without proton broadband decoupling and with selective decoupling from H-5, 7-H_3C, C(8)H_2, 9-$(H_3C)_2$, and H_3CO (Table 3) were taken for an unequivocal assignment of the signals of the carbon atoms of interest and determination of the scalar $J_{C(4)–H(5)}$ and $J_{C(10)–H(5)}$ constants. Since $J_{C(4)–H(5)}$ = 5.0 and $J_{C(10)-H(5)}$ = 1.6 Hz for the compounds obtained (Table 3), the number of bonds separating atom H(5) from atom C(4) is 3 and of atom H(5) from atom C(10) is 2. This finding is in accordance with the structure of thiazolidines **4a–c** but not with the structure of 1,3-thiazines **5a–c** [20]. Thus, this reaction proceeds to give only pyrazolylthiazolidines **4a–c**. Furthermore, the values of $^3J_{C(4)–H(5)}$ = 5.0 Hz indicates (*Z*)-configuration of the exocyclic double bond in compounds **4a–c**, which corresponds to the mechanism reported for the *trans* addition of the SH group to the triple bond in DMAD [1].

It has been reported earlier that the reaction of 5,7-diaryl2,4,5,6-tetrahydro-3*H*-1,2,4-triazepine-3-thiones with electrophilic agents such as α-halo ketones [21] and ethyl bromoacetate [22] leads to thiazolotriazepines. However, there have been no reports concerning the reactions of derivatives of 2,4,5,6-tetrahydro-3*H*-1,2,4-triazepine-3-thiones with acetylenecarboxylic acid esters. On the other hand, we might have expected that the reaction of triazepinethione **6a** with ester **2b** would be a convenient method for the synthesis of previously unreported thiazinotriazepines **8** or **9**. However, the reaction of 5,5,7-trimethyl-2,4,5,6-tetrahydro-3*H*-1,2,4-triazepine-3-thione (**6a**) with methyl phenylpropynoate (**2b**) in the presence of sodium methylate leads only to Michael adduct **7**. The conversion of triazepinethione **6a** is only 35%. Michael adduct **7** does not cyclize to give thiazinotriazepines **8** or **9** upon heating in acetic acid at 118°C for 1 h, in pyridine at 120°C for 3 h or in diglyme at 161°C for 1 h.

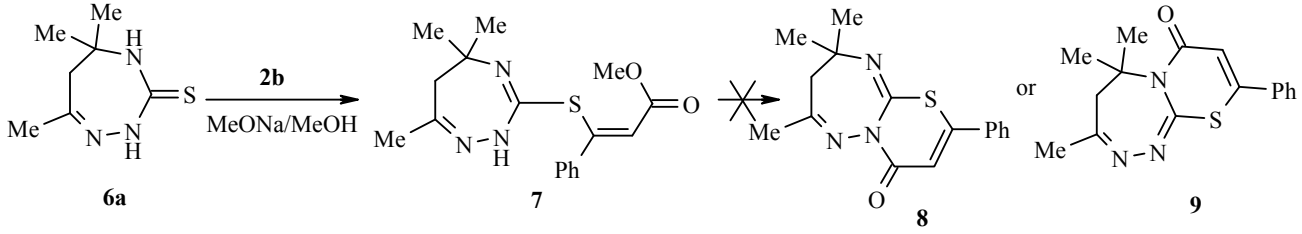
*Here and henceforward, the numbering of the atoms was selected for convenience in discussion of the NMR spectra and does not correspond to the IUPAC nomenclature numbering.

TABLE 1. Characteristics of compounds **3a–h, 4a–c,** and **11a,b**

Compound	Empirical formula	Found, *m/z* $[M+H]^+$ / Calculated, *m/z* $[M+H]^+$	R_f	Mp, °C*	Yield, % by method (reaction time, h)	
					A	B
3a	$C_{16}H_{17}N_3OS$	300.1169 / 300.1171	0.34	172–174	43 (8)	29 (15)
3b	$C_{17}H_{19}N_3O_2S$	330.1271 / 330.1276	0.29	159–161	40 (7)	
3c	$C_{10}H_{13}N_3OS$	447.1627*[2] / 447.1637	0.24	160–162	55 (4)	
3d	$C_{20}H_{17}N_3OS$	348.1180 / 348.1171	0.31	182–184	39 (10)	
3e	$C_{14}H_{13}N_3OS$	272.0856 / 272.0858	0.20	250–252	83 (2)	
3f	$C_{15}H_{15}N_3O_2S$	302.0961 / 302.0963	0.16	225–228	53 (2)	
3g	$C_{11}H_{15}N_3OS$	238.1020 / 238.1014	0.25	184–186		27 (15)
3h	$C_{17}H_{19}N_3OS$	314.1328 / 314.1327	0.36	194–196		33 (15)
4a	$C_{12}H_{15}N_3O_3S$	282.0917 / 282.0912	0.39	173–176	63	
4b	$C_{16}H_{15}N_3O_3S$	330.0917 / 330.0912	0.33	187–190	40	
4c	$C_{17}H_{17}N_3O_4S$	360.1019 / 360.1018	0.36	198–200	38	45
11a	$C_{12}H_{15}N_3O_3S$	282.0915 / 282.0912	0.47	183–185	40	
11b	$C_{14}H_{17}N_3O_3S$	308.1065 / 308.1069	0.56	82–85	38	

*Solvents: ~1:10 chloroform–hexane and then 1:5 benzene–hexane for compounds **3a,c,e,f**; ethanol for compounds **3d, 11a,b**; ~1:10 methanol–water and then ~1:5 benzene–hexane for compounds **3b, 4a**; ~1:10 chloroform–hexane for compounds **3g,h**; ~1:5 benzene–hexane and then ethanol for compound **4b**; butan-1-ol for compound **4c**.

*[2]Signal for $[2M+H]^+$.



6a **7** **8** **9**

In an attempt to obtain derivatives of thiazinotriazepines by the reaction of triazepinethione **6a** with esters **2b,e,f** in acetic acid at reflux, we were the first to find that opening of the triazepine ring and its recyclization to a pyrazoline ring occurs under these conditions to give 2-(3,5,5-trimethyl-4,5-dihydro-1*H*-pyrazol-1-yl)-4*H*-1,3-thiazin-4-ones **3a,g,h**.

The finding that the product **3a** obtained this way is identical to the product described above in the reaction of pyrazolinecarbothioamide **1a** with methyl phenylpropynoate **2b** is evidence for the structure of the products of this reaction.

TABLE 2. ^{1}H NMR Spectra of Compounds **3a–h, 4a–5c, 11a,** and **11b** in $CDCl_3$

Compound	Chemical shifts, δ, ppm (*J*, Hz)					
	R	R^1	R^2	CH_3 (3H, s)	H-5 (1H)	H-8
3a	1.75 (6H, s, $2CH_3$)		7.43–7.57 (5H, m, H Ph)	2.11	6.75 (s)	2.88 (2H, s)
3b	1.70 (6H, s, $2CH_3$)		3.79 (3H, s, OCH_3); 6.90 (2H, d, *J* = 8.0, H Ar); 7.47 (2H, d, *J* = 8.0, H Ar)	2.07	6.65 (s)	2.84 (2H, s)
3c	1.68 (6H, s, $2CH_3$)		7.30 (1H, d, *J* = 10.3, H Ar)	2.06	6.50 (d, *J* = 10.3)	2.84 (2H, s)
3d	7.21–7.32 (5H, m, H Ph)	5.78 (1H, dd, *J* = 4.2 and *J* = 11.2)	7.41–7.57 (5H, m, H Ph)	2.17	6.70 (s)	2.85 (1H, dd, *J* = 4.2 and *J* = 18.2); 3.50 (1H, dd, *J* = 11.2 and *J* = 18.2)
3e	7.18–7.30 (5H, m, H Ph)	5.73 (1H, dd, *J* = 4.1 and *J* = 11.5)	7.28 (1H, d, *J* = 10.6)	2.16	6.48 (d, *J* = 10.6)	2.83 (1H, dd, *J* = 4.1 and *J* = 18.3); 3.48 (1H, dd, *J* = 11.5 and *J* = 18.3)
3f	3.65 (3H, c, OCH_3); 6.72 (2H, d, *J* = 8.1, H Ar); 7.04 (2H, d, *J* = 8.1, H Ar)	5.51 (1H, dd, *J* = 2.5 and *J* = 11.4)	7.17 (1H, d, *J* = 10.0)	2.07	6.36 (d, *J* = 10.0)	2.73 (1H, dd, *J* = 2.5 and *J* = 18.4); 3.35 (1H, dd, *J* = 11.4 and *J* = 18.4)
3g	1.70 (6H, s, $2CH_3$)		2.20 (3H, s, CH_3)	2.09	6.34 (s)-	2.86 (2H, s)
3h	1.76 (6H, s, $2CH_3$)		2.40 (3H, s, CH_3); 7.25 (2H, d, *J* = 8.0, H Ar); 7.48 (2H, d, *J* = 8.0, H Ar)	2.13	6.76 (s)	2.90 (2H, s)
4a	1.68 (6H, s, $2CH_3$)		3.79 (3H, s, OCH_3)*	2.10	6.86 (s)	2.95 (2H, s)
4b	7.15–7.31 (5H, m, H Ph)	5.70 (1H, dd, *J* = 3.5 and *J* = 10.5)	3.82 (3H, s, OCH_3)*	2.20	6.86 (s)	2.95 (1H, dd, *J* = 3.5 and *J* = 18.2); 3.60 (1H, dd, *J* = 10.5 and *J* = 18.2)
4c	3.75 (3H, s, OCH_3); 6.81 (2H, d, *J* = 8.5, H Ar); 7.10 (2H, d. *J* = 8.5, H Ar)	5.62 (1H, dd, *J* = 3.3 and *J* = 10.6)	3.80 (3H, s, OCH_3)*	2.20	6.84 (s)	2.94 (1H, dd, *J* = 3.3, *J* = 18.7); 3.57 (1H, dd, *J* = 10.6, *J* = 18.7)
11a	1.32 (6H, s, $2CH_3$)*[2]		3.79 (3H, s, OCH_3)*	2.24	6.87 (s)	2.73 (2H, s)
11b	1.17 (3H, s, CH_3) and 1.30 (3H, s, CH_3)*[2]		3.80 (3H, s, OCH_3)*	—*[3]	6.90 (s)	2.96 (1H, t, *J* = 8.1)

*Signal for CO_2CH_3 group.

*[2]Signals for CH_3 group at atom C-9.

*[3]Multiplets for hydrogen atoms of $(CH_2)_3$ group: 1.65 (2H), 1.98 (1H), 2.13 (1H), 2.52 (1H), 2.75 (1H).

TABLE 3. ^{13}C NMR Spectra for Compounds **3a–h, 4a–c, 11a,b** in $CDCl_3$*

Compound	Chemical shifts, δ, ppm (*J*, Hz)									
	R; R^1	R^2	7-CH_3	C-2	C-4	C-5	C-6	C-7	C-8	C-9
1	2	3	4	5	6	7	8	9	10	11
3a	25.8	126.5; 129.1; 130.6; 136.0	16.3	160.6	171.3 ($^2J_{C(4)-H(5)}$ = 0.8)	115.7	149.5	158.6	52.2	67.0
3b	25.5	55.1; 114.2; 127.4; 127.9; 161.3	15.9	160.2	171.2	113.8	148.8	158.3	53.8	66.6
3c	25.7	—	16.2	160.2 ($^3J_{C(2)-H(6)}$ = 8.5)	169.0 ($^2J_{C(4)-H(5)}$ = 1.1, $^3J_{C(4)-H(6)}$ = 8.9)	118.8 ($^2J_{C(5)-H(6)}$ = 0.9)	135.8 ($^2J_{C(6)-H(5)}$ = 4.1)	158.8	54.2	66.8
3d	125.7; 127.9; 128.9; 140.3	126.4; 129.1; 130.7; 135.6	16.2	160.6	171.1 ($^2J_{C(4)-H(5)}$ = 0.9)	116.2	148.5	160.1	46.5	61.9
3e	125.7; 127.9; 28.9; 140.1	—	16.3	160.1 ($^3J_{C(2)-H(6)}$ = 8.5)	168.9 ($^2J_{C(4)-H(5)}$ = 1.2, $^3J_{C(4)-H(6)}$ = 9.2)	119.6 ($^2J_{C(5)-H(6)}$ = 1.1)	134.4 ($^2J_{C(6)-H(5)}$ = 4.7)	160.1	46.6	61.6
3f	55.2; 114.2; 127.2; 132.3; 160.0	—	16.2	159.2	168.7	119.6	134.2	160.0	46.4	61.2
3g	26.2	22.8	16.6	161.1	171.5 ($^2J_{C(4)-H(5)}$ = 1.2)	116.9	148.0	158.9	54.6	67.2
3h	26.3	21.8; 126.7; 130.2; 133.5; 141.5	16.7	161.1	172.0 ($^2J_{C(4)-H(5)}$ = 1.2)	115.3	150.0	159.1	54.6	67.4

TABLE 3 (continued)

1	2	3	4	5	6	7	8	9	10	11
4a	26.0	52.3; 166.9*[2] ($^3J_{C(10)-H3CO}$ = 3.9, $^2J_{C(10)-H(5)}$ = 1.6)	16.1	172.3	179.4 ($^3J_{C(4)-H(5)}$ = 5.0)	116.4	146.9 ($^2J_{C(6)-H(5)}$ = 1.7)	162.6 ($^2J_{C(7)-H3C}$ = 6.4, $^2J_{C(7)-H2C}$ = 7.3)	54.2	67.4
4b	125.6, 128.4; 29.1, 139.1	52.4; 166.8*[2] ($^3J_{C(10)-H3CO}$ = 3.9, $^2J_{C(10)-H(5)}$ = 1.6)	16.1	173.0	178.7 ($^3J_{C(4)-H(5)}$ = 4.9)	117.2	146.9 ($^2J_{C(6)-H(5)}$ = 1.8)	163.5	47.5	63.5
4c	55.3; 114.4; 127.2; 131.2; 59.6	52.4; 166.8	16.2	172.8	178.8	117.0	147.0	163.7	47.4	63.2
11a	30.7*[3]	52.3; 166.4*[2] ($^3J_{C(10)-H3CO}$ = 3.9, $^2J_{C(10)-H(5)}$ = 1.4)	27.2	141.4	163.2 ($^3J_{C(4)-H(5)}$ = 5.7)	115.3	141.5 ($^2J_{C(6)-H(5)}$ = 1.1)	167.9 ($^2J_{C(7)-H3C}$ = 5.0, $^2J_{C(7)-H2C}$ = 6.5)	48.0	58.0
11b	29.7; 30.0*[3]	52.3; 166.5*[2] ($^3J_{C(10)-H3CO}$ = 4.1, $^2J_{C(10)-H(5)}$ = 1.2)	–*[4]	141.10	162.8 ($^3J_{C(4)-H(5)}$ = 5.7)	115.4	141.4 ($^2J_{C(6)-H(5)}$ = 0.9)	175.4	55.4	60.3

*The J_{C-H} constants were not measured for compounds **3b,f** and **4c**; the $^2J_{C(7)-H3C}$ and $^2J_{C(7)-H2C}$ constants were measured only for compounds **4a** and **11a**; the $^2J_{C(6)-H(5)}$ constants were measured only for compounds **3c,e, 4a,b, 11a,b**; only $^2J_{C(4)-H(5)}$ constants were measured for compounds **3g,h**.

*[2]Signals for the CO_2CH_3 group.

*[3]Signals for the CH_3 groups at C(9) atom.

*[4]The chemical shifts of the carbon atoms of the $(CH_2)_3$ group: 23.8, 24.8, 36.5 ppm.

TABLE 4. IR and UV Spectra of Compounds **3a–h, 4a–c, 11a,b**

Com-pound	IR spectrum, ν, cm^{-1}	UV spectrum, λ_{max}, nm ($\varepsilon \times 10^{-4}$ $l \cdot mol^{-1} \cdot cm^{-1}$)
3a	3095, 2915, 1646, 1624, 1607, 1522, 1449, 1298, 857, 779	205 (1.4), 268 (2.6), 320 (0.8)
3b	3060, 2970, 2918, 2838, 1620, 1602, 1524, 1507, 1447, 1314, 1302, 1254, 1181, 1032, 846	205 (1.5), 270 (2.8), 328 (1.5)
3c	3024, 2968, 2933, 1620, 1593, 1493, 1350, 1315, 1284, 1245, 1155, 1106	258 (2.0), 302 (0.7)
3d	3060, 3032, 1625, 1595, 1572, 1504, 1429, 1304, 1289, 860, 771, 757, 697	206 (2.1), 268 (2.6), 318 (0.8)
3e	3033, 1624, 1594, 1492, 1420, 1358, 1296, 1211, 1115, 892	207 (0.7), 258 (2.4), 300 (0.8)
3f	3035, 2992, 2930, 1626, 1594, 1514, 1492, 1353, 1294, 1251, 1176, 1034, 893, 835	204 (0.7), 231 (0.9), 259 (1.8), 300 (0.6)
3g	3035, 3007, 1631, 1504, 1444, 1412, 1380, 1373, 1302, 1158, 1128, 1102, 1010, 932, 852, 753, 705	240 (2.91), 267 (1.2)
3h	3025, 2979, 2916, 1628, 1598, 1516, 1502, 1412, 1379,1317, 1299,1283, 1256, 1238, 1198, 1160, 962	210 (1.7), 239 (1.2), 270 (2.9), 334 (0.9)
4a	3064, 2988, 1945, 2921, 1691, 1637, 1556, 1366, 1327, 1269, 1241, 1184, 1155, 1005, 877, 770, 715, 576	207 (1.8), 222 (2.1), 256 (2.6), 319 (1.6)
4b	2974, 2952, 2929, 1706, 1695, 1562, 1373,1318, 1234, 1197, 1175, 1004, 767	210 (1.0), 245 (0.3), 327 (1.8)
4c	3070, 2997, 2951, 2840, 1693, 1555, 1515, 1368, 1324, 1246, 1232, 1203, 1170, 1031, 905, 771, 575	205 (0.9), 311 (1.7)
11a	2959, 1738, 1706, 1648, 1603, 1424, 1379, 1325, 1294, 1260, 1198, 1177, 1131, 849, 752, 725, 703, 620	205 (0.7), 225 (0.7), 326 (1.4)
11b	2965, 1730, 1702, 1640, 1613, 1424, 1421, 1305, 1291, 1288, 1173, 1101, 1053, 1020, 902, 843, 730, 710	208 (0.4), 227 (0.6), 334 (1.4)

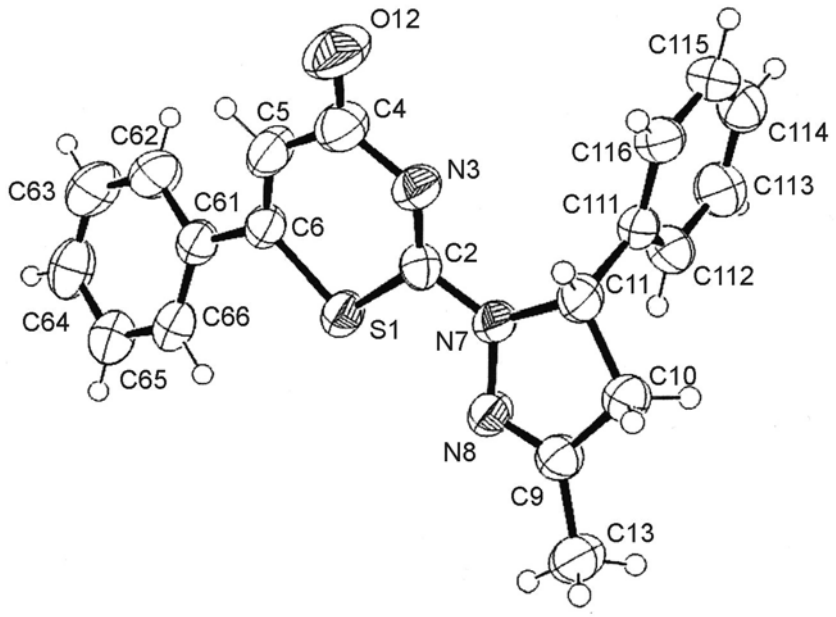


Fig. 1. Molecular structure of 2-(3-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)-6-phenyl-4*H*-1,3-thiazin-4-one (**3d**) from X-ray diffraction crystallographic analysis.

TABLE 5. Bond Lengths (*l*) in Pyrazolylthiazinone **3d**

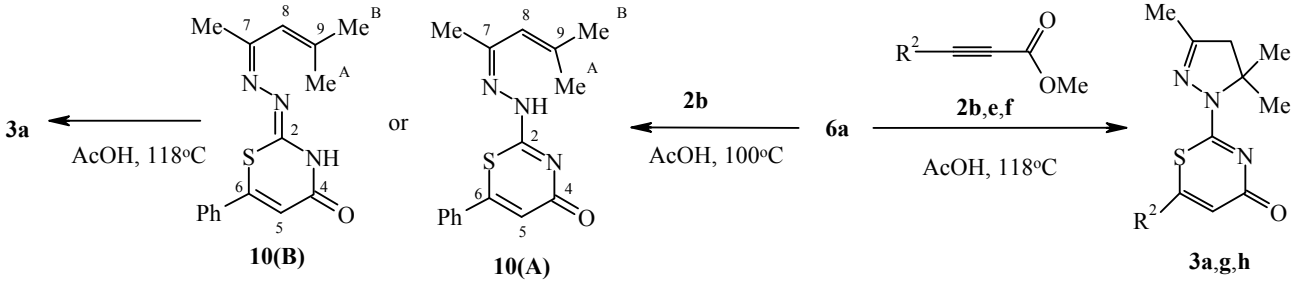
Bond	*l*, Å	Bond	*l*, Å
S(1)–C(6)	1.7453(18)	C(65)–C(66)	1.380(2)
S(1)–C(2)	1.7655(19)	N(7)–N(8)	1.3977(18)
C(2)–N(3)	1.293(2)	N(7)–C(11)	1.480(2)
C(2)–N(7)	1.337(2)	N(8)–C(9)	1.2692(19)
N(3)–C(4)	1.384(2)	C(9)–C(13)	1.486(2)
C(4)–O(12)	1.230(2)	C(9)–C(10)	1.494(2)
C(4)–C(5)	1.463(3)	C(10)–C(11)	1.537(2)
C(5)–C(6)	1.327(2)	C(11)–C(111)	1.505(2)
C(6)–C(61)	1.477(2)	C(111)–C(116)	1.367(2)
C(61)–C(62)	1.385(2)	C(111)–C(112)	1.388(2)
C(61)–C(66)	1.386(2)	C(112)–C(113)	1.379(2)
C(62)–C(63)	1.374(3)	C(113)–C(114)	1.361(3)
C(63)–C(64)	1.364(3)	C(114)–C(115)	1.382(2)
C(64)–C(65)	1.378(2)	C(115)–C(116)	1.390(2)

TABLE 6. Valence Angles (ω) in Pyrazolylthiazinone **3d**

Angle	ω, deg	Angle	ω, deg
C(6)–S(1)–C(2)	99.80(11)	C(2)–N(7)–N(8)	119.83(17)
N(3)–C(2)–N(7)	118.67(18)	C(2)–N(7)–C(11)	124.81(17)
N(3)–C(2)–S(1)	129.11(16)	N(8)–N(7)–C(11)	114.26(14)
N(7)–C(2)–S(1)	112.22(15)	C(9)–N(8)–N(7)	106.91(16)
C(2)–N(3)–C(4)	121.98(19)	N(8)–C(9)–C(13)	123.29(18)
O(12)–C(4)–N(3)	119.2(2)	N(8)–C(9)–C(10)	115.08(18)
O(12)–C(4)–C(5)	120.8(2)	C(13)–C(9)–C(10)	121.63(17)
N(3)–C(4)–C(5)	120.0(2)	C(9)–C(10)–C(11)	103.59(15)
C(6)–C(5)–C(4)	127.5(2)	N(7)–C(11)–C(111)	110.72(15)
C(5)–C(6)–C(61)	124.69(19)	N(7)–C(11)–C(10)	99.95(14)
C(5)–C(6)–S(1)	121.43(18)	C(111)–C(11)–C(10)	114.46(15)
C(61)–C(6)–S(1)	113.88(15)	C(116)–C(111)–C(112)	118.98(19)
C(62)–C(61)–C(66)	117.2(2)	C(116)–C(111)–C(11)	120.6(2)
C(62)–C(61)–C(6)	120.1(2)	C(112)–C(111)–C(11)	120.42(19)
C(66)–C(61)–C(6)	122.67(19)	C(113)–C(112)–C(111)	120.5(2)
C(63)–C(62)–C(61)	120.8(2)	C(114)–C(113)–C(112)	120.3(2)
C(64)–C(63)–C(62)	121.4(2)	C(113)–C(114)–C(115)	119.9(2)
C(63)–C(64)–C(65)	119.2(2)	C(114)–C(115)–C(116)	119.8(2)
C(64)–C(65)–C(66)	119.5(2)	C(111)–C(116)–C(115)	120.5(2)
C(65)–C(66)–C(61)	122.0(2)		

TABLE 7. Torsion Angles (φ) in Pyrazolylthiazinone **3d**

Angle	φ, deg	Angle	φ, deg
C(6)–S(1)–C(2)–N(3)	2.9(2)	N(3)–C(2)–N(7)–C(11)	–3.0(3)
C(6)–S(1)–C(2)–N(7)	–176.43(13)	S(1)–C(2)–N(7)–C(11)	176.37(13)
N(7)–C(2)–N(3)–C(4)	179.91(17)	C(2)–N(7)–N(8)–C(9)	–163.93(17)
S(1)–C(2)–N(3)–C(4)	0.6(3)	C(11)–N(7)–N(8)–C(9)	4.7(2)
C(2)–N(3)–C(4)–O(12)	174.7(2)	N(7)–N(8)–C(9)–C(13)	177.84(16)
C(2)–N(3)–C(4)–C(5)	–4.0(3)	N(7)–N(8)–C(9)–C(10)	–2.7(2)
O(12)–C(4)–C(5)–C(6)	–175.6(2)	N(8)–C(9)–C(10)–C(11)	–0.1(2)
N(3)–C(4)–C(5)–C(6)	3.1(3)	C(13)–C(9)–C(10)–C(11)	179.41(16)
C(4)–C(5)–C(6)–C(61)	–178.97(18)	C(2)–N(7)–C(11)–C(111)	–75.5(2)
C(4)–C(5)–C(6)–S(1)	1.2(3)	N(8)–N(7)–C(11)–C(111)	116.58(17)
C(2)–S(1)–C(6)–C(5)	–3.53(19)	C(2)–N(7)–C(11)–C(10)	163.50(17)
C(2)–S(1)–C(6)–C(61)	176.62(13)	N(8)–N(7)–C(11)–C(10)	–4.47(19)
C(5)–C(6)–C(61)–C(62)	23.5(3)	C(9)–C(10)–C(11)–N(7)	2.58(18)
S(1)–C(6)–C(61)–C(62)	–156.62(14)	C(9)–C(10)–C(11)–C(111)	–115.74(18)
C(5)–C(6)–C(61)–C(66)	–155.5(2)	N(7)–C(11)–C(111)–C(116)	120.17(18)
S(1)–C(6)–C(61)–C(66)	24.4(2)	C(10)–C(11)–C(111)–C(116)	–127.80(18)
C(66)–C(61)–C(62)–C(63)	1.9(3)	N(7)–C(11)–C(111)–C(112)	–60.6(2)
C(6)–C(61)–C(62)–C(63)	–177.14(19)	C(10)–C(11)–C(111)–C(112)	51.4(2)
C(61)–C(62)–C(63)–C(64)	–0.7(3)	C(116)–C(111)–C(112)–C(113)	–0.3(3)
C(62)–C(63)–C(64)–C(65)	–0.9(3)	C(11)–C(111)–C(112)–C(113)	–179.54(17)
C(63)–C(64)–C(65)–C(66)	1.3(3)	C(111)–C(112)–C(113)–C(114)	0.6(3)
C(64)–C(65)–C(66)–C(61)	–0.1(3)	C(112)–C(113)–C(114)–C(115)	–0.2(3)
C(62)–C(61)–C(66)–C(65)	–1.5(3)	C(113)–C(114)–C(115)–C(116)	–0.4(3)
C(6)–C(61)–C(66)–C(65)	177.53(17)	C(112)–C(111)–C(116)–C(115)	–0.3(3)
N(3)–C(2)–N(7)–N(8)	164.32(16)	C(11)–C(111)–C(116)–C(115)	178.93(16)
S(1)–C(2)–N(7)–N(8)	–16.3(2)	C(114)–C(115)–C(116)–C(111)	0.7(3)



2b, **3a** R^2 = Ph; **2e**, **3g** R^2 = Me; **2f**, **3h** R^2 = 4-MeC_6H_4

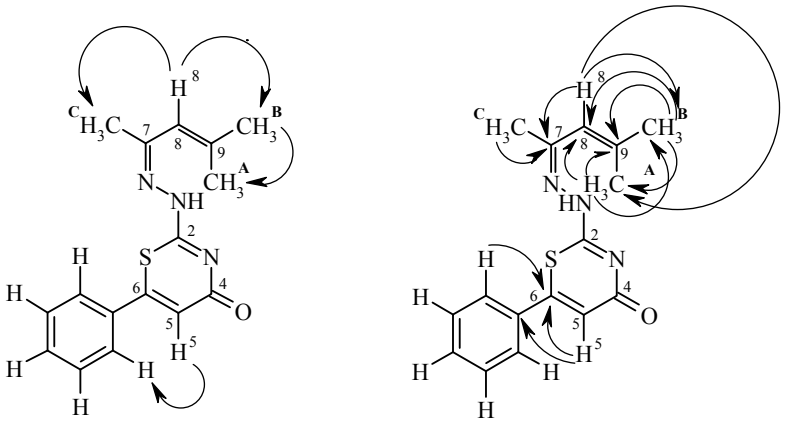
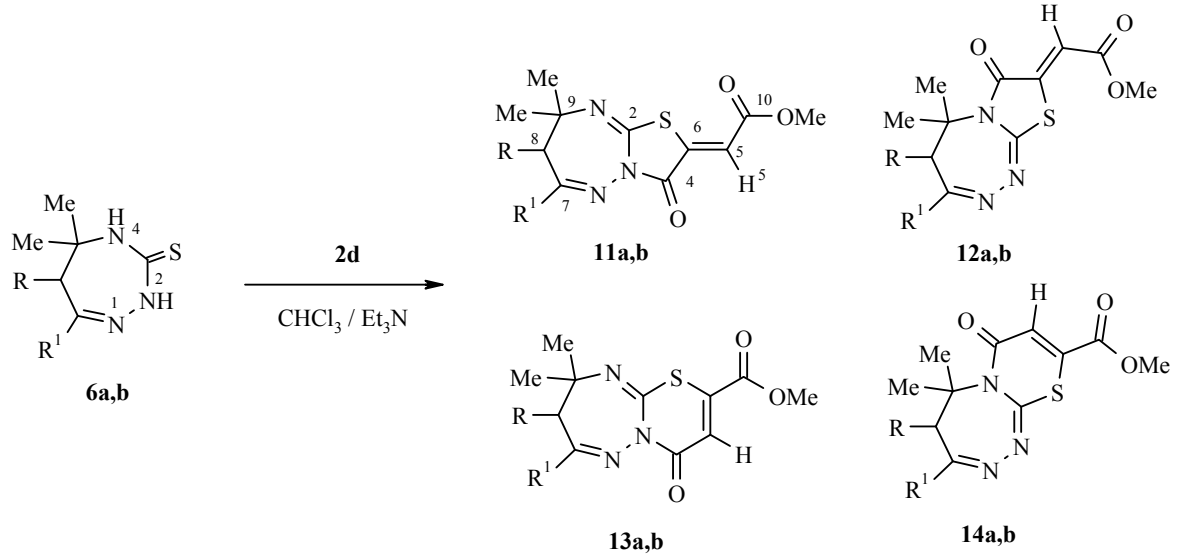


Fig. 2. Correlations in the NOESY and COLOC spectra of tautomeric form **A** of compound **10**. The correlations shown are identical for both tautomeric forms **A** and **B**.

Heating triazepinethione **6a** with ester **2b** in acetic acid at only 100°C permitted isolation of the intermediate product formed upon opening of the seven-membered ring, thiazinone **10**, which exists in solution in one of tautomeric forms **A** or **B**. Thin-layer chromatography indicated that heating intermediate **10** in acetic acid at reflux leads to pyrazolylthiazinone **3a**. The formation of thiazinone **10** suggests that opening of the triazepine ring occurs at the N(4)–C(5) bond, and closing of the pyrazoline ring occurs by forming of N(2)–C(5) bond. On the other hand, in the absence of ester **2b**, opening of the ring in triazepinethione **6a** in acetic acid at reflux does not occur.

The signals of the three methyl groups and H-8, and C(8) atoms are characteristic one in the ^{1}H and ^{13}C NMR spectra of thiazinone **10**. The correlations found in its NOESY and COLOC spectra (Fig. 2) permit an unequivocal assignment of the signals of all the protons and carbon atoms (the correlations between the benzene ring atoms are not shown).

It should be noted that there is no cross peak for atoms H-5 and C(4) in the COLOC spectrum, which may be the result of a low value of the $^{2}J_{C(4)–H(5)}$ coupling constant, characteristic for 1,3-thiazin-4-ones (Table 2 [23]). Thus, the signals for C(4) and C(2) atoms were assigned assuming that the signals for C(4) atom in 1,3-thiazin-4-one derivatives are always observed at lower field than the signals of C(2) atom (Table 2 [23]).



6, **11–14** **a** R = H, R^1 = Me; **b** R + R^1 = $(CH_2)_3$

Since there are no correlations in the NOESY and COLOC spectra for the hydrogen atom of the NH group, we cannot unequivocally determine which of the tautomeric forms (**A** or **B**) exists for thiazine **10** in solution. Furthermore, these spectra do not shed light on the configuration of the exocyclic C=N bond. However, we note that closure of the pyrazoline ring is possible only when it has (*Z*)-configuration, which is reflected in the structure of **10**.

On the other hand, by replacing the acetylenemonocarboxylic acid esters by DMAD **2d**, we were able to obtain bicyclic condensed systems containing the triazepine ring. Thus, the reaction of triazepinethiones **6a,b** with DMAD **2d** proceeds at N(2) atom through 5-*exo*-dig cyclization. Only thiazolotriazepines **11a,b** are formed from the four possible products of this reaction **11–14**.

This reaction course was confirmed by the X-ray crystallographic structural analysis of compound **11a** (Tables 8-10, Fig. 3).

It should be noted that the ^{1}H and ^{13}C NMR spectra of isomeric thiazolotriazepine **11a** and *N*-thiazolylpyrazolidine **4a** are extremely similar. The only significant difference between the spectra of these compounds is the position of the signal for C(2) atom in the ^{13}C NMR spectra (Table 3). Thus, this signal is found for thiazolotriazepine **11a** at 141.4 ppm, while it is found for isomer **4a** downfield by ~30 ppm at 172.3 ppm. Such a downfield shift for the signal of C(2) atom in pyrazoline derivatives **3a–h** and **4a–c** relative to the signal of this atom in the spectra of triazepine derivatives **11** is a general phenomenon and may be used to prove the structure of these heterocycles.

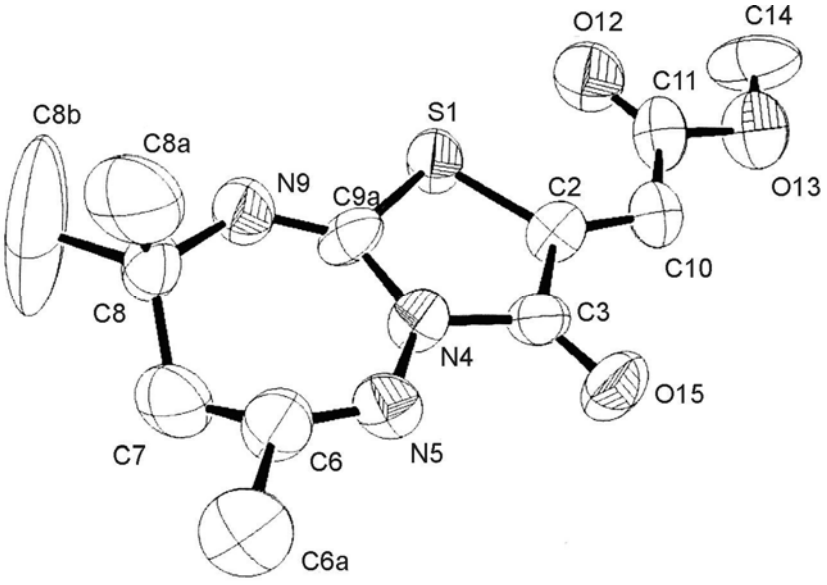


Fig. 3. Molecular structure of methyl (6,8,8-trimethyl-3-oxo-7,8-dihydro[1,3]thiazolo-[3,2-*b*][1,2,4]triazepin-2-(3*H*)-ylidene)acetate (**11a**) according to X-ray crystallographic structural analysis.

Thus, we are the first to observe that the condensation of 5,5,7-trimethyl-2,4,5,6-tetrahydro-3*H*-1,2,4-triazepine-3-thione with methyl propynoates is accompanied by opening of the triazepine ring and its recyclization to give a pyrazoline ring, leading to 2-pyrazolinyl-1,3-thiazines. The reaction of triazepinethiones with DMAD, in contrast to the reactions with methyl propynoates, proceeds with retention of the seven-membered ring and may serve as a method for the synthesis of new thiazolotriazepine derivatives. The reaction of pyrazolinecarbothioamides with esters of acetylenemonocarboxylic acids is a convenient method for the synthesis of 2-pyrazolinyl-1,3-thiazines, while the reaction with DMAD is a convenient method for the synthesis of *N*-thiazolylpyrazolidines.

TABLE 8. Bond Lengths (*l*) in Thiazolotriazepine **11a**

Bond	*l*, Å	Bond	*l*, Å
S(1)–C(2)	1.715(5)	C(6)–C(7)	1.552(5)
S(1)–C(9a)	1.785(5)	C(7)–C(8)	1.516(11)
C(2)–C(10)	1.334(7)	C(8)–N(9)	1.469(7)
C(2)–C(3)	1.500(7)	C(8)–C(8b)	1.527(5)
C(3)–O(15)	1.190(6)	C(8)–C(8a)	1.539(5)
C(3)–N(4)	1.398(6)	N(9)–C(9a)	1.265(7)
N(4)–C(9a)	1.395(7)	C(10)–C(11)	1.507(9)
N(4)–N(5)	1.396(6)	C(11)–O(12)	1.190(4)
N(5)–C(6)	1.243(7)	C(11)–O(13)	1.318(7)
C(6)–C(6a)	1.488(8)	O(13)–C(14)	1.470(10)

TABLE 9. Valence Angles (ω) in Thiazolotriazepine **11a**

Angle	ω, deg	Angle	ω, deg
C(2)–S(1)–C(9a)	92.4(2)	N(9)–C(8)–C(7)	111.8(6)
C(10)–C(2)–C(3)	121.8(5)	N(9)–C(8)–C(8b)	103.5(6)
C(10)–C(2)–S(1)	126.7(4)	C(7)–C(8)–C(8b)	117.6(11)
C(3)–C(2)–S(1)	111.4(3)	N(9)–C(8)–C(8a)	111.4(8)
O(15)–C(3)–N(4)	125.5(5)	C(7)–C(8)–C(8a)	111.6(7)
O(15)–C(3)–C(2)	124.5(5)	C(8b)–C(8)–C(8a)	100.2(14)
N(4)–C(3)–C(2)	109.9(4)	C(9a)–N(9)–C(8)	122.4(5)
C(9a)–N(4)–N(5)	129.7(4)	N(9)–C(9a)–N(4)	134.7(5)
C(9a)–N(4)–C(3)	116.0(4)	N(9)–C(9a)–S(1)	114.9(4)
N(5)–N(4)–C(3)	114.0(4)	N(4)–C(9a)–S(1)	110.2(4)
C(6)–N(5)–N(4)	122.5(5)	C(2)–C(10)–C(11)	118.3(5)
N(5)–C(6)–C(6a)	118.1(6)	O(12)–C(11)–O(13)	124.3(6)
N(5)–C(6)–C(7)	121.3(7)	O(12)–C(11)–C(10)	123.5(5)
C(6a)–C(6)–C(7)	113.6(7)	O(13)–C(11)–C(10)	111.8(5)
C(8)–C(7)–C(6)	108.4(7)	C(11)–O(13)–C(14)	111.6(6)

EXPERIMENTAL

The IR spectra were taken on an FSM 1201 spectrometer for KBr pellets. The electronic spectra were taken on an SF-2000 spectrometer for solutions in ethanol. The ^{1}H and ^{13}C NMR spectra were taken on a Bruker AM 500 spectrometer at 500 and 125 MHz, respectively, in DMSO-d_6 (for compounds **6b** and **7**) or $CDCl_3$ (for compound **10**). The chemical shifts are given relative to the signals of the residual protons (δ 7.28 and 2.50 ppm) or carbon atoms (δ 77.16 and 39.52 ppm, respectively) of the solvents. The COLOC spectrum

TABLE 10. Torsion Angles (φ) in Thiazolotriazepine **11a**

Angle	φ, deg	Angle	φ, deg
C(9a)–S(1)–C(2)–C(10)	–176.9(12)	C(6)–C(7)–C(8)–C(8a)	–47.0(7)
C(9a)–S(1)–C(2)–C(3)	0.1(10)	C(7)–C(8)–N(9)–C(9a)	–40.8(14)
C(10)–C(2)–C(3)–O(15)	–5(2)	C(8b)–C(8)–N(9)–C(9a)	–168.4(17)
S(1)–C(2)–C(3)–O(15)	178.1(13)	C(8a)–C(8)–N(9)–C(9a)	84.8(13)
C(10)–C(2)–C(3)–N(4)	179.3(11)	C(8)–N(9)–C(9a)–N(4)	7(2)
S(1)–C(2)–C(3)–N(4)	2.1(14)	C(8)–N(9)–C(9a)–S(1)	–179.2(8)
O(15)–C(3)–N(4)–C(9a)	179.9(14)	N(5)–N(4)–C(9a)–N(9)	–9(2)
C(2)–C(3)–N(4)–C(9a)	–4.1(15)	C(3)–N(4)–C(9a)–N(9)	178.1(14)
O(15)–C(3)–N(4)–N(5)	6(2)	N(5)–N(4)–C(9a)–S(1)	177.4(9)
C(2)–C(3)–N(4)–N(5)	–178.4(9)	C(3)–N(4)–C(9a)–S(1)	4.2(12)
C(9a)–N(4)–N(5)–C(6)	9.6(19)	C(2)–S(1)–C(9a)–N(9)	–177.6(10)
C(3)–N(4)–N(5)–C(6)	–177.1(12)	C(2)–S(1)–C(9a)–N(4)	–2.3(8)
N(4)–N(5)–C(6)–C(6a)	178.3(10)	C(3)–C(2)–C(10)–C(11)	179.3(11)
N(4)–N(5)–C(6)–C(7)	29.3(18)	S(1)–C(2)–C(10)–C(11)	–4(2)
N(5)–C(6)–C(7)–C(8)	–78.3(12)	C(2)–C(10)–C(11)–O(12)	9(2)
C(6a)–C(6)–C(7)–C(8)	131.5(8)	C(2)–C(10)–C(11)–O(13)	–177.7(12)
C(6)–C(7)–C(8)–N(9)	78.4(8)	O(12)–C(11)–O(13)–C(14)	–10(2)
C(6)–C(7)–C(8)–C(8b)	–162.0(11)	C(10)–C(11)–O(13)–C(14)	176.6(12)

optimized relative to the constant $J_{C–H}$ = 8 Hz of the solution of 1,3-thiazine **10** in $CDCl_3$ and the NOESY spectrum (mixing time 0.6 sec) of this solution was obtained on a Bruker DPX 300 spectrometer at 75 and 300 MHz, respectively. The high-resolution ESI mass spectra were taken on a Bruker MicrOTOF mass spectrometer with recording of the positive ions. Methanol served as the solvent. The ionizing additive was formic acid. The capillary voltage was 4500 V. The course of the reactions and purity of the products were monitored by thin-layer chromatography on Sorbfil plates using 10:5:5:1 hexane–acetone–chloroform–ethanol as the eluent.

3-Methyl-4,5-dihydro-1H-pyrazole-1-carbothiamides **1a–c** [24, 25], methyl esters of propionic acids **2b,c,e,f** [26], and 5,5,7-trimethyl-2,4,5,6-tetrahydro-3*H*-1,2,4-triazepine-3-thione **6a** [22] were obtained according to reported procedures. Methyl propynoate **2a** and DMAD **2d** obtained from Sigma-Aldrich were used without further purification.

X-ray diffraction crystallographic analysis of monocrystals 3d and 11a grown from solutions in ethanol was carried out on a Bruker SMART 1000 CCD using MoKα radiation. Unit cell parameters for monoclinic crystals of **compound 3d** ($C_{20}H_{17}N_3OS$): space group $P2_1/n$, a = 9.082(2), b = 10.811(2), c = 17.789(4) Å, β = 104.58(3)°, Z = 4, D_x = 1.365 g/cm^3, R_1 = 0.0353 ($I > 2\sigma I$), wR_2 = 0.0471, for 3712 nonzero independent reflections. Unit cell parameters for orthorhombic crystals of **compound 11a** ($C_{12}H_{15}N_3O_3S$), space group $Pn2_1a$, a = 15.012(3), b = 6.7740(10), c = 13.627(3), Z = 4, D_x =1.348 g/cm^3, R_1 = 0.0949, [$I > 2\sigma(I)$], wR_2 = 0.2273 for 2516 nonzero independent reflections, The full set of X-ray diffraction crystallographic data for compounds **3d** and **11a** was deposited in the Cambridge Crystallographic Data Center (CCDC deposits 762050 and 762051, respectively).

2-(4,5-Dihydro-1*H*-pyrazol-1-yl)-4*H*-1,3-thiazin-4-ones 3a–h. A. Ester **2a–c** (3 mmol) was added to a solution 4,5-dihydropyrazol-1-ylcarbothioamide **1a–c** (3 mmol) in glacial acetic acid (15 ml). The mixture was heated at reflux. Completion of the reaction was determined by thin-layer chromatography as indicated by disappearance of the starting compounds. Acetic acid was removed at reduced pressure. The residue was recrystallized twice to give products **3a–f**.

B. Ester **2b,e,f** (3 mmol) was added to a solution of compound **6a** (513 mg, 3 mmol) in acetic acid (15 ml). The mixture was heated at reflux for 15 h. Acetic acid was removed at reduced pressure. The residue was subjected to chromatography on silica gel using 30:1 dichloromethane–methanol as the eluent. The isolated products were recrystallized to give **3a,g,h**.

Methyl Esters of (2*Z*)-[2-(3-Methyl-4,5-dihydro-1*H*-pyrazol-1-yl)-4-oxo-1,3-thiazol-5(4*H*)-ylidene]-acetic Acids 4a–c. A. A solution of DMAD **2d** (284 mg, 2 mmol) in chloroform (5 ml) was added with stirring to a solution of 4,5-dihydropyrazole-1-carbothioamide **1a–c** (2 mmol) in a mixture of chloroform (20 ml) and triethylamine (0.28 ml, 2 mmol). The reaction mixture was maintained for 48 h at room temperature. The solvent was removed at reduced pressure. The residue was recrystallized.

B. A solution of ester **2d** (284 mg, 2 mmol) in acetic acid (5 ml) was added with stirring to a solution of 4,5-dihydropyrazole-1-carbothioamide **1c** (498 mg, 2 mmol) in acetic acid (20 ml). The reaction mixture was maintained for 48 h at room temperature. The solvent was removed at reduced pressure. The precipitate obtained was washed with ethanol (2x5 ml) and recrystallized from butan-1-ol.

5,5-Dimethyl-4,4,5a,6,7,8-hexahydrocyclopenta[*f*][1,2,4]triazepine-3(2*H*)-thione (6b). A solution of concentrated sulfuric acid (0.50 g, 5 mmol, 0.27 ml) in water (1 ml) was added with stirring to 2-(1-methylethylidene)cyclopentanone (1.24 g, 10 mmol) [27] at 15°C. A solution of ammonium thiocyanate (0.76 g, 10 mmol) in water (2 ml) was added to the mixture obtained. The reaction mixture was stirred for 2 h at room temperature. The upper oily layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic fractions were washed with water until the wash water was neutral and then dried over sodium sulfate. The solvent was removed at reduced pressure to give 1.24 g (68%) 2-(1-isothiocyanato-1-methylethyl)cyclopentanone, which was used without further purification.

10% Aqueous sodium hydroxide (2.5 ml) was added to a vigorously-stirred mixture of 2-(1-isothiocyanato-1-methylethyl)cyclopentanone (1.24 g, 6.8 mmol) and hydrazine hydrate (0.34 g, 6.8 mmol, 0.33 ml) in water (10 ml). The reaction mixture was stirred for 10 h at room temperature. The precipitate formed was filtered off and recrystallized from methanol to give 0.54 g (40%) previously unreported triazepinethione **6b**; mp 225–228°C; R_f 0.53. IR spectrum, ν, cm^{-1}: 3222, 3183, 3139, 3099, 2989, 2957, 1688, 1566, 1545, 1477, 1384, 1367, 1288, 1238, 1198, 1147, 1116, 1007, 766, 677. ^{1}H NMR spectrum, δ, ppm: 1.05 (3H, s, CH_3); 1.20 (3H, s, CH_3); 1.53 (2H, m, CH_2); 1.77 (1H, m) and 1.97 (1H, m, CH_2); 2.34 (2H, m, CH_2); 2.72 (1H, m, CH); 8.29 (1H, s, NH); 10.26 (1H, s, NH). ^{13}C NMR spectrum, δ, ppm: 23.1; 24.4; 27.5; 28.5; 34.5; 52.9; 57.7; 165.9; 175.3. Found: *m/z* 198.1069 $[M+H]^+$. $C_9H_{16}N_3S$. Calculated: *m/z* 198.1065.

Methyl Ester of (*Z*)-3-[(5,5,7-Trimethyl-5,6-dihydro-2*H*-1,2,4-triazepin-3-yl)sulfanyl]-3-phenyl-acrylic Acid (7). Methyl phenylpropynoate (**2b**) (0.16 g, 1 mmol) was added to a suspension of 1,2,4-triazepine-3-thione **6a** (171 mg, 1 mmol) in a mixture of methanol (20 ml) and 1 M solution of MeONa in methanol (0.1 ml) and heated at reflux for 10 h. The solvent was removed at reduced pressure to half of the initial volume. The precipitate formed was filtered off and recrystallized from ethanol to give 109 mg (33%) ester **7**; mp 167–170°C; R_f 0.59. IR spectrum, ν, cm^{-1}: 3198, 3022, 2977, 2950, 1721, 1714, 1634, 1534, 1453, 1428, 1274, 1265, 1192, 1164, 942, 853, 769. UV spectrum, λ_{max}, nm (ε·10^{-4} l/mol·cm): 206 (1.0), 222 (0.6), 276 (1.3). ^{1}H NMR spectrum, δ, ppm: 1.35 (6H, s, $2CH_3$); 2.02 (3H, s, CH_3); 2.49 (2H, s, CH_2); 3.67 (3H, s, OCH_3); 6.40 (1H, s, CH); 7.38 (3H, m, H Ar); 7.58 (2H, m, H Ar); 8.25 (1H, s, NH). ^{13}C NMR spectrum, δ, ppm: 25.2; 29.2; 42.4; 51.1; 61.6; 113.6; 127.5; 128.1; 129.4; 135.2; 153.6; 163.9; 168.0; 177.9. Found: *m/z* 332.1436 $[M+H]^+$. $C_{17}H_{22}N_3O_2S$. Calculated: *m/z* 332.1433.

2-[2-(1,3-Dimethylbut-2-en-1-ylidene)hydrazine]-6-phenyl-4*H*-1,3-thiazin-4-one (10). Ester **2b** (1.76 g, 11 mmol) was added to 1,2,4-triazepine-3-thione **6a** (1.71 g, 10 mmol) in acetic acid (50 ml). The mixture was maintained for 8 h at 97–100°C. The solvent was removed at reduced pressure. The residue was recrystallized from ethanol (5 ml) to give 0.9 g (30%) thiazinone **10**; mp 158–159°C; R_f 0.65. IR spectrum, ν, cm^{-1}: 3118, 3023, 2957, 2829, 1645, 1630, 1581, 1570, 1549, 1489, 1372, 1301, 1239, 1226, 841, 762, 700. ^{1}H NMR spectrum, δ, ppm: 1.93 (3H, s, 9-CH_3(**B**)); 2.12 (3H, s, 9-CH_3(**A**)); 2.15 (3H, s, 7-CH_3); 5.85 (1H, s, H-8); 6.52 (1H, s, H-5); 7.47–7.61 (5H, m, Ph); 9.48 (1H, s, NH). ^{13}C NMR spectrum, δ, ppm: 19.4 (7-CH_3);

21.9 (9-CH_3(**B**)); 28.4 (9-CH_3(**A**)); 114.7 (C-5); 124.5 (C-8); 126.8 and 129.3 (C-*o*,*m*); 131.6 (C-*p*); 136.0 (C-*i*); 144.9 (C-9); 152.8 (C-6); 153.3 (C-2); 163.5 (C-4); 163.5 (C-7). Found: *m/z* 300.1173 $[M+H]^+$. $C_{16}H_{18}N_3OS$. Calculated: *m/z* 300.1171.

Methyl Esters of (2*Z*)-(8,8-Dimethyl-3-oxo-7,8-dihydro[1,3]thiazolo[3,2-*b*][1,2,4]triazepin-2(3*H*)-ylidene)acetic Acids 11a,b. A solution of DMAD **2d** (0.284 g, 2 mmol) in chloroform (5 ml) was added to a solution of 1,2,4-triazepine-3-thione **6a** or **6b** (2 mmol) in a mixture of chloroform (20 ml) and triethylamine (0.28 ml, 2 mmol). The reaction mixture was maintained with vigorous stirring for 48 h at room temperature. The solvent was removed at reduced pressure and the residue was recrystallized from ethanol.

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