Russian Journal of Organic Chemistry, Vol. 40, No. 4, 2004, pp. 534–542. Translated from Zhurnal Organicheskoi Khimii, Vol. 40, No. 4, 2004, pp. 564–571.
Original Russian Text Copyright © 2004 by Mamedov, Gubaidullin, Nurkhametova, Litvinov, Levin.

Fused Polycyclic Nitrogen-Containing Heterocycles: VIII.* Friedel–Crafts Intramolecular Cyclization of 5-Phenylthiazole-4-carboxylic Acids—A New Route to Indeno[2,1-*d*]thiazoles

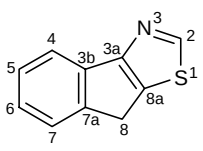
V. A. Mamedov, A. T. Gubaidullin, I. Z. Nurkhametova, I. A. Litvinov, and Ya. A. Levin

Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, ul. Arbuzova 8, Kazan, 420088 Tatarstan, Russia
e-mail: mamedov@iopc.kcn.ru

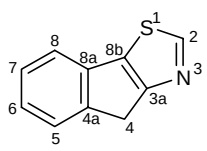
Received May 6, 2002

Abstract—Friedel–Crafts intramolecular cyclization in the presence of polyphosphoric acid of 2-substituted 5-phenylthiazole-4-carboxylic acids, which are obtained by alkaline hydrolysis of the corresponding esters, leads to indeno[2,1-*d*]thiazoles. According to the X-ray diffraction data, packing of their molecules in crystal is determined mainly by intermolecular π–π contacts, regardless of the substituent nature.

Compounds of the thiazole and benzothiazole series possess a variety of useful properties, in particular pharmacological activity. They are widely used as vulcanization accelerators and antioxidants [2], photochromic compounds [3], and dyes, as well as in manufacture of polymeric materials [4]. Unlike thiazoles and benzothiazoles, specific structural features of indenothiazoles, arising from the existence of skeletal isomers, make them convenient models for solving not only practical but also theoretical problems. However, not all theoretically possible structural isomers of indenothiazoles, differing by mutual arrangement of the thiazole ring and indene system, have been studied in sufficient detail. For example, only a few published data are available on indeno[2,1-*d*]thiazoles [5, 6], in contrast to isomeric indeno[1,2-*d*]thiazoles for which not only various simple synthetic procedures have been developed but also some practical aspects have been explored [4]. Presumably, the reason is that most known methods for the preparation of indenothiazoles are based on fusion of a thiazole ring to indene derivatives [7–12] rather than *vice versa*.



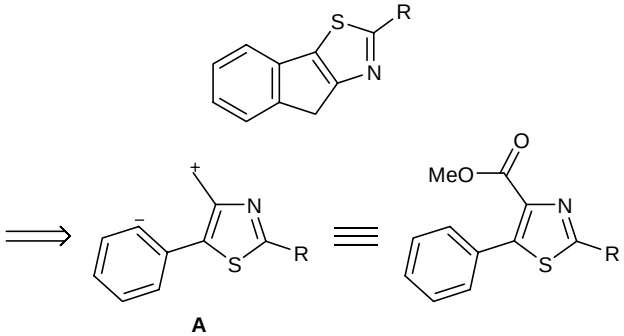
8*H*-Indeno[1,2-*d*]thiazole



4*H*-Indeno[2,1-*d*]thiazole

Retrosynthetic approach [13, 14], which was successfully applied by us to the synthesis of various fused heterocyclic systems, showed that the indeno[2,1-*d*]thiazole structure could be built up from thiazole derivatives through synthon **A** (Scheme 1); equivalents of the latter are accessible 2-substituted 5-phenylthiazole-4-carboxylic acid esters [15, 16].

Scheme 1.

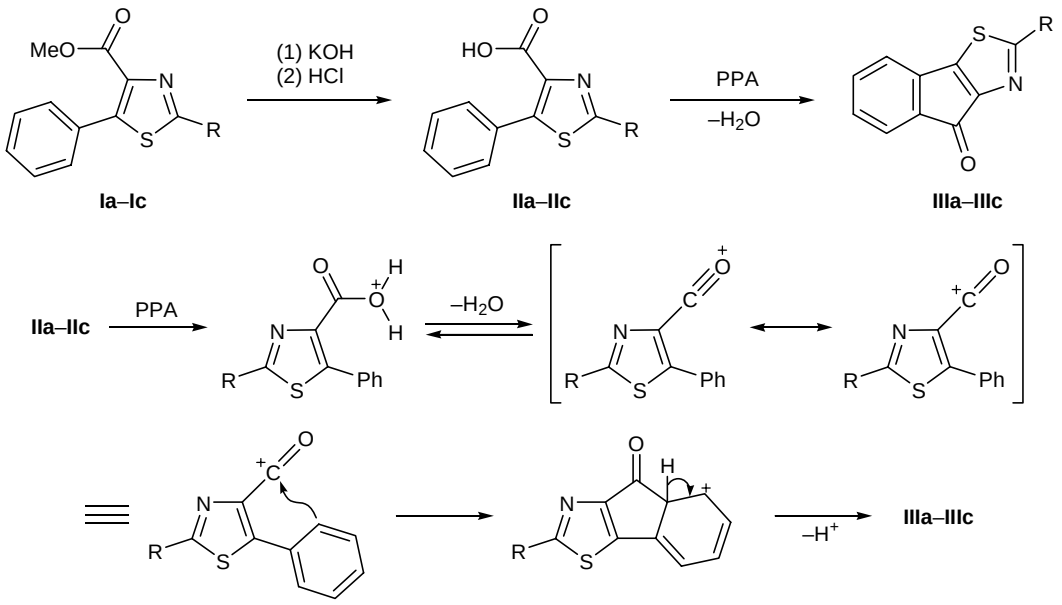


A

The location of the ester and phenyl groups at C^4 and C^5 of the thiazole ring, respectively, is spatially favorable for their interaction. However, such interaction requires that at least one of these groups be

* For communication VII, see [1].

Scheme 2.



I–III, R = H (**a**), Me (**b**), Ph (**c**).

activated. In the present work we effected conversion of 2-substituted 5-phenylthiazole-4-carboxylic acid esters **Ia**–**Ic** into the corresponding acids and intramolecular cyclization of the latter through highly electrophilic acyl cation which was generated *in situ* by the action of polyphosphoric acid (PPA).

Alkaline hydrolysis of methyl 5-phenylthiazole-4-carboxylates **Ia**–**Ic** in a boiling aqueous–methanolic solution of potassium hydroxide in 2 h afforded thiazole-4-carboxylic acids **IIa**–**IIc**. The latter were subjected to intramolecular acylation according to Friedel–Crafts [17] in the presence of PPA to obtain indeno[2,1-*d*]thiazol-4-ones **IIIa**–**IIIc** (Scheme 2). The structure of products **IIIa**–**IIIc** follows from the data of IR and NMR (^{1}H and ^{13}C) spectroscopy (Tables 1 and 2). The IR specta of **IIIa**–**IIIc** lack absorption

Table 1. IR (mineral oil) and ^{1}H NMR spectra [CD_3OD–$(CD_3)_2CO$, 1:1] of compounds **IIa**–**IIc** and **IIIa**–**IIIc**

Comp. no.	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm (*J*, Hz)
IIa	3080, 3000–2500 (a series of bands), 1690 (C=O), 970, 945, 860	7.27–7.63 m (5H, C_6H_5), 8.95 s (1H, thiazole)
IIb	3050–2500 (a series of bands), 1700 br (C=O), 1580, 1480, 1440, 1380, 1310, 1300, 1280, 1245, 1210, 1130, 980, 935	2.67 s (3H, CH_3), 7.21–7.57 m (5H, C_6H_5)
IIc	3150–2450 (a series of bands), 1690 (C=O), 1620, 1610, 1590, 1525, 1445, 1350, 1320, 1285, 1260, 1225, 1085, 1005, 925	7.23–8.37 m (10H, $2C_6H_5$)
IIIa	3070 (narrow band), 1710 (C=O), 1600, 1350, 1290, 1250, 1160, 1080, 980, 890, 830, 810, 755, 720	7.30–7.51 m (4H, C_6H_4), 9.10 s (1H, thiazole)
IIIb	1705 (C=O), 1600, 1495, 1350, 1155, 1030, 860, 765, 725	2.75 s (3H, CH_3), 7.12 d (1H, 5-H or 8-H, *J* = 7.63), 7.22 d.d.d (1H, 6-H or 7-H, *J* = 7.62, 7.00, 1.27), 7.36 d.d.d (1H, 7-H or 6-H, *J* = 7.52, 7.62, 1.28), 7.43 d (1H, 8-H or 5-H, *J* = 7.63)
IIIc	1710 (C=O), 1600, 1355, 1160, 1085, 1035, 1015, 935, 860	7.30–8.05 m (7H, C_6H_4 + C_6H_5)

Table 2. ^{13}C NMR spectra of indeno[2,1-*d*]thiazol-4-ones **IIIa**–**IIIc** (DMSO–DMSO-d_6, 4:1), δ_C, ppm (*J*, Hz)

Comp. no.	C^2	C^{3a}	C^4	C^{4a}	C^5 or C^8
IIIa	159.05 d (*J* = 219.6)	155.12 br.s	184.29 br.s	135.26 d.d.d.d (*J* = 8.9, 8.2, 1.5, 1.2)	138.88 d.d (*J* = 163.9, 7.4), 129.76 d.d (*J* = 65.9, 6.7)
IIIb	171.10 q (*J* = 7.5)	155.21 br.s	184.30 d (*J* = 5.7)	135.88 d.d.d (*J* = 7.7, 7.6, 1.1)	129.51 d.d (*J* = 165.1, 6.8), 134.73 d.d (*J* = 163.1, 6.8)
IIIc	173.09 d.d.d (*J* = 5.2, 4.0, 1.3)	157.74 s	185.58 br.d (*J* = 2.9)	136.83 d.d.d (*J* = 7.8, 7.6, 1.6)	136.07 d.d (*J* = 164.5, 6.9), 130.99 d.d (*J* = 165.3, 7.1)

Comp. no.	C^6 or C^7	C^{8a}	C^{8b}	Substituent
IIIa	123.58 d.br.d (*J* = 164.5, 8.4), 121.83 d.d.d (*J* = 165.58, 8.1, 1.5)	134.42 m	156.46 d (*J* = 14.8)	–
IIIb	123.98 d.d (*J* = 164.2, 8.6), 121.22 d.d (*J* = 166.2, 8.6)	133.90 d.d (*J* = 7.1, 7.0)	155.22 s	19.39 q (*J* = 130.57)
IIIc	124.63 d.d.d (*J* = 164.5, 7.3, 1.1), 122.76 d.d.d (*J* = 166.7, 7.1, 1.2)	135.35 d.d.d (*J* = 6.8, 6.6, 1.4)	155.72 d (*J* = 4.3)	134.04 m (C_i), 127.68 d.m (C^o, *J* = 160.6), 130.55 d.d.d (C^m, *J* = 133.8, 6.8, 6.1), 132.25 d.d.d (C^p, *J* = 162.4, 7.4, 7.5)

Table 3. Conditions of X-ray diffraction experiments and principal crystallographic parameters of compounds **IIIa**–**IIIc**

Parameter	**IIIa**	**IIIb**	**IIIc**
Color	Brown	Orange	Red
Crystal habit, mm	Prismatic 0.5×0.23×0.18	Prismatic 0.25×0.25×0.25	Rhombic 0.6×0.45×0.35
Formula	$C_{10}H_5NOS$	$C_{11}H_7NOS$	$C_{16}H_9NOS$
Molecular weight	187.22	201.25	263.32
Crystal system	Monoclinic	Rhombic	Monoclinic
Space group	*C*2/*c*	*Pbca*	$P2_1/a$
a, Å	11.094(5)	13.213(2)	12.146(4)
b, Å	8.639(5)	8.156(5)	13.606(6)
c, Å	17.286(8)	17.355(5)	15.962(6)
β, deg	98.78(2)	90.00	112.35(3)
V, Å^3	1637.3	1870.3	2440.3
Z	8	8	8
d_{calc}, g/cm^3	1.52	1.43	1.43
F(000)	768	832	1088
θ_{max}, deg	71.31	74.11	56.85
Absorption coefficient, cm^{-1}	30.444	27.018	22.090
Total number of reflections	1584	1947	2767
Number of reflections with $F^2 \geq 3\sigma(F^2)$	1370	1433	2596
Divergence factor *R*, %	3.8	3.5	6.1
wR, %	4.8	5.0	9.9
Fitting parameter *S*	1.9	1.8	4.4
Number of refined parameters	138	155	415

Table 4. Coordinates of atoms in the molecule of indeno[2,1-*d*]thiazol-4-one (**IIIa**), equivalent isotropic temperature factors of non-hydrogen atoms $B = 4/3\sum_{i=1}^{3}\sum_{j=1}^{3}(a_i a_j)B(i,j)$ (Å^2), and isotropic temperature factors of hydrogen atoms (Å^2)

Atom	*x*	*y*	*z*	*B*	Atom	*x*	*y*	*z*	*B*
S^1	0.08864(4)	0.14384(5)	0.66384(2)	4.737(9)	C^7	0.0087(2)	0.2941(2)	0.37663(9)	4.71(4)
O^4	0.3019(1)	0.6005(2)	0.58042(8)	5.18(3)	C^{8a}	0.0917(1)	0.3043(2)	0.51189(8)	3.35(3)
N^3	0.2425(2)	0.3629(2)	0.71035(8)	4.39(3)	C^{8b}	0.1222(1)	0.2725(2)	0.59642(8)	3.44(3)
C^2	0.1883(2)	0.2428(2)	0.73438(9)	4.79(4)	C^8	0.0148(2)	0.2330(2)	0.45180(9)	4.15(3)
C^{3a}	0.2046(1)	0.3791(2)	0.63143(8)	3.57(3)	H^2	0.195(2)	0.205(2)	0.788(1)	6.0(4)
C^4	0.2342(2)	0.4900(2)	0.57172(8)	3.67(3)	H^5	0.188(2)	0.595(2)	0.415(1)	6.5(5)
C^{4a}	0.1590(1)	0.4355(2)	0.49676(8)	3.48(3)	H^6	0.074(2)	0.468(2)	0.3132(9)	6.0(4)
C^5	0.1513(2)	0.4970(2)	0.42291(9)	4.28(3)	H^7	–0.036(2)	0.244(2)	0.335(1)	5.8(4)
C^6	0.0756(2)	0.4235(2)	0.3619(1)	4.88(4)	H^8	–0.028(2)	0.150(2)	0.4574(9)	4.1(4)

Table 5. Coordinates of atoms in the molecule of 2-methylindeno[2,1-*d*]thiazol-4-one (**IIIb**), equivalent isotropic temperature factors of non-hydrogen atoms $B = 4/3\sum_{i=1}^{3}\sum_{j=1}^{3}(a_i a_j)B(i,j)$ (Å^2), and isotropic temperature factors of hydrogen atoms (Å^2)

Atom	*x*	*y*	*z*	*B*	Atom	*x*	*y*	*z*	*B*
S^1	0.63525(4)	–0.20488(5)	0.08240(3)	3.350(9)	C^{8a}	0.6293(1)	0.0961(2)	–0.0138(1)	2.94(3)
O^4	0.6001(1)	0.3855(2)	0.13747(8)	5.06(3)	C^{8b}	0.6301(1)	–0.0042(2)	0.0566(1)	2.93(3)
N^3	0.6177(1)	0.0126(2)	0.19060(9)	3.52(3)	C^9	0.6236(2)	–0.2711(3)	0.2418(1)	4.59(5)
C^2	0.6248(1)	–0.1453(2)	0.1792(1)	3.40(4)	H^5	0.603(1)	0.496(4)	–0.023(1)	7.8(6)
C^{3a}	0.6205(1)	0.0911(2)	0.1208(1)	3.03(3)	H^6	0.615(1)	0.430(2)	–0.156(1)	4.7(5)
C^{4a}	0.6184(1)	0.2600(2)	0.0104(1)	3.14(3)	H^7	0.634(1)	0.172(3)	–0.192(1)	5.1(5)
C^4	0.6116(1)	0.2650(2)	0.0970(1)	3.37(3)	H^8	0.643(1)	–0.053(3)	–0.108(1)	4.2(5)
C^5	0.6143(2)	0.3856(2)	–0.0423(1)	3.94(4)	H^{91}	0.674(2)	–0.329(3)	0.239(2)	8.1(6)
C^6	0.6212(2)	0.3481(3)	–0.1201(1)	4.46(5)	H^{92}	0.571(2)	–0.328(3)	0.236(2)	9.1(7)
C^7	0.6313(2)	0.1878(3)	–0.1438(1)	4.21(4)	H^{93}	0.628(2)	–0.217(5)	0.290(3)	15(1)
C^8	0.6360(1)	0.0585(3)	–0.0906(1)	3.77(4)					

bands typical of free (3560–3500 cm^{-1}) or associated hydroxy group (2700–2500 cm^{-1}) in carboxylic acids, while the carbonyl absorption band is displaced by ~20 cm^{-1} toward higher frequencies (usually, from 1690 to 1710 cm^{-1}) (Table 1). In the ^{1}H NMR spectra we observed no multiplet signals typical of protons in unsubstituted phenyl group, but multiplets corresponding to a four-spin *ABCD* system appear in the region δ 7.0–7.6 ppm (Table 1). The number of carbon signals in the ^{13}C NMR spectra of compounds **IIIa**–**IIIc** is greater by two than in the spectra of the initial acids, and the carbonyl carbon signal shifts downfield (δ_C ~ 185 ppm; Table 2).

The molecular and crystalline structures of pure indenothiazole **IIIa**, 2-methylindenothiazole **IIIb**, and 2-phenylindenothiazole **IIIc** were examined by the X-ray diffraction method. The coordinates of atoms and some geometric parameters of molecules **IIIa**–**IIIc** are given in Tables 3–7. The molecular structures with atom numbering are shown in Figs. 1–3. Compounds **IIIa** (Fig. 1) and **IIIb** (Fig. 2) give rise, respectively, to

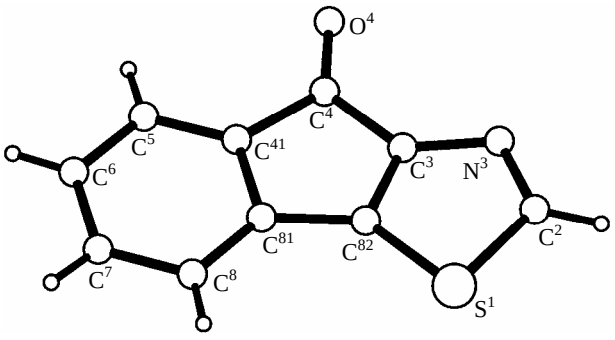


Fig. 1. Structure of the molecule of indeno[2,1-*d*]thiazol-4-one (**IIIa**) in crystal.

Table 6. Coordinates of atoms in the molecule of 2-phenylindeno[2,1-*d*]thiazole (**IIIc**), equivalent isotropic temperature factors of non-hydrogen atoms $B = 4/3 \sum_{i=1}^{3} \sum_{j=1}^{3} (a_i a_j) B(i, j)$ (Å^2), and isotropic temperature factors of hydrogen atoms (Å^2)

Atom	*x*	*y*	*z*	*B*	Atom	*x*	*y*	*z*	*B*
S^{1A}	0.49530(7)	0.48917(6)	0.33273(5)	3.73(2)	C^{13A}	0.6018(3)	0.8080(3)	0.3558(2)	4.00(8)
S^{1B}	0.15591(7)	0.49242(6)	0.16660(6)	3.65(2)	C^{13B}	0.2652(3)	0.8084(3)	0.1787(2)	4.37(9)
O^{4B}	–0.2716(2)	0.4154(2)	0.0155(2)	5.09(6)	C^{14A}	0.5645(2)	0.7115(2)	0.3502(2)	3.74(8)
O^{4A}	0.2037(2)	0.3928(2)	0.4638(2)	5.64(6)	C^{14B}	0.2245(3)	0.7126(2)	0.1706(2)	3.92(8)
N^{3B}	–0.0550(2)	0.5673(2)	0.0835(2)	3.58(6)	C^{41B}	–0.1117(2)	0.2988(2)	0.0823(2)	3.03(7)
N^{3A}	0.3639(2)	0.5511(2)	0.4175(2)	3.49(6)	C^{41A}	0.2999(2)	0.2843(2)	0.3916(2)	3.60(8)
C^{2B}	0.0578(2)	0.5932(2)	0.1227(2)	3.28(7)	C^{81A}	0.3838(2)	0.3012(2)	0.3520(2)	3.24(7)
C^{2A}	0.4400(2)	0.5811(2)	0.3828(2)	3.23(7)	C^{81B}	0.0137(2)	0.3094(2)	0.1258(2)	3.22(7)
C^{3A}	0.3482(2)	0.4533(2)	0.4037(2)	2.92(7)	C^{82A}	0.4106(2)	0.4068(2)	0.3610(2)	3.15(7)
C^{3B}	–0.0639(2)	0.4667(2)	0.0874(2)	3.10(7)	C^{82B}	0.0353(2)	0.4154(2)	0.1283(2)	3.21(7)
C^{4B}	–0.1676(2)	0.3982(2)	0.0551(2)	3.60(8)	H^{5A}	0.186(2)	0.182(2)	0.411(2)	6.2(8)
C^{4A}	0.2737(3)	0.3784(2)	0.4267(2)	3.96(8)	H^{5B}	–0.249(2)	0.201(2)	0.045(2)	2.7(5)
C^{5B}	–0.1618(3)	0.2068(2)	0.0703(2)	3.86(8)	H^{6B}	–0.115(2)	0.055(2)	0.098(2)	5.6(7)
C^{5A}	0.2576(3)	0.1896(2)	0.3966(2)	4.17(8)	H^{6A}	0.286(2)	0.060(2)	0.369(1)	2.6(5)
C^{6B}	–0.0898(3)	0.1248(2)	0.1022(2)	4.16(8)	H^{7B}	0.078(2)	0.077(2)	0.170(1)	2.6(5)
C^{6A}	0.3020(3)	0.1133(2)	0.3603(2)	4.78(9)	H^{7A}	0.403(2)	0.073(2)	0.298(2)	5.2(7)
C^{7B}	0.0322(3)	0.1370(3)	0.1441(2)	4.18(9)	H^{8A}	0.487(2)	0.232(2)	0.296(2)	3.2(6)
C^{7A}	0.3814(3)	0.1289(2)	0.3211(3)	4.80(9)	H^{8B}	0.166(2)	0.242(2)	0.176(2)	3.5(6)
C^{8A}	0.4256(3)	0.2233(3)	0.3163(2)	4.07(8)	H^{10A}	0.373(2)	0.747(2)	0.443(1)	3.1(6)
C^{8B}	0.0846(2)	0.2285(2)	0.1555(2)	3.59(8)	H^{10B}	–0.062(2)	0.756(2)	0.077(1)	2.9(6)
C^{9A}	0.4786(2)	0.6854(2)	0.3852(2)	3.11(7)	H^{11A}	0.442(2)	0.888(2)	0.440(1)	1.9(5)
C^{9B}	0.1023(2)	0.6930(2)	0.1317(2)	3.24(7)	H^{11B}	0.018(2)	0.917(2)	0.079(2)	3.6(6)
C^{10A}	0.4299(2)	0.7570(2)	0.4216(2)	3.57(7)	H^{12B}	0.213(2)	0.947(2)	0.154(1)	2.7(6)
C^{10B}	0.0239(2)	0.7714(3)	0.1023(2)	3.78(8)	H^{12A}	0.579(2)	0.939(2)	0.391(2)	5.8(8)
C^{11A}	0.4678(3)	0.8527(3)	0.4248(2)	4.52(8)	H^{13B}	0.346(2)	0.818(2)	0.199(2)	5.5(8)
C^{11B}	0.0663(3)	0.8672(2)	0.1097(2)	4.24(9)	H^{13A}	0.661(2)	0.825(2)	0.338(2)	2.6(6)
C^{12A}	0.5531(3)	0.8795(2)	0.3911(2)	4.08(8)	H^{14B}	0.289(2)	0.659(2)	0.191(2)	5.0(7)
C^{12B}	0.1858(3)	0.8851(2)	0.1487(2)	4.64(9)	H^{14A}	0.600(2)	0.641(2)	0.320(2)	5.4(8)

monoclinic and rhombic crystals with similar parameters; the independent parts of their unit cells contain a single independent molecule. The indenothiazole ring systems in molecules **IIIa**–**IIIc** are planar within the experimental error [0.02(2) Å]. Crystals of 2-phenyl-substituted indenothiazole **IIIc** are characterized by the presence of two independent molecules in the asymmetric part of a unit cell (Fig. 3). The phenyl groups in both molecules are almost coplanar to the indenothiazole plane [the dihedral angle between the indenothiazole fragment and the phenyl ring is 2.7(1)° in both molecules]. Despite similar conformations, an appreciable redistribution of bond lengths in the indenothiazole fragments is observed, which considerably exceeds the experimental error (Table 5).

Packing of molecules **IIIa**–**IIIc** in crystal is determined by weak intermolecular C–H···O, C–H···S, and π–π interactions. The O^2 atom in unsubstituted indenothiazole **IIIa** is involved in a short contact with the $H^{2'}$ proton of the neighboring molecule:

$d(H^1\cdots O^{20})$ 1.6278 Å, $\angle(O^1H^1O^{20})$ 172.76° (symmetry operation 1/2 – *x*, 1/2 + *y*, 1/2 – *z*), which gives rise to formation of zigzag chains (Fig. 4). Contiguous molecules in the chain form separate mutually orthogonal stacks via π–π interactions (dihedral angles between the planes of the adjacent molecules in a stack are equal to 0°, and the shortest distance between these planes varies from 4.06 to 4.48 Å).

For compound **IIIb** in crystal we did not reveal appreciable intermolecular contacts like C–H···X which could fit formal criteria accepted in PLATON [17]. Presumably, crystal packing of this compound is determined mainly by π–π contacts between electronic systems of the aromatic rings. In this case, layers parallel to the *y*0*z* crystallographic plane are formed (Fig. 5), and molecules **IIIb** belonging to the neighboring layers give rise to zigzag stacks. The dihedral angle between the planes of molecules in stacks varies in the range from 0 to 10°, and the interplanar distance, from 2.91 to 3.65 Å.

Phenyl-substituted indenothiazole **IIIc** is also characterized by the existence of only π–π contacts in crystal: each of the two independent molecules gives rise to dimers [the dihedral angle between the molecular planes is 0°, and the distance between the planes is 3.41(2) Å]. Insofar as the planes of independent molecules A and B form an angle of 57.7(2)°, alternating layers of molecules A and B in crystal are arranged parallel to each other, and molecules within a layer are arranged in an inclined mode (Fig. 6).

EXPERIMENTAL

The melting points were determined on a Boetius device. The IR spectra were recorded on a UR-20 spectrometer from samples dispersed in mineral oil. The ^{1}H NMR spectra of acids **IIa**–**IIc** were obtained on a Varian T-60 instrument (60.0 MHz), and of indenothiazoles **IIIa**–**IIIc**, on a Bruker MW-250 spectrometer (250.132 MHz). The ^{13}C NMR spectra were measured on a Bruker MSL-400 spectrometer at 100.6 MHz.

X-Ray diffraction experiments were performed using an Enraf–Nonius CAD-4 automatic four-circle diffractometer (20°C, λCuK_α 1.5418 Å, graphite monochromator). The principal crystallographic parameters and experimental conditions are given in Table 3. ω-Scanning for compound **IIIc** and ω/2θ-scanning for **IIIa** and **IIIb** were applied; variable scan rate, 1–16.4°/min with respect to θ. No drop in the intensity of three control reflections was observed during data acquisition. Empirical correction for absorption was introduced for compounds **IIIa** (μCu = 30.444 cm^{-1}) and **IIIb** (μCu = 27.018 cm^{-1}). The structures were solved by the direct method using SIR program [18] and were refined by the full-matrix least-squares procedure; function to be minimized $\Sigma w(|F_o| - |F_c|)^2$; extinction was not taken into account; weight scheme $4F_0^2/[\sigma(I)^2 + (0.04F_0^2)]^2$. The positions of hydrogen atoms were determined from the difference synthesis of electron density and were refined in isotropic approximation at the final stage. The coordinates of atoms and their temperature factors are listed in Tables 3–5. The calculations were performed on an Alpha Station 200 computer using MolEN software package [19]. Graphical representations of molecular

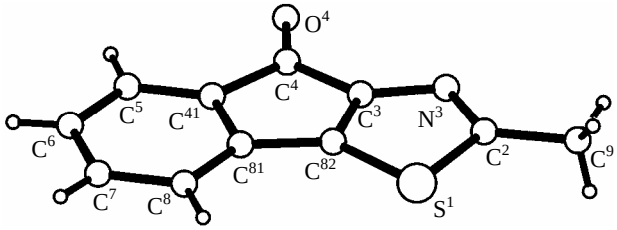


Fig. 2. Structure of the molecule of 2-methylindeno[2,1-*d*]-thiazol-4-one (**IIIb**) in crystal.

Table 7. Selected bond lengths (*d*, Å) in molecules of compounds **IIIa**–**IIIc**

Bond	IIIa	IIIb	IIIc	
			A	B
S^1–C^2	1.740(2)	1.755(2)	1.750(3)	1.776(3)
C^2–N^3	1.299(2)	1.307(2)	1.309(4)	1.320(3
N^3–C^3	1.372(2)	1.370(2)	1.350(4)	1.377(4)
C^3–C^4	1.482(2)	1.482(3)	1.498(5)	1.492(4)
C^3–C^{82}	1.371(2)	1.365(2)	1.354(5)	1.330(4)
C^4–C^{41}	1.506(2)	1.507(3)	1.480(5)	1.502(4)
C^{41}–C^{81}	1.403(2)	1.408(2)	1.406(5)	1.420(4)
C^{41}–C^5	1.373(2)	1.375(3)	1.401(5)	1.373(4)
C^5–C^6	1.396(2)	1.386(3)	1.392(5)	1.389(4)
C^6–C^7	1.387(3)	1.377(3)	1.352(6)	1.385(4)
C^7–C^8	1.395(2)	1.402(3)	1.404(5)	1.379(5)
C^8–C^{81}	1.385(2)	1.372(3)	1.388(5)	1.367(4)
C^{81}–C^{82}	1.474(2)	1.470(3)	1.469(4)	1.464(4)
C^{82}–S^1	1.693(2)	1.698(2)	1.694(3)	1.714(3)

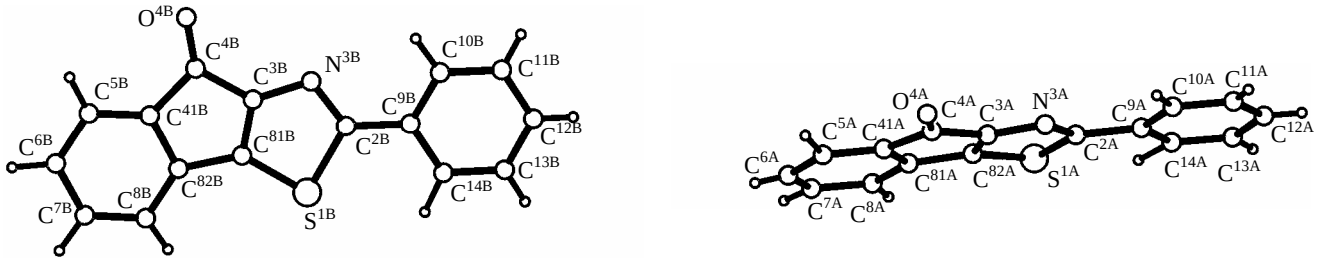


Fig. 3. Structure of two independent molecules A and B of 2-phenylindeno[2,1-*d*]thiazol-4-one (**IIIc**) in crystal.

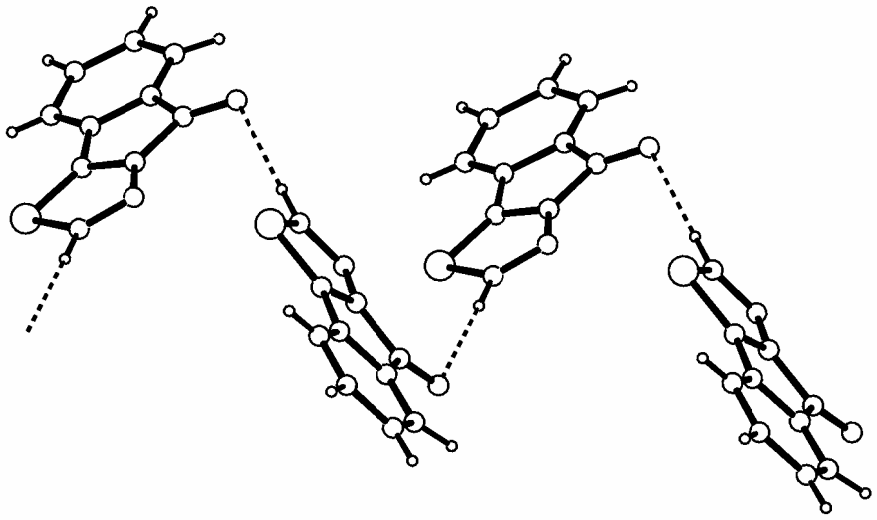


Fig. 4. Hydrogen bond system in the crystalline structure of indeno[2,1-*d*]thiazol-4-one (**IIIa**).

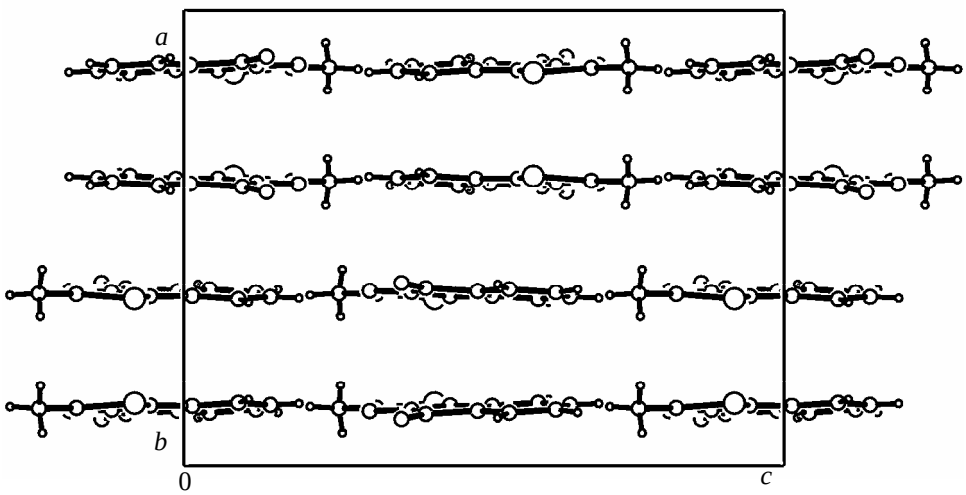


Fig. 5. Molecular stacks of compound **IIIb** in crystal. View along the 0*y* axis.

structures were obtained, and intermolecular interactions were analyzed, using PLATON software [20].

5-Phenylthiazole-4-carboxylic acid (IIa). Methyl 5-phenylthiazole-4-carboxylate (**Ia**), 2.19 g, was added to 15 ml of a 10% aqueous–methanolic solution of 0.56 g of potassium hydroxide, and the mixture was heated for 2 h under reflux. The solvent was evaporated, 10 ml of water was added to the residue, and the mixture was acidified with dilute hydrochloric acid under vigorous stirring. The precipitate was filtered off, dried in air, and recrystallized from 2-propanol. Yield 1.85 g (92%), mp 185–186°C.

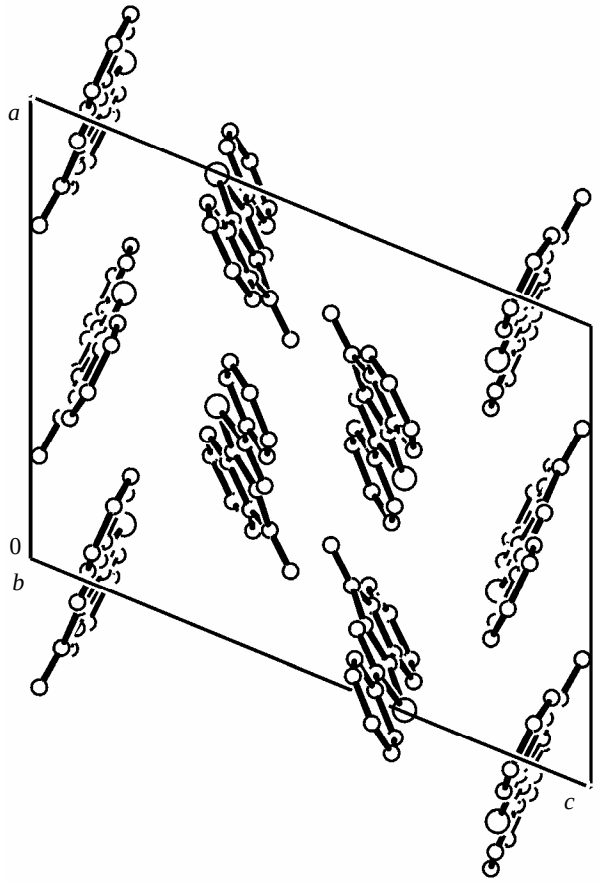


Fig. 6. Packing of molecules of 2-phenylindeno[2,1-*d*]thiazol-4-one (**IIIc**) in crystal. View along the 0*y* crystallographic axis. Hydrogen atoms are not shown.

Found, %: C 58.47; H 3.45; N 6.77; S 15.36. $C_{10}H_7NO_2S$. Calculated, %: C 58.54; H 3.41; N 6.83; S 15.61.

2-Methyl-5-phenylthiazole-4-carboxylic acid (IIb) was synthesized in a similar way from ester **Ib**. Yield 84%, mp 129–133°C. Found, %: C 60.44; H 4.0; N 6.48; S 14.56. $C_{11}H_9NO_2S$. Calculated, %: C 60.27; H 4.11; N 6.39; S 14.61.

2,5-Diphenylthiazole-4-carboxylic acid (IIc) was synthesized in a similar way from ester **Ic.** Yield 86%, mp 129–133°C. Found, %: C 68.30; H 3.84; N 5.10; S 11.48. $C_{16}H_{11}NO_2S$. Calculated, %: C 68.33; H 3.91; N 4.98; S 11.39.

Indeno[2,1-*d*]thiazol-4-one (IIIa). A mixture of 15 g of P_2O_5 and 10 ml of H_3PO_4 was heated for 1.5 h at 110–120°C. The mixture was cooled, 2.05 g of thiazolecarboxylic acid **IIa** was added, and the mixture was heated for 1.5 h at 100–140°C, cooled, and diluted with water. The precipitate was filtered off and recrystallized from toluene. Yield 1.3 g (70%), mp 157–160°C. Found, %: C 63.98; H 2.75; N 7.53; S 17.00. $C_{10}H_5NOS$. Calculated, %: C 64.17; H 2.67; N 7.49; S 17.11.

2-Methylindeno[2,1-*d*]thiazol-4-one (IIIb) was synthesized from acid **IIb** as described above for compound **IIIa**. Yield 63%, mp 122–125°C. Found, %: C 65.60; H 3.59; N 7.05; S 15.79. $C_{11}H_7NOS$. Calculated, %: C 65.67; H 3.48; N 6.97; S 15.92.

2-Phenylindeno[2,1-*d*]thiazol-4-one (IIIc) was synthesized from acid **IIc** as described above for compound **IIIa**. Yield 70%, mp 160–161°C. Found, %: C 72.89; H 3.30; N 5.32; S 12.20. $C_{16}H_9NOS$. Calculated, %: C 73.00; H 3.42; N 5.39; S 12.33.

This study was performed under financial support by the Russian Foundation for Basic Research (project nos. 03-03-32865 and 02-03-32280).

REFERENCES

1. Kalinin, A.A., Mamedov, V.A., Rizvanov, I.Kh., and Levin, Ya.A., *Russ. J. Org. Chem*., 2004, vol. 40, p. 527.
2. Kurtzer, F., *Sulphur, Selenium, and Tellurium* (Specialist Periodical Reports), London: Chem. Soc., 1970, vol. 1, p. 13; *ibid*., 1975, vol. 3, p. 14.
3. Fiorentino, M., Testaferri, L., Tiecco, M., and Troisi, L., *J. Chem. Soc., Chem. Commun*., 1977, p. 317.
4. Tolks, A.M., Kerch, G.M., Karlsone, T.A., and Irgen, L.A., *Khim. Volokna*, 1980, p. 48.
5. Gewald, K., Spies, H., and Mayer, R., *J. Prakt. Chem*., 1970, vol. 312, p. 776.
6. Dingwall, J.G., Reid, D.H., and Wade, K., *J. Chem. Soc. C*, 1969, p. 913.
7. Singh, R., Tripathe, R.C., Ashok, K., and Nitya, A., *Indian J. Chem., Sect. B*, 1989, vol. 28, p. 486.
8. Barkan, V.P., Gudrinietse, E.Yu., and Shkerite, D., *Izv. Akad. Nauk Latv. SSR, Ser. Khim*., 1975, p. 345.
9. Eur. Patent Appl. no. 230334; *Chem. Abstr*., 1987, vol. 107, no. 236698n.
10. PCT Int. Patent Appl. WO 95 24399; *Chem. Abstr*., 1996, vol. 124, no. 87003d.
11. Esses-Reiter, K. and Reiter, J., *J. Heterocycl. Chem*., 1996, vol. 33, p. 879.
12. Gudrinietse, E.Yu., *Izv. Akad. Nauk Latv. SSR, Ser. Khim*., 1980, p. 645.
13. Mamedov, V.A., Kalinin, A.A., Gubaidullin, A.T., Nurkhametova, I.Z., Litvinov, I.A., and Levin, Ya.A., *Khim. Geterotsikl. Soedin*., 1999, p. 1664.

14. Mamedov, V.A., Mustakimova, L.V., Valeeva, V.N., Nurkhametova, I.Z., Kalinin, A.A., Gubaidullin, A.T., Litvinov, I.A., Berdnikov, E.A., and Levin, Ya.A., Abstracts of Papers, *The Seventh Int. Kyoto Conf. on New Aspects of Organic Chemistry (IKCOC-7)*, Kyoto (Japan), 1997, p. 358.
15. Mamedov, V.A. and Nuretdinov, I.A., *Izv. Akad. Nauk SSSR, Ser. Khim*., 1987, p. 2856.
16. Mamedov, V.A., Nuretdinov, I.A., and Sadkova, D.N., *Izv. Akad. Nauk SSSR, Ser. Khim*., 1990, p. 2854.
17. March, J., *Advanced Organic Chemistry. Reactions, Mechanisms, and Structure*, New York: Wiley, 2000, p. 539.
18. Altomare, A., Cascarano, G., Giacovazzo, C., and Viterbo, D., *Acta Crystallogr., Sect. A*, 1991, vol. 47, p. 744.
19. Straver, L.H. and Schierbeek, A.J., *MolEN. Structure Determination System*, Nonius B.V., 1994, vol. 1, p. 2.
20. Spek, A.L., *Acta Crystallogr., Sect. A*, 1990, vol. 46, p. 34.