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Transannular sulfur–nitrogen interaction in 1,5-thiazocine derivatives: an X-ray study

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Abstract

7-Acetylbenzo[*b*]naphtho[1,8-*f*,*g*]thiazocin-8(7*H*)-one (sulfide-*N*-acetyllactam **3**) and its 13-oxide (sulfoxide-*N*-acetyllactam **4**, exhibiting polymorphy, **4a** and **4b**) have been prepared and their structures established by X-ray crystallography from diffractometer data. Compound **3** ($C_{19}H_{13}NO_2S$) crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.716(3)$, $b = 9.222(2)$, $c = 16.077(5)$ Å, $\beta = 106.68(2)°$, $V = 1521.9(7)$ Å^3, $Z = 4$, $D_c = 1.394$ g cm^{-3} and μ(Mo Kα) $= 0.22$ mm^{-1}. Compound **4a** ($C_{19}H_{13}NO_3S$) crystallizes in the monoclinic space group Pc with $a = 7.821(1)$, $b = 24.795(6)$, $c = 8.342(1)$ Å, $\beta = 101.15(1)°$, $V = 1587.2(4)$ Å^3, $Z = 4$ (two molecules, **4a**′ and **4a**″, in the asymmetric unit), $D_c = 1.40$ g cm^{-3} and μ(Mo Kα) $= 0.21$ mm^{-1}. Compound **4b** also crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.791(1)$, $b = 10.719(1)$, $c = 25.193(2)$ Å, $\beta = 96.02(1)°$, $V = 3166.4(4)$ Å^3, $Z = 8$ (two molecules, **4b**′ and **4b**″ in the asymmetric unit), $D_c = 1.394$ g cm^{-3} and μ(Cu Kα) $= 1.92$ mm^{-1}. The crystal structures were solved by direct methods and refined to $R = 0.052$ for **3**, $R = 0.088$ for **4a**, and $R = 0.048$ for **4b**, by using 9413, 4759 and 5195 reflections, respectively. Owing to the *cis*-amide structure, compounds **3** and **4** assume a boat-like conformation with transannular sulfur–nitrogen close contact; $r(S\cdots N) = 2.968(1)$ Å for **3** and 2.753(3)–2.832(2) Å for **4a**′ and **4b**″. The out-of-ring position of the sulfinyl oxygen leads to a sulfurane-like trigonal bipyramidal geometry about sulfur in **4a**′ and **4b**″; $\theta(O{=}S\cdots N) \simeq 175.8(3)$–$178.7(2)°$. The interatomic distances $r(S{=}O) = 1.483(2)$–$1.498(3)$ Å and $r(O{=}S\cdots N) = 4.245$–4.314 Å are in agreement with an S=O double bond and S···N close contact rather than with an O–S–N type molecular structure observed in spirosulfuranes. The stereochemistries of 1,5-thiazocine and 1,5-thiazonine rings are compared.

Keywords: Conformational isomerism; 1,5-Thiazocine derivative; Transannular sulphur–nitrogen interaction; X-ray crystallography

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1. Introduction

In an earlier paper [1] we described the structure of the sulfide-*N*-acetyllactam **1a** and the sulfoxide-lactam **1b**, both containing a nine-membered 1,5-thiazonine ring (Scheme 1). In these compounds the 2,2′ positions of a biphenyl ring and the ortho positions of a benzene ring are connected by amide (–NQ–CO–) and sulfur (–S–) bridges. Only the sulfoxide-lactam **1b** with an endocyclic *trans*-amide structure exhibited 1,5-type S···N close contact (2.78 Å) with a nearly linear

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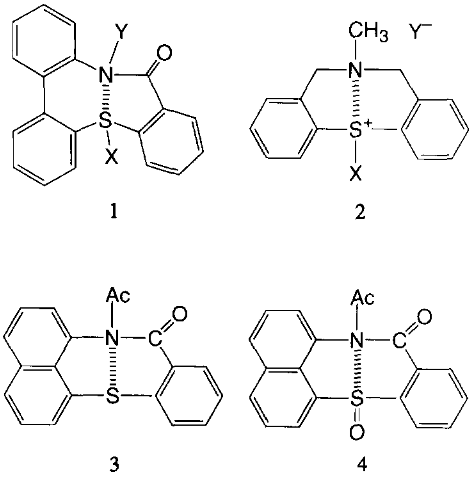
O=S$\cdots$N moiety (171°), while the sulfur and nitrogen atoms in the *cis*-amide type sulfide-*N*-acetyllactam **1a** are farther from each other 4.04 Å) than the van der Waals distance (3.35 Å according to Ref. [2]).

Previous to our work some 1,5-thiazocine derivatives were studied by X-ray diffraction (see Scheme 1) and transannular 1,5-type S$\cdots$N close contact was observed in all cases for a linear (175–179°) X–S$\cdots$N array; $r(\mathrm{S}\cdots\mathrm{N}) = 2.05$, 2.21 and 2.47 Å were found [3] for the sulfonium salts **2a**–**2c**, respectively, whereas $r(\mathrm{S}\cdots\mathrm{N})$ was 2.60 Å in the sulfoxide **2d** [3] and 2.94 Å in an *N*-aryl sulfimide with a 1,3,2,6-dioxathiazocine ring [4].

On the basis of both geometry data and MO calculations Akiba and coworkers [3] concluded that there exists a transannular hypervalent bond between sulfur and nitrogen atoms, owing to the coordination of the nitrogen lone pair to the positive sulfur center. Relatively short S$\cdots$N distances of 2.83 and 2.89 Å were observed and calculated for analogous acyclic models as well [5].

In continuation of our program aimed at clarifying the decisive roles of both the ring size and the *N*-acetyl group in the transannular sulfur–nitrogen interaction, we prepared the sulfide-*N*-acetyllactam **3** and sulfoxide-*N*-acetyllactam **4** (Scheme 1), and investigated their structure by X-ray diffraction. In these compounds the *peri*-naphthylene and *ortho*-phenylene groups are connected by amide (–NAc–CO–) and sulfur (–S–) bridges to form an eight-membered thiazocine ring.



Scheme 1. Cyclic compounds with transannular sulfur–nitrogen interaction. **1a**: X = lone pair, Y = $COCH_3$; **1b**: X = O, Y = H; **2a**: X = Cl, Y = PF_6; **2b**: X = OCH_3, Y = $SbCl_6$; **2c**: X = CH_3, Y = PF_6; **2d**: X = O^-; **3**: Ac = $COCH_3$; **4**: Ac = $COCH_3$.

1.1. Model compounds

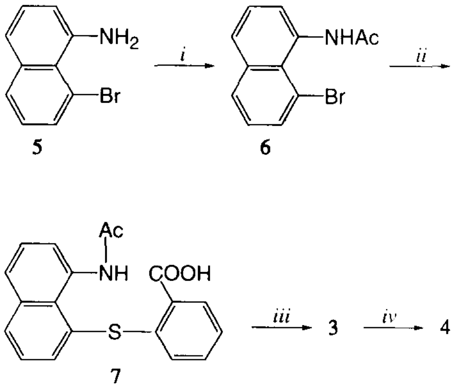
7-Acetylbenzo[*b*]naphthol[1,8-*f*,*g*]thiazocin-8(7*H*)-one (sulfide-*N*-acetyllactam, **3**) and 7-acetylbenzo[*b*]naphtho[1,8-*f*,*g*]thiazocin-8(7*H*)-one 13-oxide (sulfoxide-*N*-acetyllactam, **4**) were synthesized starting from 8-bromo-1-aminonaphthalene (**5**) which was first acetylated (**5** → **6**). The product **6** was coupled with thiosalicylic acid (**6** → **7**), then the sulfide **7** was converted to the target compounds **3** and **4** by intramolecular dehydration (**7** → **3**) followed by S-oxidation (**3** → **4**) as shown in Scheme 2.

2. Experimental

2.1. Materials

2.1.1. General

Melting points were determined on a Boetius micro melting point apparatus. IR spectra were taken on a Specord IR 75 (Zeiss, Jena) spectrophotometer. Bruker AC-80 and WM-250 spectrometers were used to obtain NMR spectra.



Scheme 2. Synthesis of model compounds. *i*: Ac_2O, pyridine, 100°C; *ii*: thiosalicylic acid, Cu_2O, pyridine–DMF, argon, reflux; *iii*: TsCl, pyridine, 100°C; *iv*: 30% H_2O_2, AcOH, 100°C.

Mass spectra were determined at 70 eV on Kratos MS-50 and MS-25-RFA spectrometers through solid probe (SP/MS) introduction; only molecular ions are listed. In the absence of clearly detectable molecular ions, chemical ionization was employed on the same instruments. Solvents were purified and dried by the usual methods; pyridine by distillation over P_2O_5. Products were dried in vacuo over P_2O_5.

2.1.2. 7-Acetylbenzo[b]naphtho[1,8-f,g]thiazocin-8(7H)-one (3)

To a solution of 8-bromo-1-aminonaphthalene [6] (**5**; 31 g, 140 mmol) in pyridine (70 cm^3) was added acetic anhydride (14.1 cm^3, 150 mmol). The mixture was heated on a steam bath for 3 h, then evaporated and the oily residue was triturated with ice-cold cc HCl. The crystalline precipitate was filtered off, washed with water and dried to give *8-bromo-1-acetylaminonaphthalene* (**6**). The crude product (34.5 g, 93%) was crystallized (charcoal) from 50% aqueous acetic acid (80 cm^3), mp 140–144°C (cf. 138–139°C in Ref. [7]).

To a solution of **6** (2.64 g, 10 mmol) and thiosalicylic acid (1.54 g, 10 mmol) in a mixture of pyridine (3.3 cm^3) and DMF (16 cm^3) was added copper(I) oxide (0.71 g, 5 mmol), and the mixture was boiled under argon atmosphere for 7 h, then poured onto ice-cold cc HCl. The precipitate was filtered off, washed with water, redissolved in aqueous $KHCO_3$, filtered off (charcoal and a small amount of Na_2S), reprecipitated with 20% aqueous HCl and, after washing with water, dried on a steam bath to yield *2-(8-acetylamino-1-naphthylthio)-benzoic acid* (**7**). The crude product (2.80 g, 83%) was crystallized from aqueous acetic acid and then from aqueous methanol, mp 252–253°C. Found: C, 67.5; H, 4.5; N, 3.5; O, 15.0; S, 9.6%; M^+, 337. Calcd. for $C_{19}H_{15}NO_3S$: C, 67.64; H, 4.48; N, 4.15; O, 14.23; S, 9.50%; MW 337.39;

Table 1
Crystal and relevant X-ray data for compounds **3** and **4**

Datum	**3**	**4a**	**4b**
Formula	$C_{19}H_{13}NO_2S$	$C_{19}H_{13}NO_3S$	$C_{19}H_{13}NO_3S$
MW	319.37	335.38	335.38
Melting point (°C)	205–217	198–213	198–213
Crystal size (mm)	0.70 × 0.70 × 0.65	0.15 × 0.45 × 0.60	0.23 × 0.25 × 0.40
Crustal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	Pc	$P2_1/c$
a (Å)	10.716(3)	7.821(1)	11.791(1)
b (Å)	9.222(2)	24.795(6)	10.719(1)
c (Å)	16.077(5)	8.342(1)	25.193(2)
β (deg)	106.68(2)	101.15(1)	96.02(1)
V (Å^3)	1521.9(7)	1587.2(4)	3166.4(4)
Z	4	4	8
D_c (g cm^{-3})	1.394	1.40	1.57
Absorption coefficient (mm^{-1})	0.22	0.21	1.92
F (000)	664	696	1392
Temp. (K)	293(2)	293(2)	293(2)
No. of unique reflections	9414	7389	6515
Data/restraints/parameters	9413/0/210	4759/0/432	5195/0/434
Goodness-of-fit on F		2.797	2.626
Goodness-of-fit on F^2	1.011		
Final R indices [$I > 2.0\sigma(I)$]	0.052		
Final R indices [$I > 3.0\sigma(I)$]		0.088	0.048
Final R_w	0.16	0.097	0.077
R indices (all data)	0.095	0.132	0.095
ρ_{max} in ΔF map (e Å^{-3})	0.55	$\lvert 0.93 \rvert$	$\lvert 0.39 \rvert$
ρ_{min} in ΔF map (e Å^{-3})	−0.43		

δ_H(80 MHz; $(CD_3)_2SO$; DSS) 1.90 (3 H, s, CH_3), 6.36–8.30 (11 H, m, ArH + NH), 10.20 (1 H, s, CO_2H); δ_C(20 MHz; $(CD_3)_2SO$; DSS) 27.2 (s, CH_3), 128.6, 128.8, 129.9 130.4, 130.6 130.9, 131.1, 131.9, 134.8, 135.6, 136.3, 137.9, 139.8, 142.5 and 146.0 (s, C_{Ar}), 171.4 (s, C=O), 171.8 (s, CO_2H); ν_{max} (KBr) (cm^{-1}) 3331vs (NH), 3150–2050br (OH), 1689vs and 1631vs (C=O).

To a solution of **7** (1.05 g, 3.1 mmol) in dry pyridine (6 cm^3) was added tosyl chloride (0.62 g, 3.3 mmol), and the mixture was heated on a steam bath for 4 h, then poured in small portions onto ice-cold 20% aqueous HCl. Upon standing (1 day) the oily precipitate crystallized, and was then filtered off, washed with 10% aqueous $KHCO_3$ and water and dried on a steam bath to give the *sulfide-N-acetyllactam* **3**. The crude product (0.98 g, 98%) was crystallized from aqueous acetone, mp 211–215°C, and after resolidification about 330°C.

Table 2
Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) with ESDs (in parentheses) for non-hydrogen atoms in compound **3**

Atom	*x/a*	*y/c*	*z/c*	U_{eq} [a]
S1	0.7372(1)	0.7211(1)	0.2123(1)	0.039(1)
N1	0.7049(1)	0.4446(1)	0.2983(1)	0.034(1)
O1	0.5076(1)	0.4888(2)	0.3227(1)	0.069(1)
O2	0.8986(1)	0.4136(2)	0.3988(1)	0.068(1)
C1	0.8448(1)	0.5970(1)	0.1831(1)	0.033(1)
C2	0.9333(1)	0.6562(2)	0.1450(1)	0.043(1)
C3	1.0144(1)	0.5665(2)	0.1125(1)	0.052(1)
C4	0.9991(1)	0.4208(2)	0.1119(1)	0.049(1)
C5	0.8858(1)	0.2034(2)	0.1428(1)	0.047(1)
C6	0.7983(2)	0.1403(1)	0.1783(1)	0.049(1)
C7	0.7363(1)	0.2243(1)	0.2276(1)	0.041(1)
C8	0.7566(1)	0.3711(1)	0.2360(1)	0.031(1)
C9	0.8356(1)	0.4440(1)	0.1914(1)	0.030(1)
C10	0.9077(1)	0.3548(1)	0.1489(1)	0.037(1)
C11	0.5856(1)	0.6465(1)	0.1492(1)	0.035(1)
C12	0.5218(1)	0.5389(1)	0.1820(1)	0.036(1)
C13	0.4004(1)	0.4885(2)	0.1325(1)	0.047(1)
C14	0.3443(1)	0.5429(2)	0.0503(1)	0.055(1)
C15	0.4065(2)	0.6500(2)	0.0180(1)	0.056(1)
C16	0.5263(1)	0.7028(2)	0.0670(1)	0.046(1)
C17	0.5741(1)	0.4888(2)	0.2732(1)	0.041(1)
C18	0.7903(1)	0.4630(1)	0.3820(1)	0.042(1)
C19	0.7473(1)	0.5519(2)	0.4465(1)	0.064(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) with ESDs (in parentheses) for non-hydrogen atoms in compound **4a**

Atom	*x/a*	*y/b*	*z/c*	U_{eq} [a]
Molecule **4a**′				
S1	0.0000	0.16381(5)	0.0000	0.0371(4)
O1	0.3722(5)	0.1934(2)	−0.2907(6)	0.080(2)
O2	0.4641(6)	0.1251(2)	0.1650(5)	0.058(2)
O3	−0.1619(5)	0.1828(2)	0.0520(4)	0.054(2)
N1	0.3083(5)	0.1362(1)	−0.0915(5)	0.037(2)
C1	−0.0032(6)	0.0916(2)	0.0113(6)	0.038(2)
C2	−0.1430(7)	0.0687(3)	0.0706(7)	0.053(3)
C3	−0.1582(8)	0.0130(3)	0.0738(7)	0.063(3)
C4	−0.0432(9)	−0.0197(2)	0.0194(8)	0.061(3)
C5	0.2227(9)	−0.0318(2)	−0.0990(7)	0.058(3)
C6	0.3593(9)	−0.0099(2)	−0.1587(8)	0.059(3)
C7	0.3835(8)	0.0452(2)	−0.1562(7)	0.051(2)
C8	0.2710(6)	0.0792(2)	−0.0999(6)	0.036(2)
C9	0.1224(6)	0.0589(2)	−0.0421(6)	0.039(2)
C10	0.1017(8)	0.0019(2)	−0.0411(7)	0.049(2)
C11	−0.0494(6)	0.1648(2)	−0.2209(5)	0.033(2)
C12	0.0779(6)	0.1660(2)	−0.3155(5)	0.035(2)
C13	0.0303(7)	0.1709(2)	−0.4840(5)	0.042(2)
C14	−0.1466(8)	0.1732(2)	−0.5589(6)	0.051(3)
C15	−0.2706(7)	0.1723(3)	−0.4622(7)	0.054(3)
C16	−0.2248(7)	0.1684(2)	−0.2942(6)	0.047(2)
C17	0.2650(6)	0.1664(2)	−0.2378(6)	0.041(2)
C18	0.4178(6)	0.1558(2)	0.0517(7)	0.042(2)
C19	0.4581(7)	0.2144(2)	0.0618(8)	0.054(3)
Molecule **4a**″				
S21	0.6773(2)	0.34458(5)	0.1860(2)	0.0395(5)
O21	1.0832(5)	0.2938(2)	−0.0467(5)	0.058(2)
O22	1.1585(6)	0.3769(1)	0.3817(5)	0.054(2)
O23	0.4983(5)	0.3342(2)	0.2182(5)	0.062(2)
N21	1.0146(5)	0.3599(1)	0.1256(4)	0.033(2)
C21	0.7043(6)	0.4167(2)	0.1966(6)	0.038(2)
C22	0.5712(7)	0.4449(2)	0.2470(7)	0.053(3)
C23	0.5757(8)	0.5018(2)	0.2461(8)	0.063(3)
C24	0.7025(8)	0.5283(2)	0.1930(8)	0.061(3)
C25	0.9730(8)	0.5287(2)	0.0795(7)	0.051(2)
C26	1.1053(8)	0.5020(2)	0.0271(8)	0.053(3)
C27	1.1129(7)	0.4457(2)	0.0408(7)	0.046(2)
C28	0.9882(6)	0.4172(2)	0.1004(5)	0.0001(6)
C29	0.8455(6)	0.4435(2)	0.1459(6)	0.034(2)
C30	0.8397(7)	0.5006(2)	0.1406(7)	0.0002(7)
C31	0.6584(6)	0.3400(2)	−0.0334(5)	0.034(2)
C32	0.7995(6)	0.3295(2)	−0.1090(5)	0.034(2)
C33	0.7694(7)	0.3194(2)	−0.2761(6)	0.045(2)
C34	0.6024(1)	0.3221(2)	−0.3676(7)	0.060(3)
C35	0.4652(8)	0.3332(2)	−0.2913(8)	0.057(3)
C36	0.4908(7)	0.3412(2)	−0.1256(7)	0.048(2)
C37	0.9784(6)	0.3249(2)	−0.0131(6)	0.037(2)
C38	1.1099(7)	0.3429(2)	0.2779(6)	0.039(2)
C39	1.1401(8)	0.2848(2)	0.3066(7)	0.051(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Found: C, 71.7; H, 4.2; N, 3.9; O, 11.8; S, 10.3%. Calcd. for $C_{19}H_{13}NO_2S$: MW, 319.37; C, 71.44; H, 4.11; N, 4.39; O, 10.01; S, 10.04%; ν_{max} (KBr) (cm^{-1}) 1694s (C=O).

Table 4
Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) with ESDs (in parentheses) for non-hydrogen atoms in compound **4b**

Atom	x/a	y/b	z/c	U_{eq} [a]
Molecule **4b**′				
S1	0.98442(5)	0.13469(6)	0.40414(2)	0.0502(3)
O1	0.6539(2)	−0.0126(2)	0.42786(8)	0.073(1)
O2	0.8906(2)	−0.2176(2)	0.36707(7)	0.075(1)
O3	1.0789(2)	0.2245(2)	0.41990(8)	0.069(1)
N1	0.8050(2)	−0.0325(2)	0.37738(7)	0.0442(9)
C1	0.9793(2)	0.1225(2)	0.33205(9)	0.048(1)
C2	1.0636(2)	0.1870(3)	0.3094(1)	0.065(1)
C3	1.0647(3)	0.1887(3)	0.2541(1)	0.077(2)
C4	0.9799(3)	0.1311(3)	0.2220(1)	0.072(2)
C5	0.7991(3)	0.0123(3)	0.2109(1)	0.068(2)
C6	0.7132(3)	−0.0453(3)	0.2321(1)	0.067(2)
C7	0.7140(2)	−0.0553(3)	0.2875(1)	0.057(1)
C8	0.8020(2)	−0.0079(2)	0.32059(8)	0.044(1)
C9	0.8916(2)	0.0586(2)	0.30045(8)	0.045(1)
C10	0.8907(2)	0.0656(2)	0.24397(9)	0.054(1)
C11	0.8542(2)	0.2263(2)	0.40390(9)	0.051(1)
C12	0.7469(2)	0.1738(3)	0.40682(9)	0.051(1)
C13	0.6564(2)	0.2533(3)	0.4137(1)	0.070(1)
C14	0.6710(3)	0.3795(3)	0.4163(1)	0.084(2)
C15	0.7771(3)	0.4303(3)	0.4123(1)	0.085(2)
C16	0.8680(3)	0.3544(3)	0.4064(1)	0.071(2)
C17	0.7273(2)	0.0377(3)	0.40568(9)	0.051(1)
C18	0.8495(2)	−0.1471(3)	0.39662(9)	0.051(1)
C19	0.8505(2)	−0.1712(3)	0.4548(1)	0.068(1)
Molecule **4b**″				
S21	0.48137(5)	−0.24265(6)	0.43118(3)	0.0501(3)
O21	0.1694(2)	−0.0773(2)	0.44616(9)	0.078(1)
O22	0.3954(2)	0.0845(2)	0.35704(7)	0.077(1)
O23	0.5738(2)	−0.3247(2)	0.45565(9)	0.073(1)
N21	0.3045(2)	−0.0836(2)	0.38673(7)	0.0440(9)
C21	0.4867(2)	−0.2585(2)	0.3596(1)	0.054(1)
C22	0.5724(2)	−0.3263(3)	0.3431(1)	0.079(2)
C23	0.5766(8)	−0.3496(3)	0.2868(1)	0.096(2)
C24	0.4929(3)	−0.3087(3)	0.2511(1)	0.093(2)
C25	0.3104(3)	−0.2005(3)	0.2289(1)	0.081(2)
C26	0.2192(3)	−0.1359(4)	0.2437(1)	0.083(2)
C27	0.2178(3)	−0.1049(3)	0.2966(1)	0.066(2)
C28	0.3053(2)	−0.1369(2)	0.33408(9)	0.048(1)
C29	0.3995(2)	−0.2107(2)	0.32182(9)	0.052(1)
C30	0.4029(3)	−0.2406(3)	0.2665(1)	0.071(1)
C31	0.3515(2)	−0.3319(2)	0.43277(8)	0.043(1)
C32	0.2439(2)	−0.2748(2)	0.42819(9)	0.043(1)
C33	0.1485(2)	−0.3466(3)	0.4349(1)	0.057(1)
C34	0.1595(2)	−0.4723(3)	0.4455(1)	0.062(1)
C35	0.2642(3)	−0.5283(3)	0.4505(1)	0.062(1)
C36	0.3616(2)	−0.4578(2)	0.4448(1)	0.055(1)
C37	0.2319(2)	−0.1375(2)	0.4214(1)	0.047(1)
C38	0.3523(2)	0.0381(2)	0.39320(9)	0.049(1)
C39	0.3532(3)	0.0975(3)	0.4465(1)	0.066(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

2.1.3. *7-Acetylbenzo[b]naphtho[1,8-f,g]thiazocin-8(7H)-one 13-oxide (4)*

To a hot solution of the crude **3** (0.98 g, 3.1 mmol) in acetic acid (5 cm^3) was added 30% aqueous hydrogen peroxide (0.31 cm^3, 3.0 mmol). The mixture was heated on a steam bath for 1 h, then evaporated and the residue was triturated with aqueous methanol. After 1 h the crystalline product was filtered off, and washed with methanol and dry ether to yield the *sulfoxide-N-acetyllactam* **4** (0.49 g, 47%), mp 198–213°C. Found: C, 68.2; H, 3.9; N, 4.2; O, 13.5; S, 9.6%; M^+, 335. Calcd. for $C_{19}H_{13}NO_3S$: C, 68.05; H, 3.88; N, 4.18; O, 14.31; S, 9.55%; MW, 335.37; δ_H(250 MHz; $(CD_3)_2SO$; DSS) 3.33 (3 H, s, CH_3), 7.75–8.55 (10 H, m, ArH); δ_C(20 MHz; $(CD_3)_2SO$; DSS) 34.7 (s, CH_3), 124.8, 126.9, 127.5, 127.7, 128.2, 130.9, 131.1, 133.0, 133.5, 133.6, 134.0, 134.8, 135.3, 141.7, and 144.5 (s, C_{Ar}), 170.6 (s, C=O), another C=O bond is missing; ν_{max} (KBr) (cm^{-1}) 1694vs (C=O), 1083, 1066, and 1027m (S=O).

2.1.4. *Crystal structure determinations*

X-ray quality single crystals were grown from acetone for **3** and from benzene–methanol mixture for **4**. Because compound **4** exhibits polymorphy, both **4a** (monoclinic space group *Pc*) and **4b** (monoclinic space group $P2_1/c$) were investigated. Table 1 summarizes the relevant data concerning the crystal structure analyses.

Intensities were recorded on an Enraf–Nonius CAD-4 diffractometer with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å radiation for **3** and **4a** by using $\omega - 2\Theta$ scans in the range $2.6° < \Theta < 40.0°$ for **3** and $2.5° < \Theta < 32.7°$ for **4a** while data for **4b** were collected with Cu Kα ($\lambda = 1.54184$ Å) in the range $3.5° < \Theta < 75.0°$. For each crystal, three standard reflections were monitored every hour. No decay correction was applied in either case. Cell constants (see Table 1) for each crystal were determined by least-squares refinement of diffractometer angles for 25 automatically centered reflections. Data were collected with the Miller indices:

3: $-19 \leq h \leq 0$ $0 \leq k \leq 16$ $-27 \leq l \leq 29$

4a: $-12 \leq h \leq 0$ $0 \leq k \leq 40$ $-13 \leq l \leq 13$

4b: $0 \leq h \leq 14$ $0 \leq k \leq 13$ $-31 \leq l \leq 31$

Data were corrected for Lorentz and polarization effects. The phase problems were solved by direct methods, by using the MULTAN program [8]. For the crystal of **4b** empirical absorption corrections (DIFABS [9]) were calculated at the end of the isotropic least-squares refinement for the positional parameters of non-hydrogen atoms. Full matrix least-squares refinement minimized $\Sigma w(\Delta F^2)$ with $w = 4F_0^2/\sigma^2(F_0^2)$, using the reflections taken with the criterion $I > 3\sigma(I)$ for **4a** and **4b**, while for **3** $\Sigma w(\Delta F^2)^2$ was minimized for the all unique reflections by the program SHELXL93 [10] with the weighting scheme: $w = 1/[\sigma^2(F_0^2)^2 + (0.1156P)^2 + 0.17P]$ (where $P = [\mathrm{Max}(F_0^2, 0) + 2F_c^2]/3$). In each case, the fractional coordinates of the hydrogen atoms were generated from

Table 5
Relevant geometric parameters for molecules **3**, **4a**$'$, **4a**$''$, **4b**$'$, and **4b**$''$ with ESDs in parentheses

Parameter	**3**	**4a**$'$	**4b**$'$	Parameter	**4a**$''$	**4b**$''$
Interatomic distances (r in Å)						
S1 ··· N1	2.968(1)	2.753(3)	2.801(2)	S21 ··· N21	2.806(3)	2.832(2)
S1–O3	–	1.492(3)	1.494(3)	S21–O23	1.498(3)	1.483(2)
S1–C1	1.782(1)	1.793(5)	1.816(2)	S21–C21	1.802(4)	1.819(3)
S1–C11	1.788(1)	1.808(4)	1.822(2)	S21–C31	1.811(5)	1.810(2)
C1–C2	1.381(2)	1.403(6)	1.383(4)	C21–C22	1.385(6)	1.346(4)
C1–C9	1.423(2)	1.411(6)	1.414(3)	C21–C29	1.421(6)	1.421(3)
C7–C8	1.372(2)	1.365(7)	1.360(3)	C27–C28	1.372(6)	1.367(4)
C8–C9	1.424(1)	1.433(6)	1.412(3)	C28–C29	1.407(6)	1.425(3)
C8–N1	1.446(2)	1.441(5)	1.452(3)	C28–N21	1.446(5)	1.445(3)
C9–C10	1.430(2)	1.422(7)	1.424(3)	C29–C30	1.418(6)	1.435(4)
C11–C12	1.394(2)	1.385(6)	1.394(3)	C31–C32	1.397(6)	1.402(3)
C12–C17	1.485(2)	1.481(6)	1.478(4)	C32–C37	1.475(6)	1.487(3)
C17–N1	1.403(1)	1.417(6)	1.432(3)	C37–N21	1.431(6)	1.410(3)
C17–O1	1.213(2)	1.219(6)	1.205(3)	C37–O21	1.198(5)	1.202(3)
C18–C19	1.495(2)	1.485(6)	1.486(3)	C38–C39	1.471(7)	1.484(4)
C18–N1	1.404(2)	1.415(6)	1.402(3)	C38–N21	1.408(6)	1.424(3)
C18–O2	1.203(1)	1.214(6)	1.199(3)	C38–O22	1.216(6)	1.197(3)
Angles (θ in deg) *Central sulfur*						
O3–S1 ··· N1	–	175.8(3)	178.4(2)	C23–S21 ··· N21	177.9(3)	178.7(2)
C1–S1 ··· N1	75.0(1)	77.8(3)	76.6(1)	C21–S21 ··· N21	76.6(1)	76.4(1)
C11–S1 ··· N1	74.1(1)	75.3(3)	74.3(1)	C31–S21 ··· N21	73.9(3)	74.8(1)
C1–S1–C11	98.9(1)	93.7(3)	95.5(2)	C21–S21–C31	95.6(3)	95.1(2)
C1–S1–O3	–	106.2(3)	104.9(2)	C21–S21–O23	105.5(4)	104.9(2)
C11–S1–O3	–	105.4(3)	105.0(2)	C31–S21–O23	105.9(4)	105.3(2)
S1–C1–C2	116.2(2)	116.2(6)	115.3(3)	S21–C21–C22	115.3(6)	117.5(3)
S1–C11–C16	119.2(2)	116.5(6)	116.1(3)	S21–C31–C36	116.3(6)	117.8(3)
Internal rings						
S1–C1–C9	123.0(2)	122.7(6)	122.9(3)	S21–C21–C29	122.6(9)	122.2(3)
C1–C9–C8	125.8(2)	124.3(7)	124.9(3)	C21–C29–C28	124.6(7)	125.5(4)
C9–C8–N1	121.9(2)	119.9(6)	120.3(3)	C29–C28–N21	120.9(6)	119.9(3)
C8–N1 ··· S1	87.8(1)	94.5(4)	93.4(2)	C28–N21 ··· S21	92.7(4)	92.9(2)
S1–C11–C12	121.6(2)	123.1(5)	123.5(3)	S21–C31–C32	123.4(5)	121.9(3)
C11–C12–C17	120.6(2)	120.6(4)	122.6(4)	C31–C32–C37	121.2(6)	121.0(3)
C12–C17–N1	115.9(2)	115.1(7)	115.0(3)	C32–C37–N21	115.1(7)	114.9(3)
C17–N1 ··· S1	81.8(1)	91.7(4)	92.9(2)	C37–N21 ··· S21	91.0(4)	88.7(2)

assumed geometries. The hydrogen positions were constrained to the corresponding heavy atoms with isotropic displacement parameters. Scattering factors were taken from standard tables [11]. Because **3a** crystallized with the polar space group *Pc* (No. 7) data were collected with Mo Kα radiation; no Flack parameter [12] was refined. All calculations were performed on a PDP-11/34 minicomputer, by using the Enraf–Nonius SDP program package [13].

Fractional atomic coordinates and mean temperature factors (U_{eq}) with ESDs (estimated standard deviations) in parentheses for non-hydrogen atoms in compounds **3**, **4a** and **4b** are listed in Tables 2–4. Because the asymmetric units in the crystal lattice of both **4a** and **4b** are built up from two similar but independent molecules (**4a**′, **4a**″ and **4b**′, **4b**″) their data, given in Tables 3–5, are distinguished by atom numbering 1–19 and 21–39 in both cases.

Lists of structure factors and anisotropic displacement parameters for non-hydrogen atoms and hydrogen atomic positions are available from one of the authors (A. Kálmán) on request.

Table 5 Continued

Parameter	3	**4a**′	**4b**′	Parameter	**4a**″	**4b**″
Amide parts						
C12–C17–O1	121.5(2)	122.4(7)	123.4(4)	C32–C37–O21	122.9(7)	121.9(4)
N1–C17–O1	122.6(2)	122.3(8)	121.6(4)	N21–C37–O21	122.8(7)	123.1(4)
C17–N1–C18	124.3(2)	123.3(6)	121.6(3)	C37–N21–C38	122.4(6)	124.3(3)
N1–C18–C19	119.0(2)	118.2(7)	117.2(4)	N21–C38–C39	118.7(7)	117.5(4)
N1–C18–O2	119.4(2)	118.8(7)	119.4(4)	N21–C38–O22	118.2(7)	119.2(4)
C19–C18–O2	121.4(2)	122.8(8)	122.7(4)	C39–C38–O22	123.0(7)	123.1(4)
Torsion angles (ϕ in deg)						
ϕ_1 S1–C1–C9–C8	−10.9(2)	4.5(6)	−3.3(3)	S21–C21–C29–C28	−7.5(5)	5.9(3)
ϕ_2 C1–C9–C8–N1	−17.8(2)	5.8(7)	−10.5(4)	C21–C29–C28–N21	−9.5(7)	12.6(4)
ϕ_3 C9–C8–N1–C17	101.6(2)	−102.8(7)	107.4(4)	C29–C28–N21–C37	106.2(7)	−106.0(4)
ϕ_3' C9–C8–N1–C18	−80.3(2)	90.4(7)	−94.6(4)	C29–C28–N21–C38	−87.5(7)	90.9(4)
ϕ_4 C8–N1–C17–C12	−35.4(2)	60.1(7)	−63.6(4)	C28–N21–C37–C32	−56.3(6)	52.0(3)
ϕ_4' C18–N1–C17–O1	−32.3(2)	42.2(8)	−38.9(3)	C38–N21–C37–O21	−40.5(7)	29.4(4)
ϕ_4'' C18–N1–C17–C12	146.6(2)	−133.8(8)	139.3(4)	C38–N21–C37–C32	138.1(7)	−146.6(4)
ϕ_4''' C8–N1–C17–O1	145.7(2)	−123.9(7)	118.2(4)	C28–N21–C37–O21	125.1(7)	−132.0(4)
ϕ_5 N1–C17–C12–C11	−53.1(1)	34.8(7)	−28.2(4)	N21–C37–C32–C31	−34.6(7)	40.6(4)
ϕ_5' O1–C17–C12–C11	125.8(2)	−141.1(8)	149.9(5)	O21–C37–C32–C31	144.0(8)	−135.4(4)
ϕ_6 C17–C12–C11–S1	3.9(2)	0.2(5)	−5.5(3)	C37–C32–C31–S21	−4.3(5)	0.4(3)
ϕ_7 C12–C11–S1–C1	89.1(2)	−92.4(7)	92.5(4)	C32–C31–S21–C21	94.1(7)	−92.5(4)
ϕ_7' C12–C11–S1–O3	–	159.6(7)	−160.4(4)	C32–C31–S21–O23	−158.0(7)	160.6(4)
ϕ_7'' C16–C11–S1–C1	−94.5(2)	92.4(7)	−94.3(4)	C36–C31–S21–C21	−93.4(7)	94.8(4)
ϕ_7''' C16–C11–S1–O3	–	−15.6(6)	12.8(3)	C36–C31–S21–O23	14.5(6)	−12.2(3)
ϕ_8 C11–S1–C1–C9	−53.8(1)	67.3(5)	−64.6(2)	C31–S21–C21–C29	−60.9(5)	61.9(3)
ϕ_8' O3–S1–C1–C9	–	174.5(8)	−171.7(4)	O23–S21–C21–C29	−169.1(8)	169.2(4)
ϕ_8'' C11–S1–C1–C2	121.3(2)	−110.1(5)	111.5(3)	C31–S21–C21–C22	114.8(5)	−113.0(3)
ϕ_8''' O3–S1–C1–C2	–	−2.9(6)	4.4(3)	O23–S21–C21–C22	6.6(6)	−5.6(4)
ϕ_9 C17–N1–C18–O2	175.5(3)	−171.6(8)	161.7(4)	C37–N21–C38–O22	168.7(7)	−166.5(4)
ϕ_9' C8–N1–C18–C19	173.5(3)	179.7(9)	−179.3(5)	C28–N21–C38–C39	−179.5(9)	179.7(5)
ϕ_9'' C17–N1–C18–C19	−8.4(1)	13.6(7)	−22.5(4)	C37–N21–C38–C39	−13.7(7)	17.9(4)
ϕ_9''' C8–N1–C18–O2	−2.6(2)	−5.5(7)	4.9(4)	C28–N21–C38–O22	2.9(7)	−4.6(4)
ϕ_{10} C9–C8–N1 ··· S1	22.3(1)	−8.4(6)	12.4(4)	C29–C28–N21 ··· S21	13.6(8)	−15.9(6)
ϕ_{11} C8–N1 ··· S1–C1	−21.1(1)	8.3(4)	−10.8(2)	C28–N21 ··· S21–C21	−13.2(4)	14.6(2)
ϕ_{12} N1 ··· S1–C1–C9	16.9(1)	−6.8(5)	7.8(2)	N21 ··· S21–C21–C29	11.1(5)	−11.0(3)
ϕ_{13} C12–C17–N1 ··· S1	47.3(1)	−35.0(10)	31.7(7)	C32–C37–N21 ··· S21	37.0(10)	−40.5(2)
ϕ_{14} C17–N1 ··· S1–C11	−36.9(1)	29.0(5)	−27.8(2)	C37–N21 ··· S21–C31	−31.9(4)	33.3(2)
ϕ_{15} N1 ··· S1–C11–C12	17.5(1)	−16.1(5)	18.1(3)	N21 ··· S21–C31–C32	19.8(5)	−18.1(2)

3. Results and discussion

Selected bond lengths, bond angles and torsion angles (with ESDs in parentheses) including data related to S···N close contacts are given for compounds **3** and **4** in Table 5.

As can be seen from Table 5 the four structures observed for compound **4** (**4a**′, **4a**″, **4b**′ and **4b**″) exhibit very similar geometry. In the following the structures **3** and **4b**′ will be discussed and compared. Geometry data quoted in the text are rounded off; the torsion angles are marked by numbering the ϕ symbols as explained in Table 5 and shown in Fig. 3 (below). The solid state conformations established for the chiral molecules **3** and **4b**′ are shown in Figs. 1 and 2 by a perspective representation of one of the enantiomers occurring in the crystal lattice.

3.1. Ring conformation

In sulfide-*N*-acetyllactam **3** and sulfoxide-*N*-acetyllactam **4** the peri (1,8) and ortho (1,2) positions of the planar naphthalene and benzene rings are connected by non-rigid amide (–NAc–CO–) and sulfur (–S–) bridges resulting in the formation of an eight-membered thiazocine ring. In an idealized case this ring should have three planar parts including the (S1,C1,C9,C8,N1) and (S1,C11,C12,C17) "aromatic sets" as well as the (C8,N1,C17,C12) "amide set" of ring atoms.

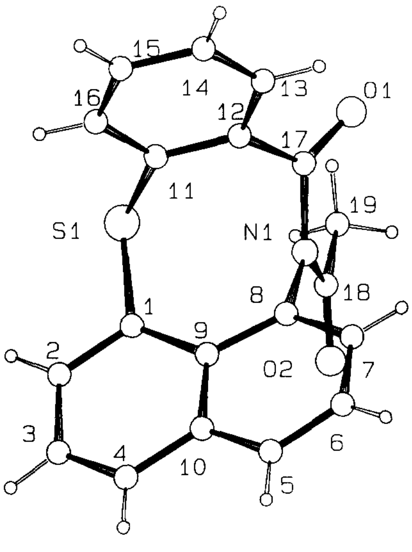


Fig. 1. Solid state conformation for compound **3** as obtained by X-ray diffraction with atom numbering scheme for non-hydrogen atoms; only one of the enantiomers occurring in the racemic crystals is represented.

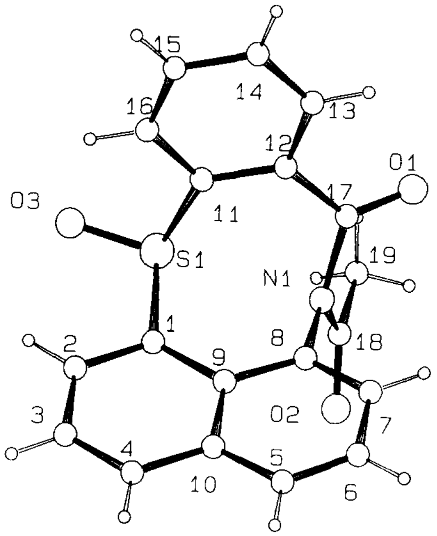


Fig. 2. Solid state conformation for one (**4b**′) of the symmetry independent molecules of **4b** as obtained by X-ray diffraction with atom numbering scheme for non-hydrogen atoms; only one of the enantiomers occurring in the racemic crystals is represented.

The deviation of ϕ_1, ϕ_2, and ϕ_3 torsion angles from the ideal 0° value (−11°, −18°, and −4° in **3**; −4°, −11°, and −6° in **4b**′) observed for the "planar" aromatic parts of the hetero ring, however, points to some steric constraint in the ring system. In the same way, the ring skeleton does not allow the endocyclic *cis*-amide moiety to assume the perfect synperiplanar conformation ($\phi_4 = -35°$ and $-63°$, $\phi'_4 = -32°$ and $-39°$ in **3** and **4b**′, respectively). Furthermore, the Csp^2 and Nsp^2 parts of the endocyclic amide group are not coplanar with the neighboring aromatic ring, as can be seen from $\phi_3 = 102°$ and $107°$ as well as from $\phi_5 = -53°$ and $-28°$ obtained for **3** and **4b**′, respectively.

The *endo-cis*-amide arrangement allows the *N*-acetyl group to assume an out-of-ring (quasi-equatorial) position which may be described by the torsion angles $\phi'_3 = -80°$ and $-95°$ as well as by $\phi_4'' = 147°$ and 139° in **3** and **4b**′, respectively. The exocyclic amide part exhibits a trans configuration in both **4** and **4b**′, i.e. the acetyl oxygen and the ring carbonyl-Csp^2 atoms are nearly antiperiplanar about the exocyclic Nsp^2–Csp^2 bond ($\phi_9 = 176°$ for **3** and 162° for **4b**′). Thus the two carbonyl oxygen atoms are located far from each other.

In the "sulfur part" of the thiazocine ring and sulfide moiety of **3** does not assume a skew conformation usually found in *o,o*′-disubstituted diaryl sulfides (see Ref. [2a]). Although the benzene ring is perpendicular to the C_{ar}–S–C_{ar} plane ($\phi_7 = 89°$), the naphthalene ring is far from being coplanar with the same plane ($\phi_8 = -54°$). In contrast, the sulfoxide moiety in **4b**′ retains the axial-twist conformation characteristic of *o,o*′-disubstituted diaryl sulfoxides (see Ref. [2b]). The benzene ring makes a dihedral angle of $\phi_7 = 93°$ with the C_{ar}–S–C_{ar} plane, which is very near to the expected right angle. At the same time, the benzene ring becomes nearly coplanar with the C_{ar}–S–O plane ($\phi_7' = 160°$). Presumably the latter position is required by the conjugative interaction between benzene ring and sulfinyl group. The same is true for the naphthalene moiety, although this ring is somewhat twisted from the position that would be perpendicular to the C_{ar}–S–C_{ar} plane ($\phi_8 = -65°$, $\phi_8' = 172°$). We may conclude, however, from the comparison of corresponding torsion angles that the aromatic ring positions in **3** and **4b**′ are nearly the same, independently of the oxidation state of sulfur.

The geometry parameters of compounds **3** and **4** lead to a chiral, boat-like molecular shape as shown in Fig. 3. The planar chirality of molecules **3** and **4b**′ represented in Figs. 1 and 2 can be denoted as p*R*. Here the naphthalene ring carrying the sulfur and nitrogen substituents in 1,8-position is regarded as the plane of chirality and the C17 atom of the ring carbonyl group is chosen as pilot atom (see Ref. [14]); the plane is viewed from the side of the pilot atom. Since the C12 → C11 → S1 sequence traces a clockwise direction, the designation of the planar chirality will be p*R*. In sulfoxide **4b**′ the p*R* ring configuration is associated with the *R* configuration as sulfur. In the same way, the configuration of the other three structures **4a**′, **4a**″, and **4b**″ can be denoted as *S*,p*S*, *R*,p*R*, and *S*,p*S*, respectively.

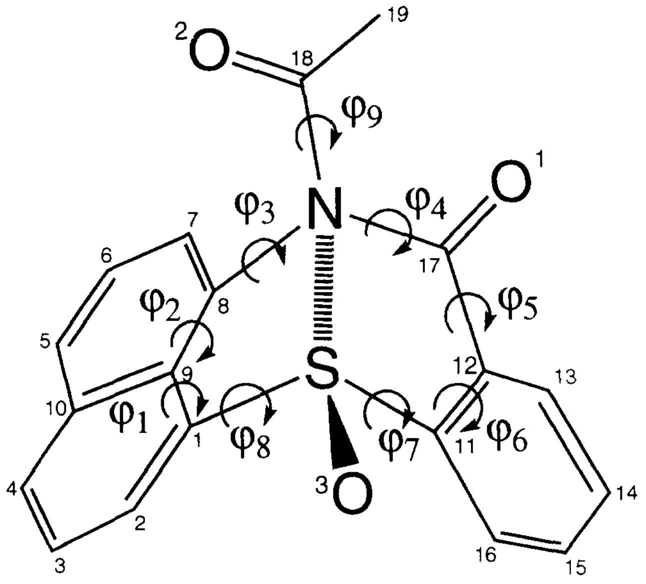


Fig. 3. Schematic representation of the actual conformations of compounds **3** (X = lone pair) and **4** (X = O) indicating the numbering of non-hydrogen atoms and ring torsion angles.

3.2. Sulfur-nitrogen close contact

The *R*,p*R* (or *S*,p*S*) configuration of the molecules of compound **4** allows the sulfinyl oxygen to assume a favorable out-of-ring (quasi-equatorial) position (e.g $\phi_7' = 160°$ and $\phi_8' = 172°$ in **4b**′), which leads to an almost linear O=S···N arrangement ($\theta = 178°$ in **4b**) with transannular sulfur–nitrogen close contact characterized by a non-bonded distance $r(\mathrm{S}\cdots\mathrm{N}) = 2.80$ Å.

All these features suggest a sulfurane-like configuration in **4** with the hetero-atoms in axial positions and the aromatic carbon atoms and lone pair in equatorial ones. The nearly rectangular $\theta(\mathrm{C_{ar}{-}S{-}O}) = 105$–$106°$ and $\theta(\mathrm{C_{ar}{-}S\cdots N}) = 74$–$78°$ angles correspond to a somewhat distorted trigonal bipyramidal geometry. The characteristic distance between the heteroatoms, $r(\mathrm{O{=}S\cdots N}) = 4.25$–$4.32$ Å is comparable with the distances $r(\mathrm{N{-}S\cdots O}) = 4.06$–$4.41$ Å found for alkylaminosulfonium compounds stabilized by sulfur–oxygen interaction [1,15]. Both this fact and the invariance of the $r(\mathrm{S{=}O}) = 1.49$ Å bond length suggest, however, that the delocalization of the lone pair (belonging to the doubly acylated nitrogen) toward the sulfur center does not result in the formation of an effective hypervalent S–N bond. This view is supported by the remarkably shorter $r(\mathrm{O{-}S{-}N}) = 3.80$–$3.87$ Å distances found for spirosulfuranes [15].

In contrast to the sulfoxide-*N*-acetyllactam **4**, a sulfurane-like configuration cannot exist at the sulfur atom in the sulfide-*N*-acetyllactam **3**. In the latter case the sulfur–nitrogen distance is significantly longer, $r(\mathrm{S}\cdots\mathrm{N}) = 2.97$ Å.

The two five-membered "half-rings" in **3** and **4** closed by a transannular S···N close contact are built up from the favorably conjugated sequences S–C(ar)1–C(ar)9–C(ar)8–N(sp^2) and S–C(ar)11–C(ar)12–C(sp^2)17–N(sp^2) with the heteroatoms in 1,5-positions. This type of structure is known to promote non-bonded interaction between sulfur and an electronegative heteroatom [16]. The S···N distances obtained for **3** and **4** (2.75–2.97 Å) are in agreement with this view. It should be mentioned, however, that only the five-membered "half-ring" fused with the naphthalene ring can be regarded as nearly planar, as shown by the intervals 7–22° and 16–47° observed for the two sets of torsion angles (ϕ_1, ϕ_2, ϕ_{10}, ϕ_{11}, ϕ_{12}) and (ϕ_5, ϕ_6, ϕ_{13}, ϕ_{14}, ϕ_{15}) listed in Table 5.

3.3. Comparison of thiazocine and thiazonine rings

By changing the 1,8-naphthylene part in **3** and **4** to a 2.2′-biphenylene part, the rather rigid thiazocine ring is enlarged to the thaizonine ring of **1a** and **1b** which is more flexible, owing to the pseudorotation about the $\mathrm{C_{ar}1{-}C_{ar}1'}$ bond in the biphenyl moiety (cf. the corresponding torsion angles $\phi = -88°$ for **1a** and $-47°$ for **1b** in Ref. [1]). As a result, the endocyclic *cis*-amide part in **1a** becomes less distorted ($\phi_4 = 28°$, $\phi_4' = 8°$) than in **3** ($\phi_4 = -35°$, $\phi_4' = -32°$), and the non-bonded S···N distance is markedly increased (from 2.97 Å in **3** to 4.05 Å in **2a**).

A comparison of the thiazocine derivative **4** with its thiazonine analog **1b** shows that a dramatic change occurs in stereochemistry, which may be attributed to the lack of an exocyclic *N*-acetyl group in **1b**. In the latter case the endocyclic amide part assumes a trans configuration ($\phi_4 = 149°$) with the quasi-axial position of the amide hydrogen causing no steric constraint. The sulfur–nitrogen transannular close contact, $r(\mathrm{S}\cdots\mathrm{N}) = 2.78$ Å, and the sulfurane-like configuration at sulfur, $\theta(\mathrm{O{=}S\cdots N}) = 171°$, which are characteristic of **1b**, do not differ significantly from those observed for **4**.

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