Synthesis of novel dibenzo-2,6,9-triazabicyclo[3.3.1]nonanes from *o*-tosylamino- and *o*-mesylaminobenzaldehydes

L. Yu. Ukhin[a]★ *and L. G. Kuz´mina*[b]

[a]*Institute of Physical and Organic Chemistry, Rostov State University, 194/2 prosp. Stachki, 344090 Rostov-on-Don, Russian Federation. Fax: +7 (863) 243 4776. E-mail: may@ipoc.rsu.ru*

[b]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 953 1279. E-mail: kuszmina@igic.ras.ru*

Condensation of *o*-tosylaminobenzaldehyde with γ-aminobutyric, 4-aminophenylthioacetic, and *p*-aminobenzoic acids and β-alanine gave 6,12-epimino-5,11-ditosyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*]-1,5-diazocines with carboxyl-containing substituents at the bridging N atoms. The structures of three products were examined by X-ray diffraction analysis. Condensation of *o*-mesylaminobenzaldehyde (prepared by the McFadyen—Stevens reaction) with NH_4OAc and primary amines afforded 6,12-epimino-5,11-dimesyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*]-1,5-diazocine derivatives.

Key words: *o*-tosylaminobenzaldehyde, amino acids, 6,12-epimino-5,11-ditosyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*]-1,5-diazocine derivatives, *o*-mesylaminobenzaldehyde, ammonium acetate, primary amines, 6,12-epimino-5,11-dimesyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*]-1,5-diazocine derivatives, X-ray diffraction analysis.

Earlier,[1] we synthesized dibenzo-2,6,9-triazabicyclo[3.3.1]nonanes from *o*-tosylaminobenzaldehyde and primary amines. Some of these compounds contained pharmacophoric phenylsulfonylamino groups at the bridging N atoms.[2] It was of interest to carry out such condensation reactions with biologically active amino acids. Incorporation of the N atom of their amino groups into bicyclic structures of the target products could change their properties and impart new kinds of biological activities.

Condensation of *o*-tosylaminobenzaldehyde **1** with γ-aminobutyric (**2a**) and *p*-aminophenylthioacetic acids (**2b**), β-alanine (**2c**), and 4-aminobenzoic acid (**2d**) gave 6,12-epiminotetrahydrodibenzo[*b*,*f*]-1,5-diazocines **3a**—**d** with carboxyl-containing substituents at position 13 (Scheme 1).

Their structures were established by X-ray diffraction analysis (see below) and confirmed by IR and NMR spectra (Table 1).

Reactions of α-amino acids with aldehyde **1** yield no carboxyl-containing diazocines.

To define the scope of this reaction, we studied the behavior of *o*-mesylaminobenzaldehyde synthesized by the McFadyen—Stevens reaction as described for *o*-tosylaminobenzaldehyde (**1**)[3,4] (Scheme 2).

It turned out that aldehyde **6** reacted with ammonium acetate and primary amines to give 6,12-epimino-5,11-dimesyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*]-1,5-diazocine derivatives **7a**—**e**; however, the yields of the products were lower than the yields of their tosyl analogs[1] (Scheme 3).

Scheme 1

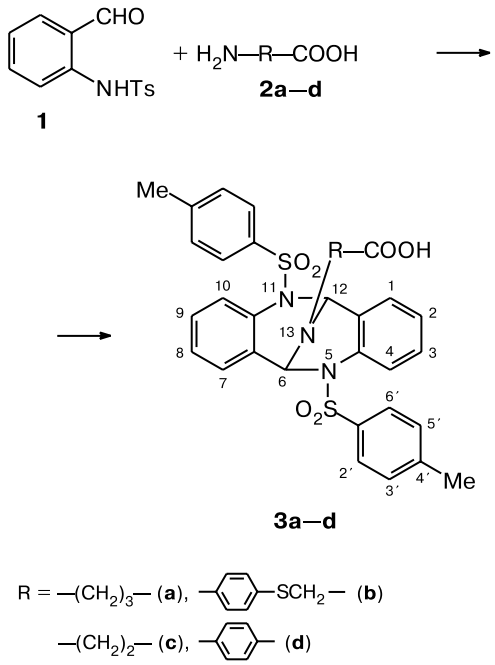

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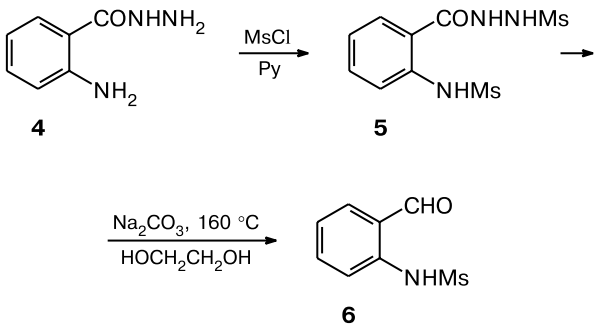
Table 1. IR and ^{1}H NMR spectroscopic data for compounds **3a—d**

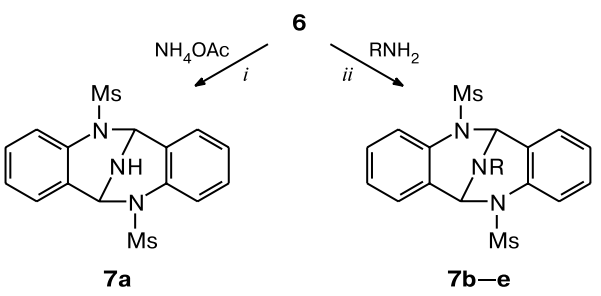
Compound	IR, ν/cm^{-1}	^{1}H NMR (DMSO-d$_6$), δ (*J*/Hz)
3a	1727, 1714 (CO), 1607, 1581, 1487 (arom.), 1334, 1160 (SO_2)	1.47, 1.63 (both m, 1 H each, CH_2); 1.94, 2.21 (both m, 2 H each, CH_2); 2.39 (s, 6 H, 2 Me); 6.03 (s, 2 H, 2 CH); 7.05—7.25 (two br.t, 4 H, C(2)H, C(3)H, C(8)H, C(9)H); 7.29 (d, 4 H, 2 C(3′)H, 2 C(5′)H, *J* = 8.2); 7.39 (br.d, 2 H, C(1)H, C(7)H); 7.58 (d, 2 H, C(4)H, C(9)H, *J* = 8.3); 7.63 (d, 4 H, 2 C(2′)H, 2 C(6′)H, *J* = 8.2)
3b*	1714, 1694 (CO), 1594, 1581, 1487, 1480 (arom.), 1341, 1154 (SO_2)	2.27 (s, 6 H, 2 Me); 3.65 (s, 2 H, SCH_2); 6.39 (d, 2 H, C(2″)H, C(6″)H, *J* = 8.6); 6.73 (s, 2 H, 2 CH); 6.86 (d, 4 H, 2 C(3′)H, 2 C(5′)H, *J* = 8.2); 7.02 (d, 4 H, 2 C(2′)H, 2 C(6′)H, *J* = 8.2); 7.10—7.22 (m, 6 H, CH (arom.)); 7.54 (dd, 2 H, C(1)H, C(7)H, ^3J = 7.5, ^4J = 1.6); 7.64 (br.d, 2 H, C(4)H, C(10)H)
3c	1727, 1714 (CO), 1607, 1581, 1487 (arom.), 1341, 1161 (SO_2)	2.10 (m, 1 H, CH_2); 2.30—2.50 (m, 9 H, 2 Me, CH_2, 1 H from CH_2); 6.08 (s, 2 H, 2 CH); 7.00—7.25 (two br.t, 4 H, C(2)H, C(3)H, C(8)H, C(9)H); 7.28 (d, 4 H, 2C(3′)H, 2 C(5′)H, *J* = 8.2); 7.38 (br.d, 2 H, C(1)H, C(7)H); 7.53 (d, 2 H, C(4)H, C(9)H, *J* = 8.2); 7.66 (d, 4 H, 2 C(2′)H, 2 C(6′)H, *J* = 8.2); 12.17 (s, 1 H, OH)
3d	1694 (CO), 1607, 1581, 1514, 1487 (arom.), 1354, 1347, 1174, 1161 (SO_2)	2.26 (s, 6 H, 2 Me); 6.54 (d, 2 H, C(2″)H, C(6″)H, *J* = 8.6); 6.83 (s, 2 H, 2 CH); 6.85 (br.d, 4 H, 2 C(3′)H, 2 C(5′)H); 6.98 (d, 4 H, 2 C(2′)H, 2 C(6′)H, *J* = 8.2); 7.15—7.35 (m, 4 H, CH (arom.)); 7.53 (br.d, 2 H, CH (arom.)); 7.65 (d, 2 H, CH (arom.), *J* = 8.0); 7.71 (d, 2 H, C(3″)H, C(5″)H, *J* = 8.6)

* In $CDCl_3$.

Scheme 2



Scheme 3



R = Me (**b**), Et (**c**), Ph (**d**), 4-MeC_6H_4 (**e**)

i. Δ, PrOH; *ii*. Δ, PrOH or AcOH.

The IR and NMR spectroscopic data for compounds **5—7** are given in Table 2.

As with *o*-tosylaminobenzaldehyde (**1**), we revealed a correlation between the basicity and reactivity of an amine in the reaction with compound **6**. The lowest yields were obtained in the reactions with aromatic amines, which are less basic than aliphatic amines by on average six orders of magnitude. However, the possibility of condensation seems to be determined by additional factors that are unclear. For instance, 4-fluoroaniline does not react with aldehyde **6**, although its basicity (pK_a = 4.54) is very close to that of aniline (pK_a = 4.60).[5]

The crystal structures of compounds **3a—c** were established by X-ray diffraction analysis (Figs 1—3; Tables 3, 4).

Both heterocycles in the bicycles exist in the sofa conformation. The angle C(1)N(3)C(8) goes out of the planes of the five-membered fragments including the N(1) or N(2) atom (C(1)N(1)C(10)C(9)C(8) or C(1)C(2)C(3)N(2)C(8)). The corresponding dihedral angles noticeably differ both for the two rings in the same molecule and for different molecules, varying from 48° to 72° (see Table 3). At the same time, the dihedral angle between the planes of the benzene rings in the phenylsulfonyl substituents, which seems to depend mainly on the packing effects in the crystal, shows a comparatively small scatter over compounds **3a—c** (from 98.4° to 104.0°).

In all the three structures, the central N(3) atom of the bicyclic system has a pyramidal bond configuration. The sum of the bond angles at the N(3) atom is 339.7° in **3a**, 347.7° in **3b**, and 334.7° in **3c**. The bond configurations of the N(1) and N(2) atoms are significantly more flattened. The sum of the bond angles at these atoms is 355.7° and 359.9° in compound **3a** and 360.0° and 358.0° in compound **3c**. The geometry of compound **3b** is slightly different. The sum of the bond angles at the N(1) atom is 357.5°, which corresponds to a virtually planar bond configuration (as in compounds **3a**

Table 2. IR and ^{1}H NMR spectroscopic data for compounds **5**, **6**, and **7a—e**

Compound	IR, ν/cm^{-1}	^{1}H NMR ($CDCl_3$), δ (J/Hz)
5*	3353, 3207 (NH), 1647 (CO), 1607, 1587, 1534, 1501 (arom.), 1341, 1327, 1167, 1154 (SO_2)	3.01, 3.04 (both s, 3 H each, Me); 7.17 (m, 1 H, CH (arom.)); 7.54 (m, 2 H, CH (arom.)); 7.85 (d, 1 H, C(6)H, J = 7.5); 9.60 (d, 1 H, NH, J = 2.5); 10.40 (s, 1 H, NH); 10.96 (d, 1 H, NH, J = 2.5)
6	3147 (NH), 1674 (CO), 1607, 1581, 1487 (arom.), 1327, 1147 (SO_2)	3.12 (s, 3 H, Me); 7.28 (m, 1 H, CH (arom.)); 7.60—7.80 (m, 3 H, CH (arom.)); 9.93 (s, 1 H, CHO); 10.62 (s, 1 H, NH)
7a*	3353 (NH), 1600, 1575, 1487 (arom.), 1354, 1341, 1327, 1167, 1161, 1154 (SO_2)	3.04 (s, 6 H, 2 Me); 4.50 (t, 1 H, NH, J = 3.0), 6.22 (d, 2 H, 2 CH, J = 3.0); 7.05—7.30 (m, 4 H, CH (arom.)); 7.89 (dd, 2 H, C(1)H, C(7)H, ^3J = 7.5, ^4J = 1.5); 7.54 (d, 2 H, C(4)H, C(10)H, J = 8.1)
7b	1607, 1587, 1581, 1487 (arom.), 1354, 1341, 1327, 1154 (SO_2)	2.52 (s, 3 H, NMe); 3.05 (s, 6 H, 2 Me), 6.04 (s, 2 H, 2 CH); 7.05—7.30 (m, 4 H, CH (arom.)); 7.44 (dd, 2 H, C(1)H, C(7)H, ^3J = 7.6, ^4J = 1.6); 7.54 (dd, 2 H, C(4)H, C(10)H, ^3J = 8.35, ^4J = 0.8)
7c	1607, 1581, 1487 (arom.), 1341, 1321, 1161, 1141 (SO_2)	1.28 (t, 3 H, Me, J = 7.2); 2.58, 2.73 (both m, 1 H each, CH_2); 3.04 (s, 6 H, 2 Me), 6.16 (s, 2 H, 2 CH); 7.05—7.30 (m, 4 H, CH (arom.)); 7.46 (dd, 2 H, C(1)H, C(7)H, ^3J = 7.6, ^4J = 1.6); 7.55 (d, 2 H, C(4)H, C(10)H, J = 8.3)
7d	1607, 1587, 1501, 1487 (arom.), 1354, 1334, 1167, 1154 (SO_2)	2.48 (s, 6 H, 2 Me), 6.94 (s, 2 H, 2 CH), 6.97—7.40 (m, 9 H, CH (arom.)); 7.59 (dd, 2 H, C(1)H, C(7)H, ^3J = 7.5, ^4J = 1.8); 7.68 (d, 2 H, C(4)H, C(10)H, J = 8.0)
7e	1607, 1600, 1587, 1514, 1487 (arom.), 1347, 1327, 1167, 1154 (SO_2)	2.26 (s, 3 H, Me); 2.48 (s, 6 H, 2 Me), 6.88 (m, 4 H, 2 CH, 2 CH (arom.)); 7.00—7.30 (m, 6 H, CH (arom.)); 7.58 (dd, 2 H, C(1)H, C(7)H, ^3J = 7.5, ^4J = 1.8); 7.68 (dd, 2 H, C(4)H, C(10)H, ^3J = 8.3, ^4J = 1.2)

* In DMSO-d_6.

and **3c**); the analogous sum of the bond angles at the N(2) atom (349.3°) suggests a noticeable pyramidal character of its bond configuration.

Hence, the geometry of the bicyclic framework in compounds **3a—c** is not rigid as regards both the bond configurations of the N atoms and the dihedral angles in the six-membered heterocycles.

Compounds **3a,b** form centrosymmetrical dimers typical of carboxylic acids through pairs of hydrogen bonds (Figs 4, 5). These hydrogen bonds in structure **3a** have the

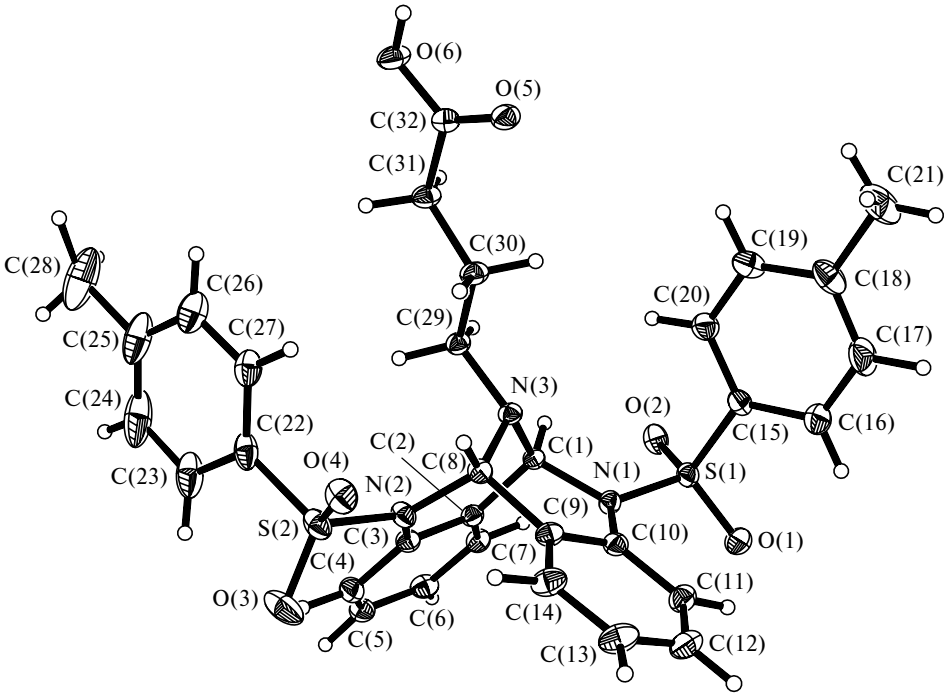


Fig. 1. Structure **3a**.

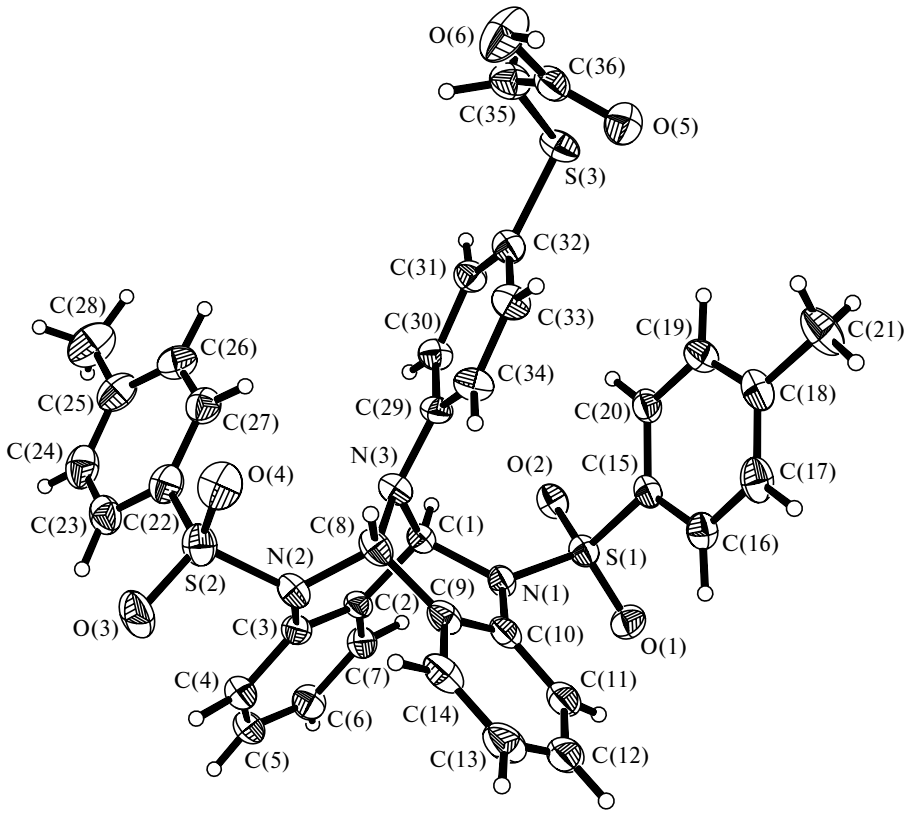


Fig. 2. Structure **3b**.

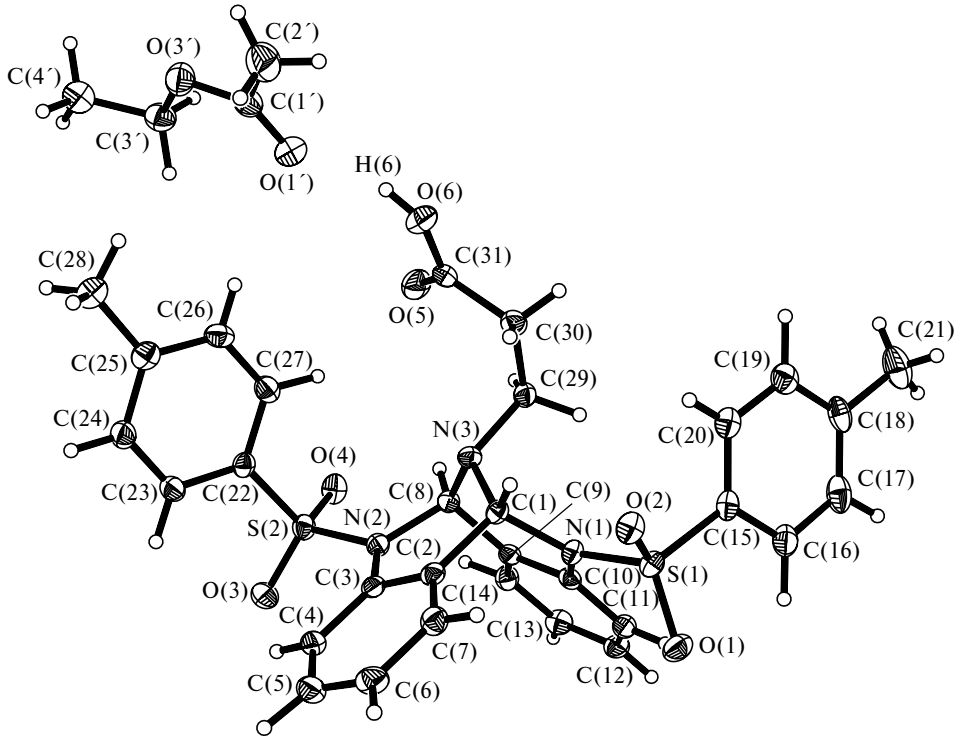


Fig. 3. Structure **3c** with a solvate molecule of ethyl acetate.

Table 3. Geometrical parameters of the 2,6,9-triazabicyclo[3.3.1]nonane fragment in compounds **3a—c**

Parameter	**3a**	**3b**	**3c**
Bond		*d*/Å	
N(1)—C(1)	1.493(2)	1.495(3)	1.521(3)
N(1)—C(10)	1.435(2)	1.442(4)	1.435(3)
N(1)—S(1)	1.651(2)	1.661(2)	1.649(2)
N(2)—C(3)	1.423(2)	1.446(3)	1.433(3)
N(2)—C(8)	1.507(2)	1.476(4)	1.484(3)
N(2)—S(2)	1.649(2)	1.673(2)	1.664(2)
N(3)—C(1)	1.447(2)	1.451(3)	1.443(3)
N(3)—C(8)	1.435(2)	1.463(4)	1.459(3)
N(3)—C(29)	1.470(2)	1.426(3)	1.479(3)
C(1)—C(2)	1.509(2)	1.522(4)	1.516(3)
C(2)—C(3)	1.402(2)	1.406(4)	1.399(3)
C(8)—C(9)	1.515(2)	1.513(4)	1.521(3)
C(9)—C(10)	1.400(2)	1.402(4)	1.403(3)
Bond angle		ω/deg	
C(1)—N(1)—S(1)	117.8(1)	120.7(2)	120.7(2)
C(1)—N(1)—C(10)	115.2(1)	113.6(2)	115.6(2)
S(1)—N(1)—C(10)	122.7(1)	123.2(2)	123.7(2)
C(8)—N(2)—S(2)	120.0(1)	118.8(2)	119.6(2)
C(8)—N(2)—C(3)	116.2(1)	112.9(2)	115.2(2)
S(2)—N(2)—C(3)	123.7(1)	117.6(2)	123.2(2)
C(1)—N(3)—C(8)	108.4(1)	108.2(2)	107.7(2)
C(1)—N(3)—C(29)	115.6(1)	118.4(2)	113.9(2)
C(8)—N(3)—C(29)	115.7(1)	121.1(2)	113.1(2)
Dihedral angle		φ/deg	
C(1),N(3),C(8)/ C(1),N(1),C(10),C(9),C(8)	59.4	48.0	72.3
C(1),N(3),C(8)/ C(1),C(2),C(3),N(2),C(8)	50.2	54.9	59.4
C(2),C(3),C(4),C(5),C(6),C(7)/ C(9),C(10),C(11),C(12),C(13),C(14)	104.0	98.4	102.0

following parameters: O(5)...H(6A) 1.77 Å, O(5)...O(6A) 2.656(2) Å, angle O(5)...H(6A)—O(6A) 170°, and angle C(32)—O(5)...H(6A) 124°.

The parameters of the hydrogen bonds in structure **3b** (see Fig. 5) (1.65 Å, 2.231(3) Å, 170°, and 120.9°, respectively) suggest a stronger interaction associated with the more pronounced electron-withdrawing properties of the substituent in the carboxyl fragment.

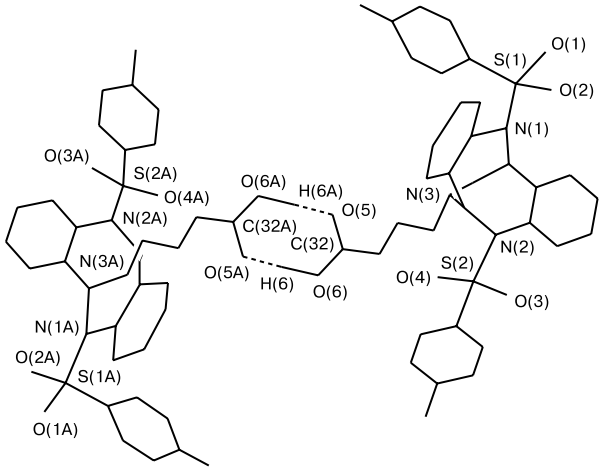


Fig. 4. Centrosymmetrical dimer in the crystal of **3a**.

A different system of weak interactions was detected in structure **3c**, in which hydrogen bonding involves a solvate molecule of ethyl acetate rather than the carboxy group of the neighboring molecule (see Fig. 3). In this structure, the distances H(6)...O(1´) and O(6)...O(1´) are 1.86 and 2.748(3) Å. These values correspond to a very weak hydrogen bond which can be identified only from the regular mutual geometries of the corresponding fragments (angle C(1´)—O(1´)...H(6) 122°, angle O(6)—H(6)...O(1´) 164.2°).

Experimental

IR spectra were recorded on a Specord IR75 instrument (Nujol). ^{1}H NMR spectra were recorded on a Varian UNITY-300 spectrometer.

***o*-Tosylaminobenzaldehyde (1)** was prepared as described earlier.[3,4]

13-(3-Carboxypropyl)-6,12-epimino-5,11-ditosyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*]-1,5-diazocine (3a). A mixture of aldehyde **1** (1.37 g, 5 mmol) and γ-aminobutyric acid (**2a**) (0.50 g, 5 mmol) in 10 mL of PrOH was refluxed for 5 h and cooled. The precipitate that formed was filtered off, washed with EtOH (3 mL), and dried in air to give colorless crystals, m.p. 224—225 °C (from ethyl acetate). The yield of compound **3a**

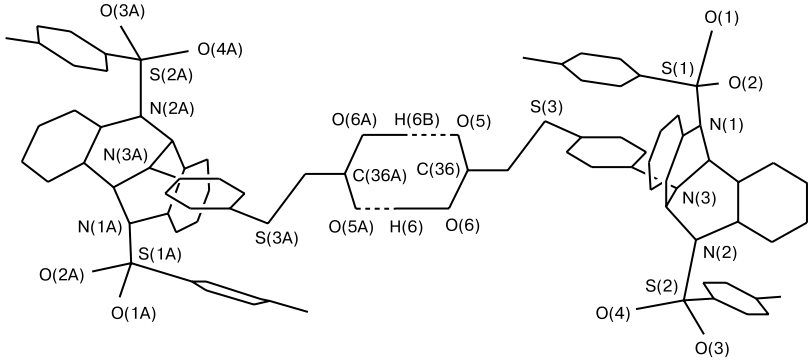


Fig. 5. Centrosymmetrical dimer in the crystal of **3b**.

Table 4. Crystallographic parameters and a summary of data collection for compounds **3a—c**

Parameter	**3a**	**3b**	**3c**
Molecular formula	$C_{32}H_{31}N_3O_6S_2$	$C_{36}H_{31}N_3O_6S_3$	$C_{35}H_{34}N_6O_8S_2$
Molar mass/kg kmol^{-1}	617.72	697.21	692.79
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	10.1866(14)	12.1487(4)	10.6092(4)
b/Å	11.2535(15)	12.5199(4)	13.1826(5)
c/Å	14.743(2)	13.0127(5)	13.6775(5)
α/deg	72.039(3)	70.247(2)	107.034(2)
β/deg	74.762(3)	67.511(2)	103.4430(10)
γ/deg	68.880(3)	70.045(2)	107.373(2)
V/Å^3	1477.7(3)	1669.18(10)	1634.73(11)
Z	2	2	2
ρ_{calc}/g cm^{-3}	1.388	1.388	1.407
$F(000)$	648	728	722
μ(Mo-Kα)/mm^{-1}	0.231	0.274	0.221
Crystal size/mm	0.34×0.26×0.18	0.18×0.12×0.10	0.18×0.10×0.08
Temperature/K	120.0(2)	120.0(2)	120.0(2)
θ range/deg	1.47—29.00	1.74—29.00	1.66—29.00
Ranges of h, k, l indices	$-13 \le h \le 12$	$-12 \le h \le 16$	$-14 \le h \le 13$
	$-15 \le k \le 10$	$-17 \le k \le 16$	$-17 \le k \le 16$
	$-20 \le l \le 18$	$-14 \le l \le 17$	$-18 \le l \le 18$
Number of measured reflections	11656	13218	10943
Number of independent reflections	7741	8534	8055
R_{int}	0.0205	0.0570	0.0370
Number of reflections with $I > 2\sigma(I)$	7741	4164	5087
Number of refined parameters	513	557	570
R factors with $I > 2\sigma(I)$			
R_1	0.0509	0.0591	0.0579
wR_2	0.1317	0.1109	0.1311
R factors for all reflections			
R_1	0.0677	0.1470	0.1062
wR_2	0.1477	0.1303	0.1473
GOOF on F^2	1.078	0.889	0.926
Residual electron density (min/max)/e·Å^{-3}	−0.397/1.079	−0.374/0.342	−0.338/0.579

was 0.60 g (39%). Found (%): C, 62.18; H, 4.99; N, 6.60; S, 10.65. $C_{32}H_{31}N_3O_6S_2$. Calculated (%): C, 62.22; H, 5.06; N, 6.80; S, 10.38.

13-[4-(Carboxymethylthio)phenyl]-6,12-epimino-5,11-ditosyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*]-1,5-diazocine (3b). A mixture of aldehyde **1** (0.55 g, 2 mmol) and 4-aminophenylthioacetic acid (**2b**) (0.20 g, 1.1 mmol) in 7 mL of AcOH was refluxed for 5 h and filtered. Methanol (3 mL) was added to the hot mother liquor. The resulting mixture was cooled with ice and the precipitate that formed was filtered off, washed with MeOH (2 mL), dried in air, and recrystallized from ethyl acetate (20 mL)—light petroleum (10 mL) to give colorless crystals, m.p. 237—240 °C. The yield of compound **3b** was 0.16 g (23%). Found (%): C, 62.14; H, 4.59; N, 5.87; S, 13.50. $C_{36}H_{31}N_3O_6S_3$. Calculated (%): C, 61.96; H, 4.48; N, 6.02; S, 13.78.

13-(2-Carboxyethyl)-6,12-epimino-5,11-ditosyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*]-1,5-diazocine (3c). A mixture of aldehyde **1** (1.37 g, 5 mmol) and β-alanine (**2c**) (0.45 g, 5 mmol) in 10 mL of PrOH was refluxed for 3 h. Then a mixture of EtOH (15 mL) and water (10 mL) was added. The resulting mixture was brought to boiling, filtered hot, and cooled in ice. The precipitate that formed was filtered off, washed with 50% EtOH (50 mL), dried in air, and recrystallized from ethyl acetate to give a 1 : 1 solvate **3c**·EtOAc. IR (solvate), ν/cm^{-1}: 1687 (CO in COOH), 1740 (CO in EtOAc). Heating of the solvate to 100—120 °C completely removed ethyl acetate to give a colorless substance, m.p. 248—250 °C. The yield of compound **3c** was 0.50 g (33%). Found (%): C, 61.30; H, 5.22; N, 7.29; S, 10.24. $C_{31}H_{29}N_3O_6S_2$. Calculated (%): C, 61.68; H, 4.84; N, 6.96; S, 10.62.

13-(4-Carboxyphenyl)-6,12-epimino-5,11-ditosyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*]-1,5-diazocine (3d). A mixture of aldehyde **1** (1.12 g, 4 mmol) and *p*-aminobenzoic acid (**2d**) (0.40 g, 3 mmol) in 15 mL of AcOH was refluxed for 4 h and cooled, while periodically scratching with a rod. The precipitate that formed was filtered off, washed with AcOH and hexane, and twice recrystallized from MeCN to give a colorless substance, m.p. 300—305 °C. The yield of compound **3d** was 0.42 g (31%). Found (%): C, 64.36; H, 4.81; N, 6.39; S, 10.12. $C_{35}H_{29}N_3O_6S_2$. Calculated (%): C, 64.50; H, 4.49; N, 6.45; S, 9.84.

2-Mesylaminobenzoic acid mesylhydrazide (5). Mesyl chloride (40 mL, 0.52 mol) was added in small portions to a stirred mixture of anthranilohydrazide (38 g, 0.25 mol) and pyridine

(90 mL), which was accompanied by the increase in the temperature of the mixture almost to boiling. The reaction mixture was refluxed for 30 min, cooled, diluted with an equal volume of MeOH and 30 mL of water, and kept in ice. The precipitate that formed was filtered off, washed with water, 30% EtOH (25 mL), and 50% EtOH (25 mL), and dried in air. The yield of compound **5** was 47 g (62%), m.p. 205 °C (from Pr^iOH). Found (%): C, 34.82; H, 4.57, N, 13.44; S, 21.17. $C_9H_{13}N_3O_5S_2$. Calculated (%): C, 35.17; H, 4.26, N, 13.67; S, 20.86.

2-Mesylaminobenzaldehyde (6). Anhydrous Na_2CO_3 (34 g, 0.32 mol) was added in small portions at 155 to 165 °C to a stirred solution of hydrazide **5** (34 g, 0.12 mmol) in 125 mL of ethylene glycol. The reaction mixture was kept at this temperature until the gas ceased to evolve completely (~30 min) and then cooled to 70—80 °C. The precipitate was filtered off and the filtrate was poured into a mixture of ice (150 g) and water (100 mL). Acetic acid (10 mL) was added to the resulting transparent solution, which was then left in a refrigerator for 12 h. The sticky precipitate that formed was separated and refluxed in 20 mL of Pr^iOH to give a friable powder. On cooling, the mixture was kept in ice for 1 h and the precipitate was filtered off, washed with cold Pr^iOH (2×5 mL) and light petroleum (5 mL). The crude product was dissolved in 20 mL of cold $CHCl_3$; the undissolved part was filtered off and washed with $CHCl_3$. The solvent was evaporated to dryness and the crystalline residue was washed with cold Pr^iOH (3 mL) and light petroleum (3 mL) and dried to give colorless crystals, m.p. 120 °C (from Pr^iOH). The yield of compound **6** was 3.0 g (14%). Found (%): C, 48.17; H, 4.69, N, 7.21; S, 16.40. $C_8H_9NO_3S$. Calculated (%): C, 48.23; H, 4.55, N, 7.03; S, 16.09.

6,12-Epimino-5,11-dimesyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*]-1,5-diazocine (7a). A mixture of aldehyde **6** (0.6 g, 3 mmol) and NH_4OAc (0.2 g, 2.5 mmol) in 5 mL of PrOH was refluxed for 2 h and cooled in ice. The precipitate that formed was filtered off and recrystallized from MeOH (75 mL) to give colorless crystals, m.p. 220 °C. The yield of compound **7a** was 0.14 g (25%). Found (%): C, 50.21; H, 4.83, N, 10.92; S, 17.26. $C_{16}H_{17}N_3O_4S_2$. Calculated (%): C, 50.65; H, 4.52, N, 11.07; S, 16.90.

6,12-Epimino-5,11-dimesyl-13-methyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*]-1,5-diazocine (7b). A mixture of aldehyde **6** (0.6 g, 3 mmol), $MeNH_2 \cdot HCl$ (0.1 g, 1.5 mmol), and NaOAc (0.12 g, 1.5 mmol) in 5 mL of PrOH was refluxed for 2.5 h. The reaction mixture was diluted with water (20 mL) and the precipitate that formed was filtered off and recrystallized from Pr^iOH. The unconsumed aldehyde **6** was separated by column chromatography on Al_2O_3 in $CHCl_3$. The yield of compound **7b** was 0.2 g (34%), colorless crystals, m.p. 227—230 °C. Found (%): C, 51.72; H, 5.05, N, 10.41; S, 15.96. $C_{17}H_{19}N_3O_4S_2$. Calculated (%): C, 51.89; H, 4.87, N, 10.68; S, 16.30.

6,12-Epimino-13-ethyl-5,11-dimesyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*]-1,5-diazocine (7c) was obtained analogously from aldehyde **6** (0.6 g, 3 mmol), $EtNH_2 \cdot HCl$ (0.15 g, 1.8 mmol), and NaOAc (0.15 g, 1.8 mmol). The yield of compound **7c** was 0.2 g (32%), colorless crystals, m.p. 205—207 °C. Found (%): C, 53.21; H, 5.34, N, 10.07; S, 15.50. $C_{18}H_{21}N_3O_4S_2$. Calculated (%): C, 53.05; H, 5.19, N, 10.31; S, 15.73.

6,12-Epimino-5,11-dimesyl-13-phenyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*]-1,5-diazocine (7d). A mixture of aldehyde **6** (0.6 g, 3 mmol) and aniline (0.14 g, 1.5 mmol) in 5 mL of AcOH was refluxed for 8 h, cooled, and diluted with water (20 mL). The precipitate that formed was filtered off and chromatographed on Al_2O_3 in $CHCl_3$ to give compound **7d** (0.11 g, 16%), colorless crystals, m.p. 247—250 °C. Found (%): C, 57.92; H, 4.93, N, 9.37; S, 13.82. $C_{22}H_{21}N_3O_4S_2$. Calculated (%): C, 58.00; H, 4.65, N, 9.22; S, 14.08.

6,12-Epimino-5,11-dimesyl-13-*p*-tolyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*]-1,5-diazocine (7e). A mixture of aldehyde **6** (0.4 g, 2 mmol) and *p*-toluidine (0.11 g, 1.0 mmol) in 3 mL of AcOH was refluxed for 4 h and cooled. A resinous product was precipitated with water, separated, dissolved in $CHCl_3$, and passed through a column with Al_2O_3. The solvent was removed and the resulting oil solidified upon trituration with light petroleum. The precipitate was filtered off and recrystallized from Pr^iOH (12 mL) to give compound **7e** (0.07 g, 15%), colorless substance, m.p. 212—215 °C. Found (%): C, 58.73; H, 5.20, N, 9.13; S, 14.00. $C_{23}H_{23}N_3O_4S_2$. Calculated (%): C, 58.85; H, 4.94, N, 8.95; S, 13.63.

X-ray diffraction analysis of compounds 3a—c. Single crystals covered with a perfluorinated oil were placed in a Bruker SMART-CCD diffractometer under a flow of cooled nitrogen. Sets of experimental reflections were collected in the ω-scan mode (Mo-Kα radiation). Crystallographic parameters and a summary of data collection for compounds **3a—c** are given in Table 4. The experimental reflections were refined with the Bruker SAINT program package.[6]

The structures were solved by the direct methods and refined by the least-squares method in the full-matrix anisotropic approximation on F^2. In all cases, hydrogen atoms were located from the electron-density difference maps and refined isotropically. All calculations were performed with the SHELXTL-Plus program package.[7]

Atomic coordinates and other experimental data were deposited with the Cambridge crystallographic data collection (CCDC, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac. The registration numbers are CCDC-232632 (**3a**), 232633 (**3b**), and 232634 (**3c**)).

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