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Dedicated to the memory of
Professor Eugen Segal (1933-2013)

NEW MULTIDENTATE POTENTIAL LIGANDS DERIVED FROM ACETYLACETONE

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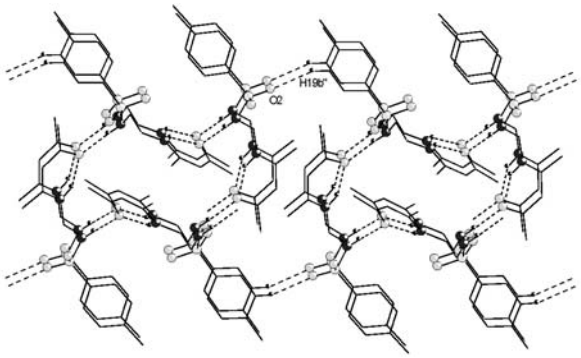
Two new potential polydentate N_x,O_y ligands based on sulphonamide groups, (*Z*)-OC(Me)CHC(Me)NH$(CH_2)_2$NHSO_2R [R = Ph (**1**), C_6H_4Me-4 (**2**)], were obtained by a condensation reaction between acetylacetone and the appropriate $H_2N(CH_2)_2NHSO_2R$ precursor. The ^{1}H and ^{13}C NMR spectra suggest the existence of only one tautomer in $CDCl_3$ solution at room temperature, *i.e.* the amino one, both for compounds **1** and **2**. The single-crystal X-ray diffraction studies revealed for compound **2** the isolation in solid state of the same tautomer found in solution. In the crystal the molecules are associated by hydrogen bonding in a 3D supramolecular network based on helicoidal polymeric chains interconnected by S=O···HC_{Ph} interactions.



INTRODUCTION

In recent years a continuous interest was manifested for a rational design of appropriate metal complexes with significant catalytic[1] or biological activity.[2] The ligands used in such systems have an important role in the fine tuning of the specific properties by controlling the electronic and structural characteristics of the active species. Among the huge number of types of ligands, most of them acting as chelating moieties, those based on sulphonamides proved to be of great importance both for catalysis and biology. Various compounds containing sulphonamide groups proved to have themselves antibacterial activity and they were used against different infections.[3-5] In most cases their metal complexes proved to have even an increased activity. Several copper-sulphonamide-based complexes were described as promising antitumor chemotherapeutic agents and their capacity to interact with DNA was investigated.[6-10] On the other hand, complexes of titanium with ligands derived from bis(sulphonamide) have shown promising catalytic activity in *rac*-lactide polymerization[11] or in asymmetric synthesis by autoinduction processes.[12-16] However, ligand modification plays a key role in controlling and improving the specific properties of a given metal complex.

Previously we reported on a new class of organophosphorus ligands containing sulphona

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mide groups, namely $[(Ph_2PX)(RSO_2)N]H$ (R = Me, Ph, $C_6H_4CH_3$-4, C_6H_4Cl-4), as well as their alkali metal salts and transition metal complexes (Cu, Ag, Pd).[17-20] At the same time, we investigated several organotin(IV) complexes with β-ketimine ligands, *i.e.* $R'_nSnCl_{4-n}[OC(Me)CHC(Me)NH(C_6H_3{}^iPr_2\text{-}2',6')\text{-}4]_x$ [n = 1 - 3, R = Me, Bu, Ph; x = 1, 2].[21,22] Here we report on a new type of ligands containing sulphonamide groups, namely (*Z*)-$OC(Me)CHC(Me)NH(CH_2)_2NHSO_2R$ [R = Ph (**1**), C_6H_4Me-4 (**2**)].

EXPERIMENTAL

The starting $H_2N(CH_2)_2NHSO_2R$ (R = Ph, C_6H_4Me-4) were prepared according to literature procedures.[23,24] RSO_2Cl (R = Ph, C_6H_4Me-4), n-BuLi (1.6 M solution in n-hexane), ethylenediamine and acetylacetone were commercial reagents. The reactions involving air-sensitive species were performed under argon, using Schlenk techniques. Elemental analyses were performed on a Flash EA 1112 analyzer. Melting points were measured on an Electrothermal 9200 apparatus and are not corrected. ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER Avance 300 instrument. The chemical shifts are reported in δ units (ppm) relative to TMS (ref. $CHCl_3$: ^{1}H 7.26 ppm and ^{13}C 77.00 ppm) respectively.

Synthesis of (Z)-N-(2'-((4-oxopent-2-en-2-yl)amino)ethyl)benzenesulphonamide, (Z)-OC(Me)CHC(Me)NH(CH$_2$)$_2$NHSO$_2$Ph (**1**)

A reaction mixture of $H_2N(CH_2)_2NHSO_2Ph$ (0.794 g, 3.96 mmol) and acetylacetone (0.397 g, 3.96 mmol) in 100 mL toluene was refluxed for 10 hours in an installation equipped with a Dean-Stark apparatus. The solvent was then removed in vacuum and the resulted colorless solid product was washed with n-hexane. Yield: 0.806 g (72%). M.p. 163 °C. Anal. Calcd. for $C_{13}H_{18}N_2O_3S$ (M = 282.36): C, 55.30, H, 6.43, N, 9.92%. Found: C, 55.21, H, 6.52, N, 9.87%. ^{1}H NMR ($CDCl_3$): 1.90s [3H, CH_3C(N)], 1.94s [3H, CH_3C(O)], 3.07s (br, 2H, CH_2N), 3.39m (br, 2H, CH_2NHSO$_2$R), 4.94s (1H, C*H*), 6.50s (br, 1H, N*H*SO$_2$R), 7.50m (3H, C$_6H_5$-*meta+para*), 7.84d (2H, C$_6H_5$-*ortho*, $^3J_{HH}$ 6.9 Hz), 10.74s (br, 1H, N*H*). ^{13}C NMR ($CDCl_3$): 18.96s [*C*H$_3$C(N)], 28.64s [*C*H$_3$C(O)], 43.02s, 43.17s (*C*H$_2$N / *C*H$_2$NHSO$_2$R), 96.11s (*C*H), 126.83s (*C*$_6$H$_5$-*ortho*), 129.05s (*C*$_6$H$_5$-*meta*), 132.50s (*C*$_6$H$_5$-*para*), 139.95s (*C*$_6$H$_5$-*ipso*), 163.63s [CH$_3$*C*(N)], 195.10s [CH$_3$*C*(O)].

Synthesis of (Z)-4''-methyl-N-(2'-((4-oxopent-2-en-2-yl)amino) ethyl)benzenesulphonamide, (Z)-OC(Me)CHC(Me)NH(CH$_2$)$_2$ NHSO$_2$C$_6$H$_4$Me-4 (**2**)

Compound **2** was prepared similarly from $NH_2(CH_2)_2NHSO_2C_6H_4$Me-4 (0.710 g, 3.32 mmol) and acetylacetone (0.333 g, 3.32 mmol). Yield: 0.684 g (78%). M.p. 119-20 °C. Anal. Calcd. for $C_{14}H_{20}N_2O_3S$ (M = 296.38): C, 56.73, H, 6.80, N, 9.45%. Found: C, 56.71, H, 6.69, N, 9.62%. ^{1}H NMR ($CDCl_3$): 1.91s [3H, CH_3C(N)], 1.97s [3H, CH_3C(O)], 2.41s (3H, C$_6$H$_4$CH_3), 3.07t (2H, CH_2N, $^3J_{HH}$ 5.4 Hz), 3.40q (2H, CH_2NHSO$_2$R, $^3J_{HH}$ 6.1 Hz), 4.96s (1H, C*H*), 5.81s (br, 1H, N*H*SO$_2$R), 7.23d (2H, C$_6H_4$-*meta*, $^3J_{HH}$ 8.0 Hz), 7.73d (2H, C$_6H_4$-*ortho*, $^3J_{HH}$ 8.2 Hz), 10.74s (br, 1H, N*H*). ^{13}C NMR ($CDCl_3$): 18.98s [*C*H$_3$C(N)], 21.50s (C$_6$H$_4$*C*H$_3$), 28.79s [*C*H$_3$C(O)], 43.16s (*C*H$_2$N + *C*H$_2$NHSO$_2$R), 96.19s (*C*H), 126.97s (*C*$_6$H$_4$-*ortho*), 129.73s (*C*$_6$H$_4$-*meta*), 136.88s (*C*$_6$H$_4$-*para*), 143.46s (*C*$_6$H$_4$-*ipso*), 163.32s [CH$_3$*C*(N)], 195.34s [CH$_3$*C*(O)].

X-ray structure determination

The details of the crystal structure determination and refinement for compound **2** are given in Table 1. Data were collected on a Bruker SMART APEX diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The crystals were attached with paraton/N oil on cryoloops and the data were collected at room temperature (297 K). The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement was used the software package SHELX-97[25] and the drawings were created with the Diamond program.[26] Intra- and intermolecular hydrogen bonds were found in the Platon program.[27]

Table 1

X-ray crystal data and structure refinement for compound **2**

Molecular formula	$C_{14}H_{20}N_2O_3S$
M	296.38
Crystal system	Monoclinic
Space group	$P2_1/n$
Temperature (K)	297(2)
a/Å	14.338(3)
b/Å	7.3803(13)
c/ Å	29.613(5)
α/°	90.000
β/°	96.982(3)
γ/°	90.000
V/Å^3	3110.4(10)
Z	8
D_{calc}/gcm^{-3}	1.266
F(000)	1264
μ(Mo-Kα)/mm^{-1}	0.217
Crystal size (mm^3)	0.29 x 0.25 x 0.23

Table 1 (continued)

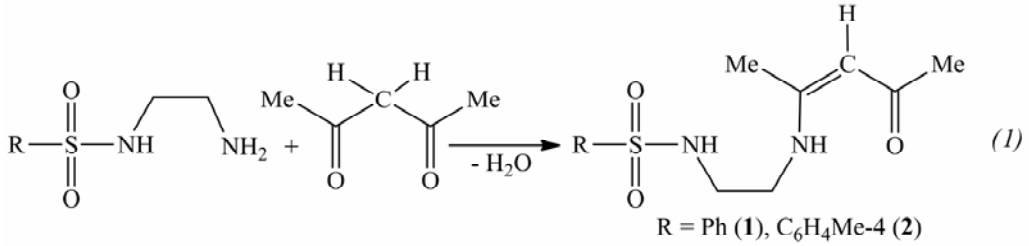
θ range for data collection (º)	1.39 to 25.00
Reflections collected	21504
Independent reflections	5461 [R_{int} = 0.0818]
Absorption correction	Multi-Scan[28]
Data / restraints / parameters	5461 / 0 / 383
Goodness-of-fit on F^2	0.953
Final R indices [$I>2\sigma(I)$][a]	R_1 = 0.0597
	wR_2 = 0.1308
R indices (all data)[a]	R_1 = 0.1357
	wR_2 = 0.1522
Largest difference peak and hole (e Å^{-3})	0.199 and –0.271

[a] Definition of the R values: $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = \{[w\Sigma(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

RESULTS AND DISCUSSION

Synthesis

The new compounds were prepared by reacting acetylacetone with the corresponding amine precursor $H_2N(CH_2)_2NHSO_2R$ in a 1:1 molar ratio, as depicted in eq. 1:



R = Ph (**1**), C_6H_4Me-4 (**2**)

After working up the reaction mixture resulted following the condensation reaction, compounds **1** and **2** were isolated as colorless solids, soluble in common organic solvents.

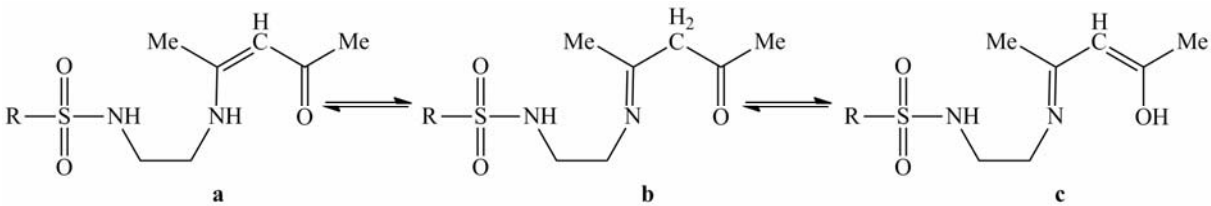
NMR Spectroscopy

The condensation reaction described by equation (*1*) might result in one of the tautomeric forms depicted in Scheme 1, or even in a mixture of the three forms in solution.

The ^{1}H and the ^{13}C NMR spectra suggest the existence of only one species at room temperature in solution, namely species **a**, in case of both compounds. This is suggested by the presence of singlet, broad ^{1}H resonances assigned to protons attached to nitrogen (δ 6.50 and 10.74 ppms for **1**; δ 5.81 and 10.74 ppm for **2**) and by the magnitude of the ^{13}C resonances at δ 195.10 ppms for **1** and 195.34 ppm for **2**, respectively, the latter being typical for the carbon atom of a C=O group.

Crystal and molecular structure of *(Z)-OC(Me)CHC(Me)NH(CH$_2$)$_2$NHSO$_2$C$_6$H$_4$Me-4* (**2**)

The compound crystallizes in the monoclinic *P2(1)/c* space group and the crystal contains two independent molecules of the same tautomer in the unit cell, designated as **2a** and **2b**, respectively, in the subsequent discussion. Their ORTEP-like diagrams and the numbering scheme are depicted in Fig. 1, while important interatomic distances and bond angles are given in Table 2.



Scheme 1

Table 2

Selected interatomic distances (Å) and angles (deg) in compound **2**

2a		**2b**	
O3−C12	1.259(4)	O6−C26	1.254(4)
C12−C11	1.394(4)	C26−C25	1.397(4)
C11−C10	1.375(4)	C25−C24	1.369(4)
C10−N2	1.332(4)	C24−N4	1.331(4)
C9−N2	1.442(4)	C23−N4	1.465(4)
C12−C14	1.513(5)	C26−C28	1.510(4)
C10−C13	1.495(4)	C24−C27	1.497(4)
N2−H2N	0.95(4)	N4−H4N	0.93(3)
O3−H2N	1.85(4)	O6−H4N	1.85(4)
N1−H1N	0.85(3)	N3−H3N	0.85(3)
C8−N1	1.464(4)	C22−N3	1.458(4)
S1−N1	1.593(3)	S2−N3	1.605(3)
S1−C1	1.754(3)	S2−C15	1.756(3)
S1−O1	1.427(3)	S2−O4	1.432(3)
S1−O2	1.433(2)	S2−O5	1.428(3)
O3−C12−C11	122.9(3)	O6−C26−C25	123.1(3)
O12−C11−C10	125.2(3)	C26−C25−C24	125.5(3)
C11−C10−N2	121.0(3)	C25−C24−N4	121.9(3)
C9−N2−C10	127.5(3)	C23−N4−C24	124.4(3)
C9−N2−H2N	123(2)	C23−N4−H4N	121.0(19)
C10−N2−H2N	110(2)	C24−N4−H4N	114.2(19)
C8−N1−S1	120.3(2)	C22−N3−S2	118.5(3)
C8−N1−H1N	114(3)	C22−N3−H3N	114(2)
S1−N1−H1N	117(3)	S2−N3−H3N	113(2)
C1−S1−N1	107.36(16)	C15−S2−N3	108.16(16)
C1−S1−O1	108.31(16)	C15−S2−O4	106.72(17)
C1−S1−O2	106.44(16)	C15−S2−O5	107.85(18)
N1−S1−O1	106.02(17)	N3−S2−O4	107.52(19)
N1−S1−O2	108.01(16)	N3−S2−O5	106.64(17)
O1−S1−O2	120.12(17)	O4−S2−O5	119.52(18)
N2−H2N−O3	143(3)	N4−H4N−O6	135(3)

Both molecules **2a** and **2b** exhibit a basically planar OC(Me)CH(Me)CN(H)C skeleton, with an acidic hydrogen attached to the nitrogen atom. The carbon-oxygen distances [C12−O3 1.259(4) Å for **2a** and C26−O6 1.254(4) Å for **2b**] are typical for C=O double bonds [*cf*. C_{sp}^3−O 1.43 Å, C_{sp}^2=O 1.23 Å].[29] Within a OCCCN fragment the carbon-carbon bonds are of similar length [C12−C11 / C11−C10 1.394(4) / 1.375(4) Å for **2a** and C26−C25 / C25−C24 1.397(4) / 1.369(4) Å for **2b**] and of intermediate magnitude between the theoretical lengths of single C−C and double C=C bonds [*cf*. C_{sp}^3−C_{sp}^3 1.54 Å, C_{sp}^2=C_{sp}^2 1.34 Å].[29] For each of the nitrogen atoms which are part of the OCCCN fragments two nitrogen-carbon bonds of different length were observed. Thus, the nitrogen-carbon bonds resulted following the condensation reaction are significantly shorter [C10−N2 1.332(4) Å for **2a** and C24−N4 1.331(4) Å for **2b**] than the other ones [C9−N2 1.442(4) Å for **2a** and C23−N4 1.465(4) Å for **2b**] which correspond to the primary amine derivatives used as starting materials. These bond lengths are consistent with double C=N and single C−N bonds [*cf*. C_{sp}^2=N 1.34 Å, C_{sp}^3−N 1.54 Å].[29] Moreover, the sum of the experimental bond angles at N2 (360.5º) and N4 (359.6º) are close to 360º, thus suggesting an sp^2 hybridisation for these nitrogen atoms and consequently a delocalization of the π electrons over the OCCCN fragments to which they belong in the molecules **2a** and **2b**. We can conclude that the compound is crystallized in the form of the same tautomer as suggested by the NMR data in solution. The second nitrogen atom

(the amidic one), which is present in both molecules **2a** and **2b**, has an sp^3 character as suggested by the sum of the experimental bond angles (351.3º for N1 atom in **2a** and 345.5º for N3 atom in **2b**, respectively). A pattern which has to be noted is due to the chiral nature of these nitrogen atoms which have three different substituents. Taking into account the nitrogen chirality in solid state the crystal of **2** is formed by a racemic mixture of (S_{N1})-**2a** / (R_{N1})-**2a** and (S_{N3})-**2b** / (R_{N3})-**2b** (see Fig. 2).

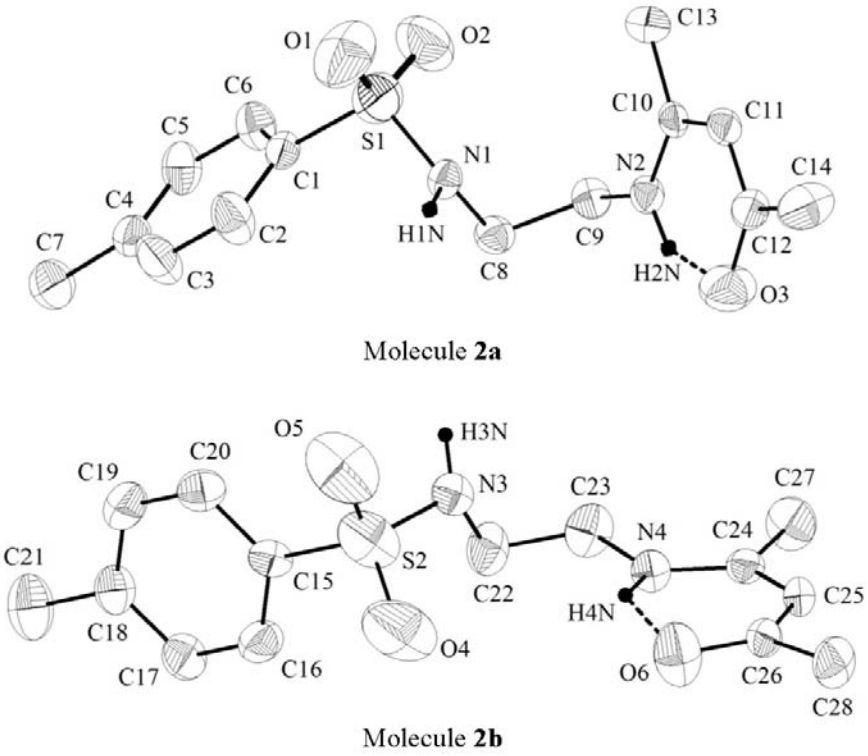


Fig. 1 – ORTEP representation at 30% probability and atom numbering scheme for the two independent molecules in the crystal of compound **2**. Only hydrogen atoms bound to nitrogen and the intramolecular N−H···O interactions are shown.

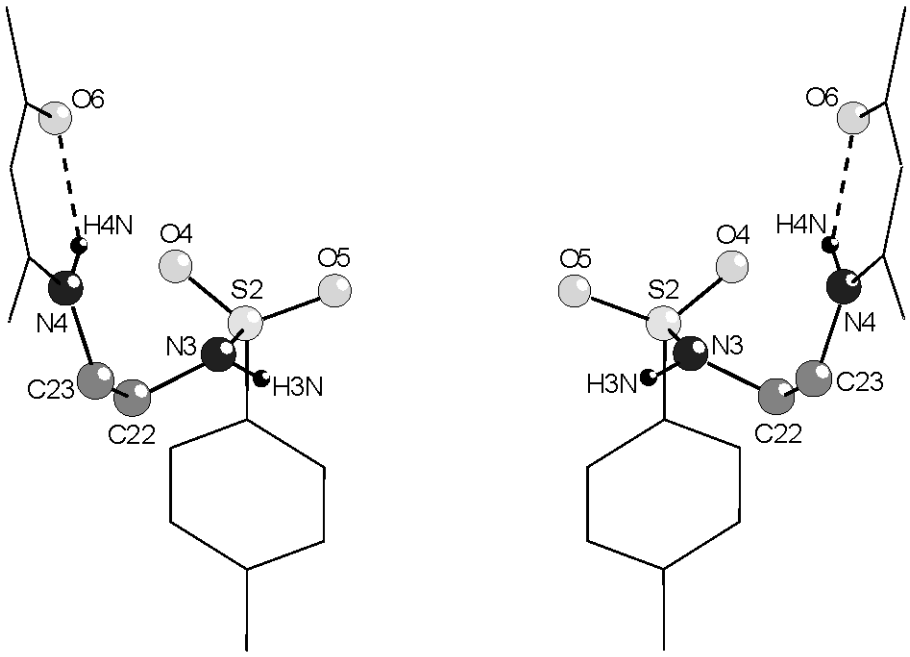


Fig. 2 – (S_{N3})-**2b** (*left*) and (R_{N3})-**2b** (*right*) isomers in the crystal of **2**.

Several intramolecular and intermolecular O···H hydrogen bonding are established in the solid state. In each molecule the acidic hydrogen attached to the sp^2 nitrogen atom is involved in a strong intramolecular hydrogen bonding to the oxygen of the OC(Me)CH(Me)CN(H)C skeleton [O3···H2N 1.85(4) Å for **2a** and O6···H4N 1.85(4) Å for **2b**] resulting in a planar six-membered ring.

Intermolecular O···H hydrogen bonding which involves the amidic hydrogen [O3···H3Na 1.98(3) Å and O6···H1N 2.01(3) Å] are established between alternating independent molecules, *i.e.* (S_{N1})-**2a** / (R_{N3})-**2b** (see Figure 3) and (R_{N1})-**2a** / (S_{N3})-**2b** isomers, respectively, generating *P*-helicoidal and *M*-helicoidal chain polymers. Parallel chains of the same type, *i.e.* either *P*- or *M*-helicoidal, are further connected into a supramolecular layer assembly by additional inter-chain, weaker O···H hydrogen bonding [O2···H19" 2.47 Å] (Fig. 4).

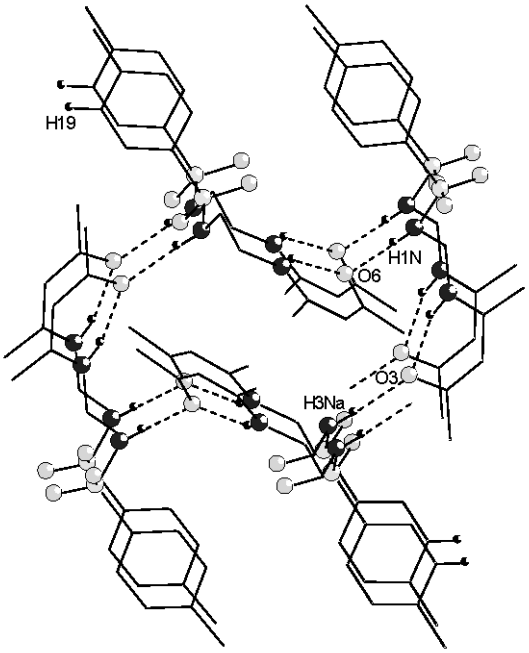


Fig. 3 – *P*-Helicoidal chain polymer from alternating (R_{N1})-**2a** and (S_{N3})-**2b** isomers in the crystal of **2**. Symmetry equivalent position 1 − x, -0.5 + y, 0.5 – z is given by "a".

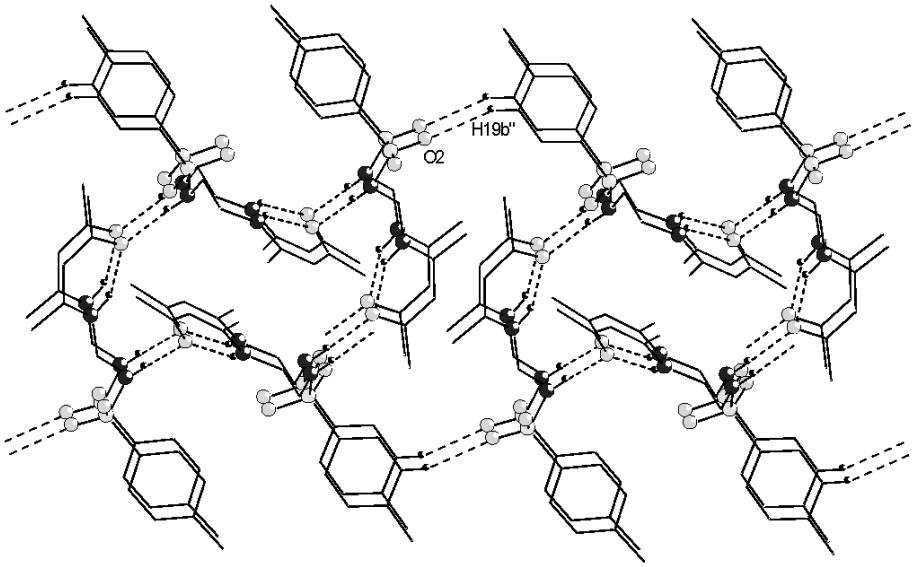


Fig. 4 – Supramolecular layer network built from *P*-helicoidal chains in the crystal of **2**. Symmetry equivalent position 1 + x, y, z is given by "double prime".

CONCLUSIONS

New potential multidentate N_x,O_y-ligands based on sulphonamide groups, (*Z*)-OC(Me)CHC(Me)NH$(CH_2)_2$NHSO_2R [R = Ph (**1**), C_6H_4Me-4 (**2**)], were obtained and characterized by multinuclear NMR in solution. The same tautomeric form was found to be present both in solution and in solid-state, as suggested by the molecular structure determined for **2** by single-crystal X-ray diffraction. In the crystal of **2** a supramolecular network is established based on O···H hydrogen bonds.

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Supplementary material

CCDC 1009727 contains the supplementary crystallographic data for compound **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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