Supplementary Material

Novel convenient approach to 1,4,2-benzodithiazine-1,1-dioxides and 1,2,3-benzoxathiazine-2,2-dioxides

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Description of X-Ray diffraction studies

Full crystallographic details have been deposited at Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for these materials should quote the full literature citation and reference numbers CCDC 2127303 (**5**), CCDC 2127304 (**8c**) and CCDC 2127305 (**10**).

Crystal data for compound 5: $C_{12}H_6Cl_3NO_2S_2$, M = 366.65, monoclinic, space group *P2₁/c*, *a* = 8.9999(4), *b* = 17.3770(8), *c* = 9.2128(4)Å, *β* = 104.343(3), V = 1395.89(11)Å^3, Z = 4, d_c = 1.745, μ 0.953 mm^{-1}, F(000) 736, crystal size ca. 0.06 × 0.18 × 0.29 mm. All crystallographic measurements were performed at ambient temperature on a Bruker Smart Apex II diffractometer operating in the ω scans mode. The intensity data were collected for reflections within $\theta_{max} \leq 29.3°$ using Mo-Kα radiation (λ = 0.71073 Å). The intensities of 12580 reflections were collected (3670 unique reflections, R_{merg} = 0.0606). The structure was solved by direct methods and refined by the full-matrix least-squares technique in the anisotropic approximation for non-hydrogen atoms using the Bruker SHELXTL program package [1]. All CH hydrogen atoms were found in DF synthesis and refined isotropically. Convergence was obtained at R1 = 0.0441 and wR2 = 0.0880 for 2214 observed reflections with $I \geq 2\sigma(I)$, R1 = 0.0932 and wR2 = 0.1058, GOF = 1.012 for 3670 independent reflections, 205 parameters, the largest and minimal peaks in the final difference map 0.43 and –0.40 e/Å^3. The naphthalene system is a bit twisted, thus maximal deviation of fitted atoms from least square plane reached 0.055Å. The S1C1C2S2C11N1 six-membered ring is also non-planar and has an inflection along the line S1S2 with the dihedral angle between the planes S1C1C2S2 and S1N1C11S2 of 7.8°, thus, conformation that the ring is a flattened boat. The C11 N1 bond lengths is 1.268(3)Å which is typical for carbon-nitrogen double bond in organic compounds. The S-C bonds in molecule were found in the range 1.717-1.757(3)Å and S1N1 is 1.624(2)Å. In general, geometric characteristics of the cycle are very close to found in analogous 6-membered cycles in related compound [2, 3].

Crystal data for compound 8c: $C_{10}H_8Cl_3N_1O_5S_1$, M = 360.60, triclinic, space group *P-1* , *a* = 7.8642(18), *b* 8.5693(18), *c* = 11.242(3)Å, *α* = 72.078(7), *β* = 83.803(8), *γ* = 78.805(7)º, V = 706.2(3)Å^3, Z = 2, d_c = 1.696, μ 0.812 mm^{-1}, F(000) 364. All crystallographic measurements were performed at RT on a Bruker Smart Apex II diffractometer operating in the ω scans mode. The intensity data were collected for reflections within $\theta_{max} \leq 26.5°$ using Mo-Kα radiation (λ = 0.71073 Å). The intensities of 7287 reflections were collected (2887 unique reflections, R_{merg} = 0.0459). The structure was solved by direct methods (SIR92) and refined by the full-matrix least-squares technique in the anisotropic approximation for non-hydrogen atoms using the CRYSTALS program package [4], [5]. All CH hydrogen atoms were placed at calculated positions and refined as 'riding' model. The hydrogen atoms supported nitrogen atom were found in DF synthesis and refined isotropically. Convergence was obtained at R1 = 0.0852 and wR = 0.0524, GOF = 1.115 for 1596 observed reflections with $I \geq 3\sigma(I)$, R1 = 0.1360 and wR = 0.0620, for all 2875 reflections, 181 parameters, the largest and minimal peaks in the final difference map 1.09 and –0.89 e/Å^3.

In compound **8c** the phenyl cycle C1-C6 is slightly non-planar due to the strength of the stresses caused by the presence of a non-planar C3NSO cycle. The C1C2C3C5C6 atoms occupy positions in the plane, and C4 atoms deviate from this plane by 0.118Å, thus the C3C4C5 atoms making plane with main plane dihedral angle of 8.4°. The C3C4C7N1S1O1 ring has a twisted half-boat conformation with O1C3C4C7N1 atoms aproximatelly in the plane and O1S1N1 atoms making with the previous plane dihedral angle of 45.9°. The bond lengths of S1-N1 and S1-O1 have values of 1.626(4) and 1.589(4) Å, respectively, which is close to values observed for compound **5**. The S=O double bonds are almost equivalent (mean value is 1.413 Å) and very close to values found in compound **5** and other related compounds.

Crystal data for compound 10: $C_{10}H_{10}Cl_3NO_6S$, M = 378.62, monoclinic, space group *P2₁/c*, *a* = 9.5311(2), *b* = 9.9314(2), *c* = 16.4675(4)Å, *β* = 104.5400(10)º, V = 1508.84(6)Å^3, Z = 4, d_c = 1.667, μ 0.769 mm^{-1}, F(000) 768. All crystallographic measurements were performed at RT on a Bruker Smart Apex II diffractometer operating in the ω scans mode. The intensity data were collected for reflections within $\theta_{max} \leq 26.8°$ using Mo-Kα radiation (λ = 0.71073 Å). The intensities of 15144 reflections were collected (3156 unique reflections, R_{merg} = 0.0459). The structure was solved by direct methods (SIR92) and refined by the full-matrix least-squares technique in the anisotropic approximation for non-hydrogen atoms using the CRYSTALS program package [4, [5]. All CH hydrogen atoms were found in DF synthesis and refined isotropically. Convergence was obtained at R1 = 0.0382 and wR = 0.0410 for 2504 observed reflections with $I \geq 3\sigma(I)$, R1 = 0.0491 and wR = 0.0506, GOF = 1.101 for all 3146 reflections, 190 parameters, the largest and minimal peaks in the final difference map 0.75 and –0.59 e/Å^3.

Description of growth-regulating assay studies

The growth-regulating effect of compounds (**3b,e,f**) was studied on model monocotyledonous Winter wheat "Bezosta" and dicotyledonous plants *Barbarea arcuata* according to the described method of Sergeeva [6]. Commonly used regulators of plant growth are known to be Ivin (2,6-dimethylpyridine-1-oxide) [7], Nortiol (potassium 3-carboxynorbornane-5-ene-2-carboxylate) [8], they were selected as reference compounds. The experiments were performed in Petri dishes on agar medium. Test solutions of compounds (**3b,e,f**) in dimethyl sulfoxide with a mass fraction of the compounds 0.01 - 0.001 - 0.0001%.

10 g of agar-agar is added to 1.0 L of water, heated to complete dissolution and cooled to 35-40 °C. 37 mL of this solution was poured into each Petri dish and 1 mL of the solution of the test substance was added. In a blank experiment, 1 mL of water was added instead of the test substance. 15 Grains of wheat are sown on hardened agar-agar in each Petri dish, covered with lids and placed for 3 days in a thermostat at a temperature of 24-26 °C. After incubation, Petri dishes with wheat seedlings are kept in daylight at a temperature of 19-21 °C for 5 days. The results are recorded on the ninth day after the experiment. The results obtained are recorded as a percentage of the blank experiments obtained for the root system of plants weight (g), stem length (mm), green mass (g) and seeds germination (%). The repetition of experiments with each content of the substance is fourfold. The experiments are repeated three times. The obtained experimental data are listed in Table 1.

Table 1. The results of laboratory studies of the growth-regulating activity of 3-trichloromethyl-1,4,2-benzodithiazine-1,1-dioxides (**3b,e,f**) and reference compounds 2,6-dimethyl-pyridine-1-oxide (**Ivin**) and potassium 3-carboxynorbornane-5-ene-2-carboxylate (**Nortiol**) in experiments on Winter wheat "Bezosta" and *Barbarea arcuata*.

Compound	Mass Fraction, (%)	Experimental data (in % relative to control) Winter wheat ("Bezosta")				Experimental data (in % relative to control) *Barbarea arcuata*			
		Weight of Roots (g)	Height of Stems (mm)	Green mass (g)	Seeds germination (%)	Weight of Roots (g)	Height of Stems (mm)	Green mass (g)	Seeds germination (%)
3b	0.01	106.1	96.0	112.5	104.0	173.7	114.7	116.1	105.7
	0.001	110.7	96.2	108.6	100.0	190.4	106.9	124.2	105.0
	0.0001	126.7	93.4	112.0	114.0	171.9	97.8	110.5	106.9
3e	0.01	107.6	98.3	104.9	95.0	130.3	110.4	111.2	103.9
	0.001	111.9	97.3	105.4	95.0	148.5	108.5	117.0	109.8
	0.0001	106.9	103.3	100.6	93.3	123.8	87.9	104.0	107.8
3f	0.01	136.7	95.3	122.9	114.0	134.1	98.2	101.1	100.7
	0.001	127.5	95.4	110.8	114.0	136.4	91.1	101.1	102.0
	0.0001	127.8	94.5	113.2	100.0	138.6	83.5	101.8	103.5
Water	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Nortiol	0.01	104.2	102.6	93.3	-	-	-	-	-
	0.001	100.6	97.9	94.9	-	136.4	104.3	111.2	-
	0.0001	97.0	101.5	98.0	-	-	-	-	-
Ivin	0.01	88.8	70.3	89.5	-	-	-	-	-
	0.001	102.5	73.3	101.9	-	151.7	108.3	112.9	100.5
	0.0001	101.4	68.1	95.7	-	-	-	-	-

The data indicate that 1,4,2-benzodithiazine derivatives (**3b,e,f**) proved to be powerful stimulators of root growth of monocotyledonous and especially dicotyledonous plants and are 10-40% more effective than ivin and nortiol. At the same time, compounds (**3b,e,f**) have higher growth-regulating activity than reference compounds at much lower concentrations. It is important to note that 3-trichloromethyl-1,4,2-benzodithiazine-1,1-dioxides (**3b**), (**3f**) have a low toxicity.

Acute toxicity of the tested compounds was studied in laboratory experiments on white mice, males and females weighing 20-22 g by oral administration of a solution of the drug in dimethyl sulfoxide using a probe. The results of the experiment are recorded 24 hours after the introduction of the substance. Statistical processing of the results and calculation of median lethal dose (LD_{50}) were determined by the method of Litchfield and Wilcoxon in the modification of Roth [9] (Table 2).

Table 2. Acute toxicity of 3-trichloromethyl-1,4,2-benzodithiazine-1,1-dioxide (**3f**), (**3b**)

Compound	LD_{50}, mg/kg
Ivin	1700
Nortiol	2950
3b	2000
3f	2000

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