Molecular Structure and Properties of *N*,*N*'-Disulfinyl-1,2-diaminobenzene

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Abstract—According to X-ray diffraction data, N,N'-disulfinyl-1,2-diaminobenzene in crystal exists as a planar Z,Z isomer. On heating or under the action of catalytic amounts of water, as well as in reactions with LiN(SiMe₃)₂ or PCl₅ in 1:1 or 1:2 molar ratios it quantitatively converts into 2,1,3-benzothiadiazole. According to ¹⁵N NMR data, this transformation is accompanied by deshielding of the nitrogen atoms by 18 ppm.

Cyclic arylenazathienes of general formula **I** at certain values of the *a*, *b*, and *c* indices form a unique sequence of alternating every 2π electrons ten-, twelve-, fourteen-, and more- π -electron (hetero)aromatic and antiaromatic systems [1]. Studies on such systems are useful for further development of the concept of (anti)aromaticity, especially in relation to nontraditional objects.



At present 10π -electron 2,1,3-benzothiadiazoles II, [3–6], 12π -electron 1,3,2,4-benzodithiadiazines III [6–10], and 14π -electron 1,3,5,2,4-benzotrithiadiazepines IV [1, 6, 11] have been synthesized and characterized as possessing a planar geometry and a united molecular π system. Further members of this series, beginning with 16π -electron V, are still unknown [1]. No prohibition on their existence, in any case in regard to stability of azathiene chains, evidently exists. Acyclic analogs of 16, 18, and 20π -electron systems I having -N=S=N-S-N=S=N- [12], -S-N=S=N-S-N=S=N [13], and -S-N=S=N-S-N=S=N-S- [14] chains, respectively, have been obtained and structurally characterized.

A priori a convenient starting material for preparing V might be N,N'-disulfinyl-1,2-diaminobenzene VI [15, 16], but the information on this compound is controversial. Thus, the synthesis of VI from 1,2-diaminobenzene and SOCl₂ in boiling benzene has been described [15]. At the same time, the same reaction in boiling toluene or in the presence of HCl acceptor (for instance, pyridine) in ether leads to compound II [17].

The aim of this work was to test the procedure for preparing compound VI, described in [15], to characterize this compound, and study its utility for synthesis of heterocycles like V.

Compound **VI** can actually be prepared by a slightly modified procedure [15] in a practically quantitative yield.

According to X-ray diffraction data, compound **VI** in crystal exists as a planar Z,Z isomer (Fig. 1). Selected bond lengths, Å, and bond angles, deg, in compound **VI** are as follows: $C^{1}-N^{1}$ 1.387(4), $N^{1}-S^{1}$ 1.511(3), $S^{1}-O^{1}$ 1.449(3), $C^{2}-N^{2}$ 1.385(4), $N^{2}-S^{2}$ 1.521(3), $S^{2}-O^{2}$ 1.443(3), $C^{1}-C^{2}$ 1.423(4) Å; $C^{1}N^{1}S^{1}$ 133.1(2), $N^{1}S^{1}O^{1}$ 121.52(17), $C^{2}N^{2}S^{2}$ 132.6(2), $N^{2}S^{2}O^{2}$ 120.74(17), $C^{3}C^{2}N^{2}$ 124.5(3), $C^{1}C^{2}N^{2}$ 116.1(3), $C^{6}C^{1}N^{1}$ 124.8(3), $C^{2}C^{1}N^{1}$ 116.7(3)°. The bond lengths and bond angles in the N=S=O groups coincide, within the experimental error, with that in other structurally characterized compounds of

the general formula Ar-N-S=O {they all have Z configuration, both planar (Ar = 4-BrC₆H₄ [8]) or nonplanar (Ar = $2,6-F_2C_6H_3$ [19] or $2,4,6-(t-Bu)_3C_6H_2$ [20]} and close to mean values [21]. The C^1-C^2 bond in VI [1.423(4)Å] is considerably longer than in 1,2diaminobenzene (1.406 [22]). In the PM3-optimized geometry of VI, which well reproduces experimental data, this bond length is 1.427Å. According to the calculations, the elongation of the C^1-C^2 bond in going from 1,2-diaminobenzene to compound VI is connected with decrease in its order (1.32 and 1.26, respectively). The contribution of mutual repulsion of the N=S=O groups in compound VI in this effect is evidently negligible, because the C-C-N, C-N=S, and N=S=O angles in VI and 4-BrC₆H₄NSO coincide. Moreover, in the closest analog with bulky substituents on nitrogen, N,N-bis(5-chloro-o-phenylenedioxy)-1,2-diaminobenzene [23], the C^1-C^2 distance is as small as 1.402 Å.

In the crystal of compound **VI** intermolecular interactions lead to formation of layers with shortened $(C^5-)H^5\cdots S^1$ [2.85(4) Å] and $O^1\cdots S^2$ (3.265 Å) contacts (Fig. 2)



Fig. 1. Crystal structure of compound VI.



Fig. 2. Crystal packing of compound **VI** (projection along the *a* axis). RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 71 No. 7 2001

Compound VI is thermally unstable, and on short boiling in *o*-xylene it quantitatively cyclizes to give compound II. Compound VI is extremely sensitive to water, and already on contact with moist air it quickly



converts to *N*-sulfinyl-1,2-diaminobenzene (**VII**) [16] and then to compound **II** in quantitative yield.

Attempted conversion of compound VI to the possible precursors of the target heterocycle V [compounds VIII and IX, with subsequent ring closure under the action of SCl₂ or $(Me_3Si)_2N-S-N(SiMe_3)_2$, respectively] via standard 1:2 reactions with LiN·(SiMe₃)₂ [10] or PCl₅ [24], too, gave nothing more than compound II. Analogous result was obtained with the corresponding 1:1 reactions. Apparently, the modification of one NSO group in compound VI under the action of one or another reagent is accompanied by fast intramolecular condensation of the modified fragment with the second NSO group, thus leading to II.



The δ_N and δ_O values in the ¹⁵N and ¹⁷O NMR spectra of compound VI (311.9 and 416 ppm, respectively) are characteristic of the Ar-N=S=O group [25–28]. They practically coincide with those in N-sulfinyl-2-fluoroaniline [25, 26]. In going from compound **VI** to compound **II** (δ_N 329.9 ppm), the nitrogen atom is deshielded by 18 ppm. As the transformation of -N=S=O to N=S=N (for example, in going from Ph–N=S=O to Ph–N=S=N–Ph) results in enhanced (by 20 ppm [29]) shielding of the nitrogen atom, it can be proposed that the effect observed in the case of the $VI \rightarrow II$ transformation is integral in nature, with prevalence of deshielding due to heteroaromatic ring closure. These data are in agreement with the fact that the signal of compound II in the ^{15}N NMR spectra is shifted downfield by ~32 ppm from that of Ph–N=S=N–Ph [29, 30].

Clearly, the facility of transformation to **II** considerably restricts the utility of compound **VI** in heterocyclic synthesis. At the same time, this compound, being now thoroughly characterized, is an interesting ligand for the coordination chemistry of the Ar–N=S=O group [31, 32].

EXPERIMENTAL

The ¹H, ¹³C, ¹⁵N, and ¹⁷O NMR spectra were measured for CDCl₃ solutions on a Bruker DRX-500 spectrometer at 500.13, 125.76, 50.68, and 67.80 MHz, respectively, against TMS, liquid NH₃, and D₂O. The mass spectra were obtained on a Finnigan MAT MS-8200 spectrometer (electron impact, 70 eV). The UV spectra were taken on a Specord UV-Vis spectrophotometer for heptane solutions.

X-ray diffraction experiment was performed with a crystal of compound VI $(0.52 \times 0.36 \times 0.12 \text{ mm})$ on a Bruker P4 diffractometer at -50° C (Mo K_{α} radiation, graphite monochromator, $2\theta/\theta$ -scanning in the range $2\theta < 50^{\circ}$ C). The crystal is triclinic, *a* 7.420(3) Å, b 7.830(2) Å, c 8.246(2) Å, α 109.57(2)°, β 114.90°, γ 93.17(3)°, V 398.5 Å³, space group P-1, Z 2, C₆H₄. $N_2O_2S_2$, d_{calc} 1.669 g/cm³, μ 0.622 mm⁻¹. Intensities of 1195 unique reflections were measured. Absorption correction was determined empirically from the azimuthal scanning curves for 7 reflections (transmission 0.41-0.77). The structure was solved by the direct method using the SHELXS-86 program (positions of hydrogen atoms were calculated geometrically) and refined by the least-squares method in the fullmatrix anisotropic-isotropic (for H atoms) approximation using the SHELXL-97 program. The structure was refined on all F^2 to wR^2 0.160 and S 1.102; 126 parameters were refined (*R* 0.0534 for 1062 $F > 4\sigma$). Coordinates and thermal parameters for non-hydrogen atoms are given in the table.

The syntheses described below were carried out in absolute solvents under argon.

N,*N*'-Disulfinyl-1,2-diaminobenzene (VI). A solution of 25 ml of SOCl₂ in 15 ml of CCl₄ was added dropwise at 0°C to a solution of 7.56 g of 1,2-diaminobenzene in 60 ml of CCl₄. The reaction mixture was refluxed for 2 h, the resulting orange-red solution was evaporated under reduced pressure, and the residue was crystallized from a 3:1 hexane– CCl_4 mixture containing a little $SOCl_2$ to obtain 13.73 g (98%) of compound VI as bright golden yellow crystals, mp 56–57°C (agrees with [15]). Mass spectrum, M^+ (m/z), 199.9739, calculated for $C_6H_4N_2S_2$ measured 199.9714. ¹H NMR spectrum, δ , ppm: 8.08 (H^{3,6}), 7.37 (H⁴, H⁵) (agrees with [16]. ¹³C NMR spectrum, δ_{C} , ppm; 135.3 (C¹, C²) 129.8 (C⁴, C⁵), 126.5 (C³, C_{0}^{6}). ¹⁵N NMR spectrum: δ_{N} , ppm: 311.9 t (*J* 1.0 Hz). ¹⁷O NMR spectrum: δ_0 416 ppm ($\Delta v_{1/2}$ 170 Hz). UV spectrum, λ_{max} , nm (log ϵ): 335 (3.95 sh), 314 (4.03), 240 (3.77).

2,1,3-Benzothiadiazole (II). *a*. A solution of 1.00 g of compound VI in 10 ml of *o*-xylene was refluxed (144°C) until decoloration and then distilled in a vacuum to obtain 0.63 g (92%) of compound II as a colorless oil, bp $63-64^{\circ}C$ (1.5 mm), that crystallized on handling, mp $43-44^{\circ}C$.

b. Compound **VI**, 1.00 g, without protection from air moisture quickly converted to a red oil (compound **VII** [16]). Mass spectrum, m/z: 154 (M^+). ¹H NMR spectrum agrees with that described in [16]. This compound solidified to colorless crystals of

Atomic	coordin	ates (:	$\times 10^4$) and	equiva	lent	isotr	opic
parameter	s (Å ² ,	$\times 10^3$)	for	non-hy	drogen	atoms	in	VI

Atom	x/a	y/b	z/c	U _{eq}
S^1	-1176(1)	1867(1)	-5682(1)	51(1)
S^2	2021(1)	8591(1)	774(1)	43(1)
O^1	-3100(4)	499(4)	-6929(4)	79(1)
O^2	1380(4)	9699(3)	2136(4)	56(1)
\mathbf{N}^{1}	-919(4)	3584(3)	-3989(4)	39(1)
N^2	574(4)	6840(3)	-965(4)	35(1)
C^1	-2230(4)	4245(4)	-3252(4)	33(1)
C^2	-1423(4)	5980(4)	-1615(4)	33(1)
C^3	-2653(6)	6708(5)	-801(6)	44(1)
C^4	-4642(6)	5759(6)	-1587(6)	55(1)
C^5	-5423(5)	4059(6)	-3162(6)	54(1)
C ⁶	-4247(5)	3318(5)	-3979(5)	47(1)

compound II (purified by vacuun sublimation), yield 0.65 g (95%).

c. To a stirred solution of 6.68 g of LiN(SiMe₃) in 50 ml of hexane, a solution of 4.00 g or 8.00 g of compound **VI** in 100 ml of hexane was added dropwise with stirring at -70° C. The mixture was heated to room temperature within 2 h and then 5 ml of Me₃SiCl was added. The precipitate was filtered off, the solvent was removed at reduced pressure, and the residue was crystallized from hexane and sublimed in a vacuum to obtain 2.05 g (75%) or 4.46 g (82%) of compound **II** at 2:1 and 1:1 reagent molar ratios, respectively.

d. A mixture of 1.00 g of compound **VI**, 20 ml of CCl_4 , and 2.08 g or 1.04 g of PCl_5 was stirred at 40°C until real solution had formed (~30 min). The solvent was removed at reduced pressure, and the residue was sublimed in a vacuum and crystallized from hexane to obtain 0.54 g (80%) or 0.58 g (85%) of compound **II** at 2:1 and 1:1 reagent molar ratios, respectively.

Compound II was identified by the melting point, ¹H NMR spectrum, UV spectrum, and low-resolution mass spectrum, which were in agreement with published data. ¹⁵N NMR spectrum, δ_N , ppm: 329.9 t (*J* 0.5 Hz). For the ¹⁵N NMR spectra of the other compounds I, see [1, 10, 34].

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RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 71 No. 7 2001

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