Accepted Manuscript

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PII: S0022-2860(16)30767-0

DOI: 10.1016/j.molstruc.2016.07.083

Reference: MOLSTR 22786

To appear in: Journal of Molecular Structure

Received Date: 3 June 2016

Revised Date: 15 July 2016

Accepted Date: 18 July 2016

Please cite this article as: V.M. Petrov, N.I. Giricheva, S.N. Ivanov, V.N. Petrova, G.V. Girichev, Molecule 1,5-C₁₀H₆(SO₂Cl)₂ as prototype of conformational properties of naphthalene sulfonyl derivatives, *Journal of Molecular Structure* (2016), doi: 10.1016/j.molstruc.2016.07.083.

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Molecule 1,5-C₁₀H₆(SO₂Cl)₂ as Prototype of Conformational Properties

of Naphthalene Sulfonyl Derivatives

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Conformational composition of the vapor (T=413(5) K) and the conformer structures of 1,5-naphthalenedisulfonylchloride (1,5-NaphDSC) have been studied by a combined gas-phase electron diffraction and mass spectrometry (GED/MS) method complemented by quantum chemical calculations. According to quantum chemical calculations at DFT/B3LYP/cc-pVTZ and MP2/cc-pVTZ theory levels, the molecule 1,5-NaphDSC possesses four conformers differing mutual orientation of the two SO₂Cl groups.

GED data clearly indicate that only two conformers, whose structures are characterized by deviation of two S-Cl bonds from perpendicular position relative to the plane of the naphthalene skeleton (syn-symmetry C_2 and anti-symmetry C_i), are present in vapor at 413 K.

The following geometrical parameters of these conformers were obtained from the experiment (Å and degrees; uncertainties are in parentheses): $r_{h1}(C-H) = 1.098(9)$, $r_{h1}(C-C)=1.405(3)$, $r_{h1}(C-S)=1.781(4)$, $r_{h1}(S-O)=1.426(3)$, $r_{h1}(S-C)=2.056(4)$, $\angle C-C_S-C = 122.9(1)$, $\angle C_S-S-Cl = 101.8(6)$; C9-C1-S-Cl =71.2(12), C10-C5-S-Cl =71.2(12)-syn conformer; C9-C1-S-Cl =71.2(12), C10-C5-S-Cl=71.2(12) - anti-conformer.

The presence of $C_9H_n^+$ ions in the mass spectra of naphthalenesulfonyl chlorides, which are absent in the mass spectrum of naphthalene, may be attributed to the weakening of two C–C bonds adjacent to the substituent of the naphthalene skeleton. This reflects in the geometric parameters of 1,5-NaphDSC.

The barriers to internal rotation of sulfonyl chloride groups were calculated. It is shown that the low-energy syn- and anti-conformers are structurally rigid, in contrast to high-energy conformers with one or two S-Cl bonds, lying in the plane of the naphthalene skeleton.

The dependence of C1-C2, C-S, S-Cl bond lengths from SO₂Cl groups orientation relative to naphthalene skeleton is discussed in terms of NBO-analysis of electron density distribution.

The relationship between conformational properties of molecule and some physicochemical characteristics of the 1,5-NaphDSC compound is discussed.

Keywords: 1,5-naphthalenedisulfonylchloride, molecular structure, gas-phase electron diffraction, mass spectrometry, quantum chemical calculations, conformational properties, transition barriers

Introduction

The conformational properties of monosubstituted naphthalene molecules such as: 1naphthalenesulfonyl chloride (1-NaphSCl), 2-naphthalenesulfonyl chloride (2-NaphSCl) [2], 1- and 2-naphthalene sulfonyl amides [3] and 2-naphthalenesulfonyl fluoride [2] were determined by GED and quantum chemical methods. It was shown that 1- and 2monosubstituted naphthalenes (1-NaphSO₂X and 2-NaphSO₂X (X=F, Cl, NH₂)) demonstrate the different conformational properties and have a different number of conformers. The molecule 1-NaphSCl has two conformers, and 2-NaphSCl - only one. It should be pointed out that the S–X bond deviation from orthogonal position relative to the naphthalene frame by about 20° is characteristic for the most stable conformer in 1- and 2-monosubstituted naphthalenes. In contrast, SO₂X substituent in benzene moiety is characterized by the exactly orthogonal position of the S–X bond with respect to the ring [4-6].

The correlation between nonequivalence of the C–C bonds in the naphthalene frame and spatial orientation of the SO_2NH_2 substituents in 1-Naph SO_2NH_2 and 2-Naph SO_2NH_2 was discussed in Ref. 3. It was shown that the S–N bond deviates in different directions from the short C1–C2 bond of the naphthalene frame depending on 1- or 2-position of the substituent in these molecules.

The structure of 1,5-disubstituted naphthalene 1,5-Naph $(SO_2X)_2$ in a gas phase has not been studied yet, although such investigations can not only disclose the conformational properties of the gaseous compound, but predict conformations that may be implemented in crystals [e.g., 7-12]. In crystals of different compounds the SO₂X group can possess a different spatial location relative to the plane of the naphthalene frame, as well as the different relative orientation with respect to other substituents.

Detailed knowledge about the conformation properties of 1,5-naphthalenedisulfonyl derivatives is important because these compounds are used as crosslinking agents in the synthesis of macromolecular compounds - polysulfones, polysulfonamides and are the base for a synthesis of highly thermostable polymers and adhesives [13,14], polymer membranes [15,16] , fluorescent probes [17] etc.

The 1,5-naphthalenedisulfonylchloride (1,5-NaphDSC) is used for synthesis of many other 1,5-naphthalenedisulfonyl derivatives, and the knowledge of conformational properties of this compound seems to be important for understanding the reaction mechanisms. In this connection it is interesting to see the relationship between conformational properties of molecule and some physicochemical characteristics. So the conformational features of the 1,5-NaphDSC can be related to the kinetics of hydrolysis of this compound in aqueous *i*-PrOH mixtures [18] manifested by sharply nonmonotonic dependence of the activation parameters on solvent composition. Two sharp minima of activation enthalpy are detected at 0.014 and 0.018 m.f. *i*-PrOH, what the authors [18] attribute to the selective hydration of two 1,5-NaphDSC conformers.

The 1.5-NaphDSC is a suitable object for electron diffraction study. The scattering ability of chlorine atoms of this compound is high compared with that of the nitrogen or oxygen atoms in 1,5-Naph $(SO_2X)_2$ (X = NH₂, OH), and this makes the reliability to determine the spatial locations of two SO₂X groups relative to the naphthalene frame in the case of 1,5-NaphDSC also significantly higher.

The present work reports the structural and electronic characteristics of the 1,5-NaphDSC conformers and its correlation with molecular structures of monosubstituted 1-NaphSC studied previously [1].

Experimental

1,5-NaphDSC was synthesized by reaction of 1.5-naphthalenedisulfonic acid (1,5-NaphDSAc) with a threefold molar excess of PCl₅. The product was recrystallized from a hexane/propan-2-ol mixture (80/20 vol.%) to obtain a sample melting point 183 °C (mp. = $183 \degree C$ [19,20]).

The diffraction patterns were recorded using a combined EMR-100/APDM-1 apparatus, which allows carrying out synchronous gas electron diffraction and mass spectrometric (GED/MS) experiments [21]. The sample was evaporated from a stainless steel (X18H10T) effusion cell with the ratio of the cross sectional area of the internal cylindrical part to the area of the effusion hole equals to 150. A temperature of the effusion cell was measured by a

W/Re-5/20 tungsten-rhenium thermocouple. Accurate wavelengths of electrons were determined from the diffraction patterns of the polycrystalline ZnO recorded before and after patterns of the sample. Main conditions of the GED/MS experiment are listed in the Table 1.

Table 1.

Conditions of the synchronous GED/MS experiments.

nozzle-to-plate distance, mm	338	598
electron beam current, <mark>µ</mark> A	1.4	1.0
temperature of effusion cell, K	413(5)	412(5)
accelerating voltage, kV	88.3	89.0
ionization voltage, V	50	50
exposure time, s	100	45
residual gas pressure, Torr	$1.4 \cdot 10^{-6}$	$2.0 \cdot 10^{-6}$
scattering angles, Å-1	2.5-30.0	1.3-17.1

The optical densities of the diffraction patterns were measured by a computercontrolled MD-100 (Carl Zeiss, Jena) microdensitometer [22]. Molecular scattering intensity were calculated as $sM(s) = \frac{I(s) - G(s)}{G(s)} \cdot s$, where I(s) is a total experimental scattering intensiter function and G(s) is a backward function

ty function and G(s) is a background function.

Table 2 lists mass-spectra of 1,5-NaphDSC recorded simultaneously with electron diffraction patterns. All of the observed ions originate from a single molecular form ($C_{10}H_{6^-}(SO_2Cl)_2$). Neither thermal destruction nor volatile admixtures were detected in the mass-spectra.

Table 2.

Ions relative abundance in mass spectrum of saturated vapor over 1,5-NaphDSC ($U_{ioniz}=50V$) recorded simultaneously with the diffraction pattern, and mass spectra of 1-NaphSC and naph-thalene $C_{10}H_8$ for comparison.

ion	m/e,	1,5-NaphDSC	1-NaphSC		C10H8
	а.е.м.				
		our data	[1]	[23]	[23]
$C_{10}H_6(SO_2^{37}Cl)_2^+$	328	14			
$C_{10}H_6S_2O_4^{35}Cl^{37}Cl$	326	58			

$C_{10}H_6(SO_2^{35}Cl)_2^+$	324	72			
$C_{10}H_6S_2O_4^{37}Cl^+$	291	37			
$C_{10}H_6S_2O_4^{35}Cl^+$	289	92			
$C_{10}H_7SO_2^{37}Cl^+$	228	41 ^a	24	11.0	
$C_{10}H_7SO_2^{35}Cl^+$	226	98 ^a	48	29.2	
$C_{10}H_7SO_2^+$	191		29	16.7	
$C_{10}H_7SO^+$	175		-	3.9	
$C_{10}H_7^{37}Cl^+$	164	31 ^a	18	10.4	
$C_{10}H_7^{35}Cl^+$	162	76 ^a	42	32.1	
$C_9H_6^{-35}Cl^+$	149	30			
$C_9H_6S^+$	146	18			
$C_{10}H_7O^+$	143		8.8	3.9	
$C_8H_6S^+$	134	32			·
$^{13}C_1^{12}C_9H_7^+$	128	19 ^a	11	25.0	11 ^b
$C_{10}H_7^+$,	127	100 ^a	100	100	100 ^b
$C_{10}H_6^+$	126	20 ^a	30	13.6	10.8 ^b
$C_9H_7^+$	115	20 ^a	10	6.3	-
$C_8H_n^+$	100-103 ^c	23	12	6.3	8.2
$C_{7}H_{3}^{+}$	87	15		2.1	-
$C_6H_n^+$	74-77 ^c	32	22	10.2	3.4
$C_5H_n^+$	63-65 [°]	25	15	10.8	6.8

^a Ion contains the number of hydrogen atoms smaller by one (and one a.m.u.) than that written in the formula.

^b Ion contains the number of hydrogen atoms bigger by one (and one a.m.u.) than that written in the formula.

^c Group of ions with different number of hydrogen atoms; intensity of ion involved in group is given.

Quantum chemical calculations

Quantum chemical (QC) calculations were performed using Gaussian 03 program package [24]. DFT/B3LYP [25] and MP2 [26,27] methods with cc-pVTZ [28-29] basis sets were chosen. Geometry optimization and calculation of the frequencies were performed for all the stationary points on the PES of 1,5-NaphDSC.

By analogy with the 1-NaphSC, which has two conformers, 'skewed' (C9-C1-S-Cl) = $71.4(21)^{\circ}$) and 'planar', in which the S–Cl bond lies in the plane of the naphthalene frame[1], we supposed the molecule 1,5-NaphDSC has four conformers differing mutual orientation of two groups SO₂Cl: 'skewed-skewed-syn' – conformer I, 'skewed-skewed-anti' - conformer II, 'skewed-planar' - conformer III, and 'planar- planar' - conformer IV (Fig. 1). QC calculations at MP2/cc-pVTZ and DFT/B3LYP/cc-pVTZ theory levels show that all of these conformers cor-

respond to a minima on the PES.



Fig. 1 The 1,5-NaphDSC conformers: 'skewed-skewed-syn' – conformer I, 'skewed-skewed-anti' - conformer II, 'skewed-planar' - conformer III and 'planar-planar' - conformer IV.

Relative total energies ΔE , relative Gibbs free energies ΔG°_{T} for conformers of 1,5-NaphDSC along with the relative conformer ratios χ in a gas phase at the temperature of GED experiment are summarized in Table 3.

Table 3.

Calculated (B3LYP/cc-pVTZ) relative total energies ΔE , relative Gibbs free energies ΔG°_{T} of conformers of 1,5-NaphDSC molecule and the conformer ratio χ in gas phase at T=413 K.

	conformer I	conformer II	conformer III	conformer IV
	'skewed-	'skewed-skewed-	'skewed-planar'	'planar-planar'
	skewed-syn'	anti'		
ΔE^{a} , kcal/mol	0.02	0.0	3.73	7.44
ΔG°_{413} , kcal/mol	0	0.01	3.22	6.57
v_1^{b}, cm^{-1}	32.4	33.5	25.4	25.2
χ, mol %	49.8	49.2	1.0	0.02

^a relative total energies ΔE calculated by MP2/cc-pVTZ are 0, 0.01, 4.09 and 8.17 kcal/mol for I, II, III and IV conformers, correspondently

^b lowest frequency

The nature of stabilization of the certain geometry configurations of 1,5-NaphDSC was interpreted in terms of the NBO-analysis [30]. Chemcraft program [31] was used for the visualization of the molecular structures and orbitals.

Structural analysis

According to mass-spectra, the saturated vapor of 1,5-NaphDSC at the temperature of GED/MS experiment contains the single molecular form $C_{10}H_6(SO_2Cl)_2$.

Geometry configuration of this molecule was described by 12 independent parameters accounting for the nonequivalence of the bond lengths C-C in the naphthalene skeleton, the deviation of bonds C1-S from bisection of corresponding bond angles C9-C1-C2, the out-of-plane movement of S atom and the internal rotation of the sulfonyl chloride groups around the bonds C1-S (Fig. 1). The set of independent parameters included: five bond lengths C2-H, C1-C2, C1-S, S-O1, S-Cl, five bond angles C9-C1-C2, C9-C1-S, C1-S-Cl, C1-S-O1, O1-S-Cl, dihedral angle C10-C9-C1-S describing the movement of the sulfur atom out of the naphthalene plane and two φ 1(C9-C1-S-Cl) and φ 2(C10-C5-S-Cl) torsion angles taking into account the rotation of the two SO₂Cl groups whose initial values depend on the conformers symmetry. All bond lengths C-H in the naphthalene fragment were assumed to be equal and to bisect corresponding bond angles C-C-C. The differences Δ r(C-C) arising due to nonequivalence of the bond lengths C-C were taken from the QC calculations at B3LYP/cc-pVTZ level of theory and were not included in variation during the least-squares procedure. The same adoption was made for the C-C-C bond angles.

The geometry of the molecule was investigated in terms of r_{h1} -structure. Vibrational corrections ($\Delta r = r_a - r_{h1}$) were calculated using program Shrink [32] assuming curvilinear relations between Cartesian and internal coordinates. The force field used in this calculation was obtained from B3LYP/cc-pVTZ calculations. The vibrational amplitudes for the terms possessing the close internuclear distances were refined in groups corresponding to the peaks on the radial distribution curve f(r) (Fig. 2). Structural analysis was performed utilizing modified KCED-35 program which is similar to the algorithm described in [33].

Two correlation coefficients happened to possess magnitude larger than 0.7: $p_2/p_5 = -0.80$, $p_6/p_7 = -0.73$ (p_i in Table 4).

Experimental structural parameters of 1,5-NaphDSC corresponding to the theoretical sM(s) curve which is in the best agreement with experimental data are listed in Table 4. Experimental and theoretical scattering intensity curves are given in the Fig. 3.

Table 4.

Experimental (GED) and calculated (B3LYP/cc-pVTZ)/(MP2/cc-pVTZ) structural parameters of 1,5-NaphDSC conformers (distances in Å, angles in deg.) in comparison with parameters of monosubstituted 1–NaphSC.

			1,5-NaphDSC				1–NaphSC	
	confor skewed- sk'	rmer I kewed-syn'	conformer II 'skewed-skewed-anti'		conformer III 'skewed-planar'		conformer 'skewed'	
Parameters	GED ^a r _{h1} structure	QC r _e structure	GED^{a} r_{h1} structure	QC r _e structure	c r _e stru skewed SO ₂ Cl group	C acture planar SO ₂ Cl group	$\operatorname{GED}^{\mathrm{a}},$ r_{h1} structure [1]	QC r _e structure [1]
C-H ^b	$1.098(9)^{a} p_{l}^{b}$	1.079/1.080	$1.098(9)^{a} p_{I}^{b}$	1.081/1.080	1.079/1.080	1.079/1.080	1.082(6) <i>p</i> ₁	1.081/1.081
C1-C2, (C5-C6) ^c	1.376(3) <i>p</i> ₂	1.371/1.379	1.376(3) <i>p</i> ₂	1.371/1.379	1.371/1.378	1.366/1.378	$1.380(3)p_2$	1.373/1.380
C2-C3, (C6-C7) ^c	1.408(3) (<i>p</i> ₂)	1.404/1.403	1.408(3) (p ₂)	1.404/1.403	1.404/1.403	1.406/1.403	1.413(3) (<i>p</i> ₂)	1.406/1.406
C3-C4, (C7-C8) ^c	1.373(3) (<i>p</i> ₂)	1.368/1.377	1.373(3) (<i>p</i> ₂)	1.368/1.377	1.368/1.376	1.367/1.376	1.375(3) (<i>p</i> ₂)	1.368/1.376
C4-C10, (C8-C9) ^c	1.422(3) (<i>p</i> ₂)	1.417/1.415	1.422(3) (<i>p</i> ₂)	1.417/1.415	1.418/1.416	1.417/1.416	1.422(3) (<i>p</i> ₂)	1.415/1.414
C1-C9, (C5-C10) ^c	1.431(3) (<i>p</i> ₂)	1.426/1.422	1.431(3) (p ₂)	1.427/1.422	1.427/1.422	1.429/1.422	1.434(3) (<i>p</i> ₂)	1.427/1.422
C9-C10	1.440(3) (<i>p</i> ₂)	1.435/1.439	1.440(3) (<i>p</i> ₂)	1.435/1.438	1.435	/1.438	1.439(3) (p ₂)	1.432/1.434
(C-C) ^b	1.405(3)	1.401/1.403	1.405(3)	1.401/1.403	1.401	/1.403	1.407(3)	1.400/1.402
C-S	$1.781(4) p_3$	1.797/1.772	1.781(4) <i>p</i> ₃	1.797/1.772	1.797/1.772	1.810/1.782	$1.764(5) p_3$	1.791/1.769
S-Cl	$2.056(4) p_4$	2.114/2.072	$2.056(4) p_4$	2.114/2.072	2.114/2.072	2.111/2.068	$2.051(5) p_4$	2.121/2.077
S=O ^b	1.426(3) <i>p</i> ₅	1.444/1.441	1.426(3) <i>p</i> ₅	1.444/1.441	1.444/1.441	1.444/1.442	1.425(3) <i>p</i> ₅	1.444/1.441
C9-C1-C2, (C10-C5-C6) ^c	$122.9(1) p_6$	122.5/122.7	122.9(1) p ₆	122.5/122.7	122.6/122.7	122.2/122.2	$122.5(1)^{a} p_{6}$	122.6/122.9
C9-C1-S, (C10-C5-S) ^c	122.7(3) <i>p</i> ₇	122.6/122.0	122.7(3) <i>p</i> ₇	122.6/122.0	122.5/122.8	116.6/115.8	122.1(5) <i>p</i> ₇	122.3/121.8
C1-S-Cl, (C5-S-Cl)	101.8(6) <i>p</i> ₈	101.2/99.8	101.8(6) <i>p</i> ₈	101.2/ 99.8	101.2/99.8	104.2/103.1	$101.5(10) p_8$	101.4/99.8
C-S-O ^b	109.3(4) p ₉	110.2/110.1	109.3(4) p ₉	110.2/110.1	110.2/110.1	109.3/109.1	110.2(7) <i>p</i> ₉	110.5/110.3
O-S-Cl ^b	106.2(2) p_{10}	106.2/106.5	106.2(2) <i>p</i> ₁₀	106.2/106.5	106.2/106.5	106.2/106.4	106.4(3) p_{10}	105.9/106.2
φ1(C9-C1-S-Cl)	71.2(12) <i>p</i> ₁₁	72.7/70.3	71.2(12) <i>p</i> ₁₁	72.7/70.3	72.9/70.3		71.4(21) p_{11}	73.0/70.4
φ2(C10-C5-S-Cl)	71.2(12)	72.7/ 70.3	288.8(12)	287.3/289.7		180/180		
φ(C10-C9-C1-S), (φ(C9-C10-C5-S)) ^c	178.0(32) p_{12}	179.1/179.1	178.0(32) p_{12}	179.3/179.4	179.0/179.3	179.6/180	179.3(55) <i>p</i> ₁₂	179.2/179.2

		ACCEPTED MANUSCRIPT							
conformer ratio χ, mol %	51.4(49) p_{13}	50.3	48.6(49) <i>p</i> ₁₃	49.7	0	0	100	-	
R _f , %, GED		3.34						3.68	

^a Total error limit in interatomic distances was estimated as $\sigma = [(2.5\sigma_{\rm LS})^2 + (0.002r)^2]^{1/2}$; total error in angles and in mole fraction was taken to be equal $3\sigma_{\rm LS}$ (all in the units of last significant digit).

^b Average values.

[°] Parameter in 'skewed-planar' conformer III.

-PMA

Results and discussion

Fragmentation of 1,5-NaphDSC by electron ionization

In Table 2 the mass spectra of disubstituted 1,5-NaphDSC, monosubstituted 1-NaphSC and naphthalene molecules are compared. The distinctive feature of the massspectrum of 1,5-NaphDSC containing two sulfonyl chloride groups as compared to the massspectrum of 1-NaphSC appears in the increasing of the relative intensities of the ions occurring due to elimination of the atoms (groups of atoms) of substituents. The ions with a lack of chlorine atom of one sulfonyl chloride group as well as ions with a lack of whole sulfonyl chloride group are the most probable to form. One more feature of the mass spectrum of 1.5-NaphDSC is the presence of $C_9H_6Cl^+$, $C_9H_6S^+$, and $C_8H_6S^+$ ions. The formation of the first of them is similar to the appearance of $C_9H_7^+$ and $C_{10}H_7Cl^+$ ions in the mass spectrum of monosubstituted sulfonyl chloride and related to the detachment of the C-SO₂Cl moiety belonging to one of substituents and the elimination of the SO₂ group of the second substituent. Possibly $C_9H_6Cl^+$ ion consists of two cyclic fragments: five- and six-membered (with the Cl atom as a substituent). The $C_9H_6S^+$ ion seems to consist of two cyclic six-membered fragments, one of which involves a sulfur atom, and the $C_8H_6S^+$ ion consists of the same six-membered fragment and the five-membered one remaining after the loss of the C-SO₂Cl group by the second substituent.

The common feature of the mass-spectra of mono- and disubstituted naphthalene sulfonyl chlorides is the predominance of the ions forming by loss or destruction of the substituents over those, which are formed by destruction of the naphthalene fragment. Besides, one can find signals corresponding to the ions $C_9H_n^+$ in the spectra of naphthalenesulfonylhalides while they are absent or have very low intensity in the spectrum of naphthalene. It may be connected with weakening of the bonds C-C adjacent to a substituent that appears in the elongation of these bonds and decreasing of the Wiberg bond indexes [34] (Table 5) as compared with unsubstituted naphthalene.

Table 5.

The bond lengths r(C–C) and Wiberg bond indexes Q(C–C) by scheme [34] for naphthalene, 1- NaphSC and 1,5-NaphDSC.

Molecule	r(C1-C2),	Q(C1-C2)	r(C1-C9),	Q(C1-C9)
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	Å		Å	
$C_{10}H_8$	1.370	1.561	1.416	1.280
$1-C_{10}H_7SO_2Cl$	1.380(3)	1.512	1.434(3)	1.239
$1.5-C_{10}H_6-(SO_2Cl)_2$	1.376(3)	1.515	1.431(3)	1.243

Conformational composition of the 1,5-NaphDSC vapor according to GED data and QC calculations.

According to Table 3 the calculated relative conformer ratios χ indicate that only two conformers I and II can be present in the 1,5-NaphDSC vapor at the temperature of the GED experiment.

This is confirmed by Figure 2 which shows the experimental function f(r) and the difference curves between the experimental and theoretical functions $\Delta f(r)$, corresponding to each of the conformers.



Fig. 2. Experimental (dots) and theoretical (lines) radial distribution curves f(r) and their differences $\Delta f(r)$ for the separate conformers of 1,5-NaphDSC (b-e) and for the optimal conformers ratio (a):

a) conformer I:conformer II $(51.4(49)\%:48.6(49)\%, R_f=3.34\%);$

- b) 'skewed- skewed-syn' conformer I, R_f=3.85%;
- c) 'skewed- skewed-anti' conformer II, R_f=3.64%;
- d) 'skewed-planar' conformer III, R_f=7.15%;
- e) 'planar- planar' conformer IV, R_f=9.47%



Fig. 3. Experimental (dots) and calculated (for the optimal I/II conformers ratio - lines) molecular intensities sM(s) and their differences $\Delta sM(s)$ for the long (a) and short (b) nozzle-to-plate distances.

According to Figure 2 it can be argued that the structure of conformers III and IV do not satisfy GED data, while the theoretical functions f(r) of both conformers I and II are very close to the experimental function and with each other despite the difference in the distances between Cl atoms of the two SO₂Cl groups, which equal 7.34 and 8.36 Å in the I(syn) and II(anti) conformers, respectively. The proximity of the O...O distances between these groups (7.73 (2), 7.97, 7.99 and 8.94 Å in conformer I and 7.54 (2), 7.89, 8.08 and 8.99 Å in conformer II) results in the similarity of theoretical functions f(r) of conformers I and II as well.

The scanning of conformer ratio with relaxation of the geometric parameters of conformers I and II was undertaken (Fig.4).

For the individual conformer II, disagreement factor R_f between experimental and theoretical functions sM(s) is 3.64%, for conformer I R_f is 3.85%. The lowest $R_f = 3.34\%$ corresponds to the conformers mixture with mole fractions ($\chi_{I=}43\%(25), \chi_{II=}57(25)\%$). According to Hamilton criterion [35] at the significance level of 0.05 the models of individual conformers may be excluded from consideration. The result of simultaneous refinement of structural parameters and conformer ratio is in agreement with this conclusion (Fig.2).

Thus, the GED data as well as QC calculations indicate that saturated vapor of 1,5-NaphDSC at 413(5) K consists of the conformers I and II mixture with approximately equal mole fractions.



Fig. 4. The dependence of R_f value on the mole fraction of conformer I of 1,5-NaphDSC.

Conformational properties and features of conformers geometric structure

Molecule 1,5-NaphDSC has two coordinates associated with internal rotation SO₂Cl groups about C1-S and C5-S bonds (numbering of atoms is shown in Fig. 1). The conformational properties of 1,5-NaphDSC were determined from the torsional potential functions $U(\varphi 1, \varphi 2)$ of the SO₂Cl group obtained by scanning $\varphi 1(C9-C1-S-Cl)$ angle with a step 10 degrees and an relaxation of other parameters including the $\varphi 2(C10-C5-S-Cl)$ torsion angle. Two different starting positions of the other SO₂Cl group ($\varphi 2$ equals 72.7° or 180°) were

used.

In Figure 5 the U(φ 1/72.7°) is the potential function of the first SO₂Cl group internal rotation when the starting value of φ 2(C10–C5–S–Cl) angle is equal to 72.7°. The U(φ 1/180°) potential function corresponds to scanning the angle φ 1 when the starting value of φ 2 angle is 180°. It should be noted that at scanning of the PES along the coordinate φ 1, the geometrical parameters and spatial position of the second sulfonyl chloride group remain practically unchanged, indicating the independent rotation of the two substitutes.

The calculations predict the existence of three minima of the U(φ 1/72.7°) potential function. The minimum at φ 1/ φ 2=72.7°/72.7° corresponds to conformer I ('skewed-skewed-syn'), the minimum at φ 1/ φ 2=287.3/72.7° is connected with existence of conformer II ('skewed-skewed-anti'), at last the minimum at φ 1/ φ 2=180/72.7° corresponds to conformer III ('planar- skewed'). In turn, the minima of the U(φ 1/180°) function correspond to conformers III ('skewed-planar', φ 1/ φ 2=72.7/180°), IV ('planar-planar', φ 1/ φ 2=180/180°) and enantiomer III* ('skewed-planar', φ 1/ φ 2=287.3/180°).

As seen from the U(φ 1/72.7°) plot, conformers I and II are the most stable structures in comparison with conformers III and IV. The barriers to internal rotation of the sulfonyl chloride group for these conformers exceed considerably the thermal energy (0.8 kcal/mol) corresponding to the temperature of the GED experiment. Therefore, the conformers I and II can be considered as rigid molecular systems and the harmonic vibration approximation can be used to describe their nuclear dynamics. In contrast, the conformers III and IV have to be regarded as a non-rigid molecular systems due to the shallow potential well at φ 1=180°, which is not deeper than 0.4 kcal/mol. Note that the lowest vibrational mode for both conformers III and IV corresponds to the torsional motion of the "planar" SO₂Cl group, and only five levels of this vibration mode fit in the potential wells of conformers III and IV. However, both III and IV conformers were excluded from consideration during structural analysis of experimental data because they possess the high total energies.



Fig. 5. Potential functions of internal rotation $U(\varphi 1/72.7^{\circ})$ and $U(\varphi 1/180^{\circ})$ of the sulfonyl chloride group of 1.5-NaphDSC as calculated by B3LYP/cc-pVTZ method. Minima correspond to conformers I, II, III, IV and enantiomer III*.

The statistical analysis of X-ray data [36] showed that in crystal the naphthalene sulfonic derivatives exist in the conformations with the bond S-X of SO₂X group in skewed or in planar positions with respect to the naphthalene skeleton, and skewed conformation meets about 9 times frequently than planar conformation. On a qualitative level, there is a correspondence between the relative energies of skewed and planar conformers of free molecules, calculated by B3LYP/cc-pVTZ method, and the probability of their structures realization in crystals.

Table 4 shows the experimental and calculated geometrical parameters of the most stable conformers I and II as well as the calculated parameters of conformer III having the sulfonyl chloride groups in skewed and in planar positions. Comparing the geometric characteristics of conformers shows that the parameters of the naphthalene skeleton and SO₂Cl group parameters in conformers I and II are close, while there is a difference in C1-C2, C-S, S-Cl bond lengths (Tabl. 4) and Wiberg bond indexes as well as in atomic charges (Tabl. 6) for sulfonyl chloride groups in skewed and in planar positions of conformer III.

These features can be explained in terms of NBO-analysis of the electron density distribution. Due to donor-acceptor interaction of the π (C1-C2) and σ *(S-Cl) orbitals in skewed conformers the electron density transfer from the bonding to the antibonding NBOs takes place. As a result, both bonds become weaker, and the bond C-S, in contrast, a more strong

(Fig. 6, Table 6), leading to a corresponding change in the lengths and Wiberg bond indexes compared to similar ones for sulfonyl chloride groups in planar positions in which this interaction is absent.



Fig. 6 The donor-acceptor interaction of the π (C1-C2) and σ *(S-Cl) orbitals for sulfonyl chloride group in skewed position

It is noted that the planar structure of naphthalene skeleton is kept in all conformers, and the Siamese C9-C10 bond is longer than the other C-C bonds in the skeleton. The data presented in Table 5 indicate that the introduction of the SO₂Cl substituent in the naphthalene framework lowers the Wiberg bond indexes of the two C–C bonds adjacent to the substituent.

The relationship between conformational properties and some physicochemical characteristics of 1,5-NaphDSC.

Table 6 shows the some characteristics of 1,5-NaphDSC conformers and skewed conformer of 1-NaphSC.

Table 6. The dipole moment values (μ), the energies of frontier orbitals, NBO atomic charges (q), Wiberg bond indexes (Q) and wave numbers of stretching S-Cl vibrations for 1,5-NaphDSC conformers and skewed conformer of 1-NaphSC (B3LYP/cc-pVTZ).

Y	1-NaphSC	1,5-NaphDSC ^a				
Parameters	skewed conformer	conformer	conformer	conformer III		
		Ι	II	skewed	"planer"	
				SO ₂ Cl group	SO ₂ Cl group	

μ, D	5.426	0.949	0.0	1.2	252	
E _{HOMO} , eV	-6.920	-7.676	-7.674	-7.	615	
E _{LUMO} , eV	-2.588	-3.308	-3.296	-3.	150	
q(Cl)	-0.279	-0.266	-0.266	-0.266	-0.251	
q(S)	2.088	2.086	2.086	2.086	2.068	
q(O)	-0.874	-0.870	-0.870	-0.870	-0.863	
q(C1)	-0.269	-0.261	-0.261	-0.261	-0.337	
q(C2)	-0.161	-0.156	-0.156	-0.154	-0.174	
q(C9)	-0.048	-0.045	-0.045	-0.042	-0.046	
Q(C-S)	0.8529	0.8441	0.8441	0.8434	0.8267	
Q(S-Cl)	0.6843	0.6943	0.6947	0.6952	0.7036	
$v_s(S-Cl), cm^{-1}$	338.5	341.9(16) ^b	341.2(0)	341.	4(12)	
$v_{as}(S-Cl), cm^{-1}$	-	343.1(9)	343.3(27)	342	.5(8)	

^a For 'planar-planar' conformer IV the dipole moment value is 0, $v_s(S-C1)=343(0)$, $v_{as}(S-C1)=340.7(22)$ cm⁻¹, $E_{HOMO}=-7.56$ eV. $E_{LUMO}=-2.92$ eV.

^b Intensity in brackets, km/mole.

In conformers I and II of 1,5-NaphDSC the NPA charges are practically identical, as well as the energies of the frontier orbitals. Other orientation of SO₂Cl groups leads to changing NPA charges in the groups as well as to increasing the energies of frontier orbitals of conformers III and IV. However, the energies of HOMO and LUMO orbitals of any 1,5-NaphDSC conformer are significantly lower the energies of frontier orbitals of 1-NaphSC (Table 6) and, especially, of the frontier orbitals ($E_{homo} = -6.09$, $E_{lumo} = -1.30$ eV) of the naphthalene molecule. Thus, the introduction of the second SO₂Cl group in monosubstituted naphthalene greatly increases electron acceptor ability.

At the same time, the values and directions of the dipole moments of 1,5-NaphDSC conformers are different (Table 6). Thus, the conformer ratio may affect the physicochemical properties of the compound. For example, the vibrational spectra of the conformers will be different. Since conformers II and IV have a center of symmetry, the symmetric vibrations activity in IR spectrum will be absent, and the spectra will contain smaller number of bands than the spectrum of conformers I and III which do not have a center of symmetry.

Due to that the 1,5-NaphDSC conformers have the different dipole moments, they will interact with the solvent differently, and their relative energy and the conformer ratio in the solvent may change in comparison with the gas phase. Thus, in an aqueous medium the Gibbs free energy difference ΔG^{0}_{298} of conformers I and II is 0.53 kcal/mol (calculation by PCM method) in comparison with 0.02 kcal/mol in gas phase. Besides, the dipole moment of the conformer I increases from 0.95 to 1.35 D at the transition from the gas phase to the aqueous medium.

Obviously, the different conformers ability to hydration is the reason for appearance of two sharp minima of activation enthalpy of 1,5-NaphDSC hydrolysis on the concentration dependence of the aqueous *i*-PrOH mixtures [18]. At specific compositions of the aqueous i-PrOH mixture some hydrate V-structures are formed in bulky water which possess maximal complementarity to the structures of hydration shells for each of the 1,5-NaphDSC conformers.

Conclusion

By GED and quantum chemical methods it was established that gas phase of 1,5-NaphDSC at T = 413 (5) K contains two conformers with syn and anti S-Cl bonds orientations of two sulfonyl chloride groups. The S-Cl bonds have skewed towards the longer C-C bonds of naphthalene skeleton, i.e., position of the sulfonyl chloride groups is the same as in a stable conformer of monosubstituted 1- NaphSC [1].

The introduction of two electron withdrawing SO₂Cl substituents in the naphthalene framework significantly lowers the energy of frontier orbitals and increases the lengths of the two C–C bonds adjacent to the substituent. The weakening of these C-C bonds is confirmed by the presence of $C_9H_n^+$ ions in the mass spectra of naphthalene sulfonyl halides which are absent or have very low abundence in the mass spectrum of naphthalene.

Though four conformers of 1,5-NaphDSC have close NPA-charges on the atoms and energy frontier orbitals, they differ by a magnitude and direction of the dipole moment, by the number of bands in the IR spectra and by the interaction with the solvent. The different conformers abilities to hydration may be the reason for appearance of two sharp minima of activation enthalpy of 1,5-NaphDSCh hydrolysis [18] on the concentration dependence of the aqueous i-PrOH mixtures.

For conformer III of 1,5-NaphDSC it is shown that the bond lengths C1-C2, C-S, S-Cl

depend on SO_2Cl groups orientation with respect to the naphthalene skeleton. Within the NBO-analysis the explanation for this fact is given.

Detected structural features of the 1,5-NaphDSC conformers allow to predict the conformational properties of unstudied mono- and disubstituted naphthalenes.

Acknowledgement

This work was supported by Russian Ministry of Education and Science (Project No 4.1385.2014K).

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Highlitght

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Graphical abstract

