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Crystal and Molecular Structure of 2-Ethylthio-3-phenyl-1,3,4-thiadiazolium Tetrafluoroborate

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Synopsis. 2-Ethylthio-3-phenyl-1,3,4-thiadiazolium tetrafluoroborate (**2**) was synthesized by the reaction of 3-phenyl-1,3,4-thiadiazole-2(3*H*)-thione (**1**) with triethyloxonium tetrafluoroborate (Meerwein's reagent) in acetonitrile at room temperature. A structural investigation of **2** was carried out on the basis of such spectral data as ^{1}H NMR and ^{13}C NMR spectroscopies and X-ray analysis. The crystallographic data of **1** and **2** are as follows: Orthorhombic space group of $P2_12_12_1$, a=10.116(2), b=13.199(2), c=6.690(2) Å, V=893.3(3) Å^3, and Z=4 for **1**, orthorhombic space group of $Pbca$, a=16.449(6), b=15.291(3), c=10.833(2) Å, V=2725(2) Å^3, and Z=8 for **2**, respectively.

During the course of our studies concerning the synthetic and structural investigation of 1,3,4-thiadiazine and 1,3,4-thiadiazole analogs we observed that the 1,3,4-thiadiazine and 1,3,4-thiadiazole rings were stabilized by on effective conjugation between the π bond and a pair of electrons on the sulfur atom.[1—3] Our preceding paper[4] reported that the structure of 3-phenyl-1,3,4-thiadiazol-2(3*H*)-one was found to be best interpreted by a joining of two adjacent resonance structure of 3pπ–2pπ–2pπ–2pπ (–S–C=N–N–) and 2pπ–2pπ ($\rangle$C=O) by the use of a spectroscopic investigation and X-ray analysis. We thus wish to obtain a structural investigation of 3-phenyl-1,3,4-thiadiazole-2(3*H*)-thione and 2-alkylthio-3-phenyl-1,3,4-thiadiazolium salt.

In this report, we describe a synthesis of 2-ethylthio-3-phenyl-1,3,4-thiadiazolium tetrafluoroborate (**2**) and discuss the structural characteristics of 3-phenyl-1,3,4-thiadiazole-2(3*H*)-thione (**1**) and **2** based on the spectroscopic properties and X-ray crystallography.

Experimental

Synthesis of 2. A mixture of thiadiazole **1** (0.387 g, 2.0 mmol), which was prepared as described in a preceding paper,[5] and triethyloxonium tetrafluoroborate (Meerwein's reagent, 1.01 g, 5.3 mmol) in acetonitrile (10 ml) was stirred for 1 d at room temperature under an argon atmosphere; it was then evaporated to give an oily residue. The residue was treated with water (5 ml) and diethyl ether (5 ml) to give a precipitate of **2**, which was collected by filtration and dried. Yield, colorless plate crystals (from acetone) 0.487 g (78%); mp 158—159 °C; ^{1}H NMR (CD$_3$CN) δ=1.56 (3H, t, J=7.3 Hz), 3.75 (2H, q, J=7.3 Hz), 7.66—7.77 (5H, m), and 9.37 (1H, s); ^{13}C NMR (CD$_3$CN) δ=12.7 (CH$_3$), 34.3 (CH$_2$), 125.8, 131.0, 132.9, 136.9 (each phenyl group), 154.1 (C-5: J_{CH}=229 Hz), 181.7 (C-2); IR (KBr) 1495, 1120, 1084, 1036 cm^{-1}; UV (in acetonitrile) $\lambda_{\max}$ ($\varepsilon_{\max}$) 240 (6800), 287 (8150); MS m/z (rel intensity) 222 (P-HBF$_4$, 13), 161 (48), 77 (100). Found: C, 38.86; H, 3.63; N, 9.11%. Calcd for $C_{10}H_{11}N_2S_2BF_4$: C, 38.73; H, 3.58; N, 9.03%.

X-Ray Data Collection, Structure Solution and Refinement.[6] Diffraction data were obtained on a Rigaku AFC-5R four-circle diffractometer at ambient temperature. Crystal data and details concerning measurements for **1** and **2** are summarized in Table 1. The standard reflections were monitored every 50 measurements; the decay of their intensities was 5%. Reflection data were corrected for both Lorentz and polarization effects. Empirical absorption corrections were applied. The structures were solved by a direct method[7] and refined anisotropically for non-hydrogen atoms by block-diagonal least-squares calculations. The reliability factors are defined as $R=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$. $R_w=\{\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$. The atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[8] Hydrogen atoms were included as a fixed contribution in the last cycle; their temperature factors were assumed to be isotropic. The calculations were performed on

Table 1. Crystallographic Data and Some Experimental Conditions

	Colorless rectangular crystal **1**	Colorless triangular crystal **2**
Formula	$C_8H_6N_2S_2$	$C_{10}H_{11}N_2S_2BF_4$
Formula weight	194.27	310.13
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$Pbca$
a/Å	10.116(2)	16.449(6)
b/Å	13.199(2)	15.291(3)
c/Å	6.690(2)	10.833(2)
V/Å^3	893.3(3)	2725(2)
Z	4	8
Density/g cm^{-3}	1.444	1.512
Crystal size/mm	0.25×0.25×0.20	0.40×0.40×0.40
Radiation	Mo $K\alpha$	Mo $K\alpha$
λ (Mo $K\alpha$)/Å	0.71069	0.71069
μ (Mo $K\alpha$)/cm^{-1}	5.15	4.05
Scan mode	ω–2θ	ω–2θ
Scan rate/° mm^{-1}	16	16
Scan range/°	1.37+0.30 tan θ	1.42+0.30 tan θ
2θ range/°	2—55	2—55
Number of observed reflections	1231	3535
Reflections used in refiment	888 ($F_o>3\sigma(F_o)$)	1035($F_o>3\sigma(F_o)$)
F(000)	400	1264
R	0.032	0.065
R_w	0.036	0.071

$R=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$. $R_w=\{\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$, where $w=1/\sigma^2(F_o)$.

a VAX computer by using the program system TEXAN.[9] The final R and R_w values were 0.032 and 0.036 for **1** and 0.065 and 0.071 for **2**, respectively. The final parameters for non-hydrogen atoms for **1** and **2** are given in Table 2.

Results and Discussion

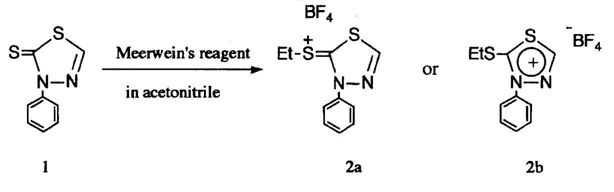
The thiadiazolium **2** was prepared by a reaction of thiadiazolethion **1** with triethyloxonium tetrafluoroborate (Meerwein's reagent) in acetonitrile under an argon atmosphere in fairly good yield (78%) (Scheme 1).

The spectroscopic data of **2** supported the assigned structure. The ^{1}H NMR signals of the heterocyclic protons (5-position) and the ^{13}C NMR signals of the carbons of 5-position for **2** and **1** are different from each other regarding the chemical shifts and coupling constants, because the methine signals of proton and carbon of **2** shifted to a lower field (1.38 ppm for ^{1}H NMR, 10 ppm for ^{13}C NMR spectra) and indicated a greater coupling constant (J_{CH}; 12 Hz) compared with that of **1**. However, in spite of the chemical shift of the C-2, having a sulfonio group in **2** instead of a thioxo group in **1** shows almost a similar value as that of **1**.

Table 2. Final Atomic Coordinates of **1** and **2** Together with Their Standard Equivalent Isotropic Temperature Factors

Atom	x	y	z	B_{eq} a)
1				
S(1)	0.9173(1)	0.15367(7)	0.4767(1)	4.25(4)
S(2)	0.8178(1)	−0.05930(8)	0.4076(2)	4.71(5)
N(1)	1.0050(3)	0.0149(2)	0.2141(5)	3.2(1)
N(2)	0.9897(3)	−0.0807(2)	0.1317(5)	4.1(1)
C(1)	0.8956(4)	−0.1262(3)	0.2208(7)	4.6(2)
C(2)	0.9226(3)	0.0429(2)	0.3631(5)	3.2(1)
C(3)	1.1103(3)	0.0767(2)	0.1378(5)	3.1(1)
C(4)	1.2222(4)	0.0907(3)	0.2509(6)	3.8(2)
C(5)	1.3250(5)	0.1486(3)	0.1741(8)	4.6(2)
C(6)	1.3132(5)	0.1920(3)	−0.0132(8)	4.9(2)
C(7)	1.2010(5)	0.1774(3)	−0.1231(7)	4.6(2)
C(8)	1.0971(4)	0.1188(3)	−0.0504(6)	3.9(2)
2				
S(2)	0.8083(1)	0.1066(2)	0.0965(2)	4.7(1)
S(1)	0.7990(2)	0.1161(2)	0.3789(2)	5.5(1)
F(1)	0.2445(4)	0.1031(7)	0.7677(6)	14.0(6)
F(2)	0.3563(4)	0.0646(5)	0.8567(5)	10.3(4)
F(3)	0.3576(4)	0.1170(5)	0.6670(5)	10.0(4)
F(4)	0.3280(6)	0.1970(5)	0.8292(8)	15.1(7)
N(1)	0.6823(4)	0.1422(4)	0.2138(5)	3.8(3)
N(2)	0.6579(4)	0.1484(5)	0.0912(6)	5.1(4)
C(2)	0.7595(5)	0.1209(5)	0.2330(6)	3.7(4)
C(1)	0.7204(5)	0.1310(7)	0.0228(7)	5.3(5)
C(3)	0.6214(5)	0.1623(6)	0.3060(7)	3.8(4)
C(4)	0.6027(6)	0.0992(6)	0.3945(8)	5.0(5)
C(5)	0.5427(6)	0.1225(7)	0.4807(8)	5.6(5)
C(6)	0.5048(6)	0.2017(8)	0.476(1)	5.5(6)
C(7)	0.5240(6)	0.2595(6)	0.389(1)	5.4(5)
C(8)	0.5832(5)	0.2410(6)	0.3009(8)	4.4(4)
C(9)	0.9067(6)	0.1013(7)	0.3474(8)	5.7(5)
C(10)	0.9316(7)	0.0114(9)	0.330(1)	8.4(8)
B(1)	0.3235(7)	0.119(1)	0.777(1)	5.3(6)

a) $B_{\mathrm{eq}}=(4/3)\{\sum_{i}\sum_{ij}B_{ij}\boldsymbol{\alpha}_i\cdot\boldsymbol{\alpha}_j\}$.



Scheme 1.

X-Ray crystal analyses of **1** and **2** were carried out; the results are given in Tables 1 and 2 and Fig. 1. Each of the planes (A, B, C) defined by the 1,3,4-thiadiazole ring atoms (S(2), C(1), N(1), N(2), and C(2)), the 1,3,4-thiadiazole ring containing side chain atoms (S(2), C(1), N(1), N(2), C(2) and S(1)) and the phenyl ring atoms (C(3), C(4), C(5), C(6), C(7), C(8)) are almost planar; the deviations from planes A, B, C are 0.0029, 0.0153, and 0.0025 Å for compound **1** and 0.0013, 0.0179, and 0.0038 Å for compound **2**. On the other hand, the dihedral angles between planes A and C are 73° for **1** and 56° for **2**. These values indicate that the C(2)–S(1) groups are, interestingly, almost coplanar with the heterocyclic plane, while the phenyl rings are not coplanar with the heterocyclic plane. Thus, conjugation interactions are present between the double-bond in the 1,3,4-thiadiazole ring and the C(2)–S(1) group, and are absent between the 1,3,4-thiadiazole ring and the phenyl ring. The lengths of N(1)–N(2) (1.39 Å), N(2)–C(1) (1.29 Å), and S(1)–C(2) (1.71 Å), for **2** are longer than those of N(1)–N(2) (1.38 Å), N(2)–C(1) (1.27 Å), and

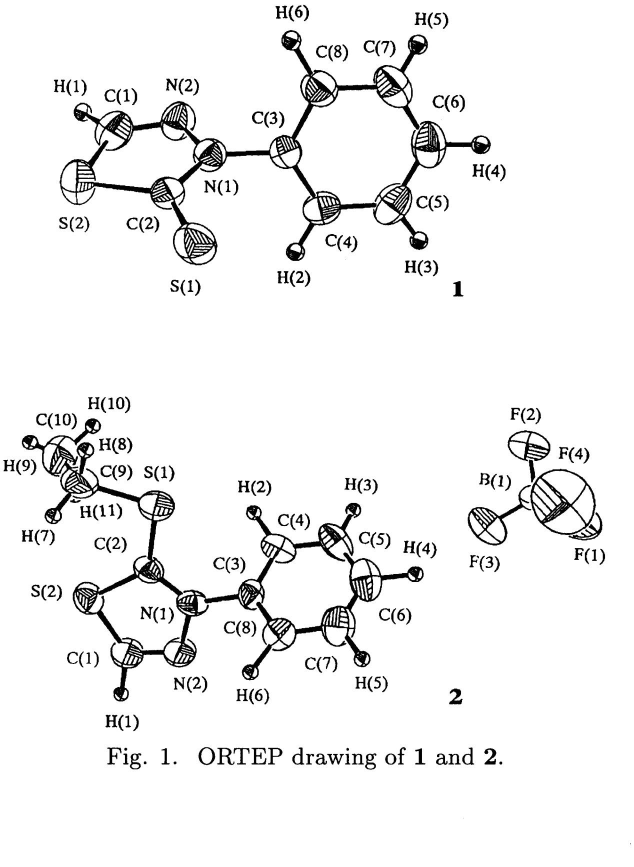


Fig. 1. ORTEP drawing of **1** and **2**.

S(1)–C(2) (1.64 Å) for **1**; however, the lengths of C(2)–S(2) (1.64 Å), S(2)–C(1) (1.69 Å), and N(1)–C(2) (1.32 Å), for **2** are shorter than C(2)–S(2) (1.74 Å), S(2)–C(1) (1.72 Å), and N(1)–C(2) (1.35 Å) for **1**. These values indicate that although the double-bond character of C(2)–S(2), S(2)–C(1), and N(1)–C(2) increases, the double-bond character of N(2)–C(1) and S(1)–C(2) decreases in the ring of **2** by conversion of **1** into **2**.

All of these observations suggest that the structure of **2** should be like the 1,3,4-thiadiazolium structure **2b** rather than the sulfonium structure **2a**.

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