

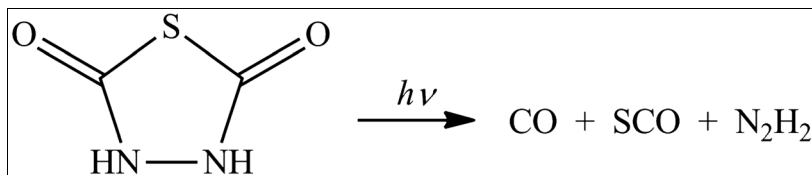
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Single crystals of 1,3,4-thiadiazolidine-2,5-dione (**1**) have been grown and the X-ray crystal structure showed the molecule to be planar with sp^2 -hybridized nitrogen atoms. Density functional theory calculations of nucleus-independent chemical shifts profiles show that **1** is non-aromatic. From actinometry, it was found that continuous photolysis of **1** in methanol at $\lambda = 254$ nm resulted in a decomposition with the quantum yield $\Phi = 0.076(7)$ mol/Einstein at room temperature.

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INTRODUCTION

The heterocyclic compound 1,3,4-thiadiazolidine-2,5-dione (**1**) has interestingly been shown to undergo photolysis in solution giving CO, OCS, and N_2H_2 (diazene) as shown in Figure 1 [1]. In the presence of various alkenes in the solution during the photolysis, the generated diazene was shown to hydrogenate the double bonds in high yields. Furthermore, the diazene is interesting, because it is an intermediate in the reduction of dinitrogen to ammonia, a reaction that takes place in the enzyme nitrogenase, where the catalytic site includes one molybdenum, seven iron ions, and an interstitial carbon atom [2]. In the free state, diazene is extremely unstable, decomposing to N_2 and N_2H_4 [3]. With the aim of studying the chemistry of photolytically generated diazene in solution, we have carried out a more detailed investigation of the properties of **1**, and we present here the X-ray crystal structure of **1** along with a density functional theory study (DFT) of the aromaticity of **1** and finally chemical actinometry of the photolysis shown in Figure 1.

RESULTS AND DISCUSSION

Synthesis. The synthesis of **1** reported by Rüfenacht [4] involves gaseous phosgene as shown in Figure 2. As an alternative to handling this extremely poisonous gas we, analogous to Diederich [5], found that the commercially available triphosgene, bis(trichloromethyl)carbonate, a stable solid at room temperature, can be used as well. We carried out the first step in Figure 2 in 3 M hydrochloric acid in which both triphosgene and 5-methoxy-3*H*-1,3,4-thiadiazol-2-one are insoluble. However, during 2 days of stirring of the reaction mixture,

the solid triphosgene reacted quantitatively, according to NMR, giving solid 5-methoxy-3*H*-1,3,4-thiadiazol-2-one.

Crystal structure. Figure 3 shows the X-ray crystal structure of **1** along with the unit cell showing the intermolecular hydrogen bonds, and selected bond distances and angles are listed in Table 1. It is noteworthy that the geometry around the nitrogen atoms is close to trigonal planar with the atoms being sp^2 -hybridized. This results in a planar geometry of **1**, consistent with the ionic resonance structure **1a** shown in Figure 4. The C–N and C–O bond distances in **1** fall in the range found in amides typically being 1.32–1.35 Å and 1.22–1.24 Å, respectively [6]. The C–S bond distance of averagely 1.785 Å is seen to lie in between the $C(sp^2)$ -S distance found in $C=C-S-C$ type molecules (1.75 Å) and non-aromatic tetrahydrothiophenes (1.83 Å) [6]. This should be compared with the shorter C–S bond distance of 1.71 Å found in aromatic thiophenes [6]. This suggests that the C–S bond in **1** has little, if any, π character. The N–N bond distance in **1** is similar to the

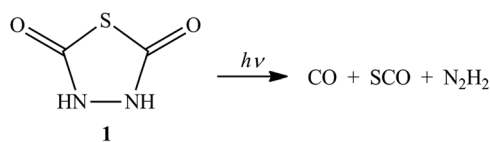


Figure 1. Molecular structure and photolysis of **1**.

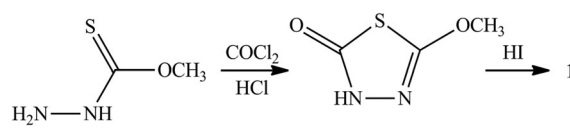


Figure 2. Reaction scheme in the synthesis of **1**.

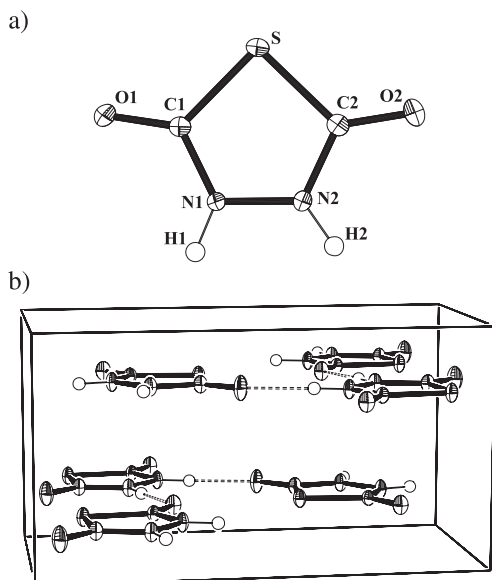


Figure 3. X-ray crystal structure of **1** (a) showing the layer structure and intermolecular hydrogen bonds (b).

Table 1

Selected distances (Å) and angles (o) in **1**.

S-C1	1.7822(14)	C1-S-C2	90.61(6)
S-C2	1.7870(15)	O1-C1-N1	124.78(13)
C1-O1	1.2319(16)	O1-C1-S	125.98(10)
C1-N1	1.3363(17)	N1-C1-S	109.24(10)
N1-H1	0.8800	C1-N1-N2	115.52(11)
N1-N2	1.3835(15)	C1-N1-H1	131.2
C2-O2	1.2238(17)	N2-N1-H1	113.3
C2-N2	1.3368(17)	O2-C2-N2	124.33(13)
N2-H2	0.8781	O2-C2-S	126.67(11)
		N2-C2-S	109.01(10)
		C2-N2-N1	115.63(11)
		C2-N2-H2	120.1
		N1-N2-H2	124.3

distances found in pyrazoles (1.37 Å) and much longer than found in C–N=N–C (*cis*) type molecules (1.24 Å) [6]. The structure consists of layers of **1** with N–H...O intermolecular hydrogen bonds and the N–O distance around 2.69 Å is typical for a strong hydrogen bond [7]. Figure 5 shows the hydrogen bond pattern. A structure refinement where the hydrogen bond was considered to be O–H...N gave significantly higher *R*-values. The distance between the layers is 3.10 Å. In this context, it should be mentioned that Enchev and Angelove [8] reported an *ab initio* study of the tautomerism of **1** (Figure 4) and similar molecules, and it was concluded that tautomer **1a** is preferred over **1b** in accordance with our findings.

DFT calculations. Because the crystal structure showed **1** to be planar, the question of the aromaticity of the ring presents itself. It is often of interest to probe

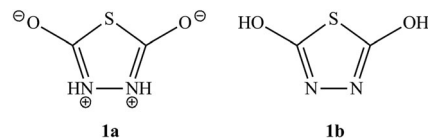


Figure 4. Resonance form (**1a**) and tautomeric form (**1b**).

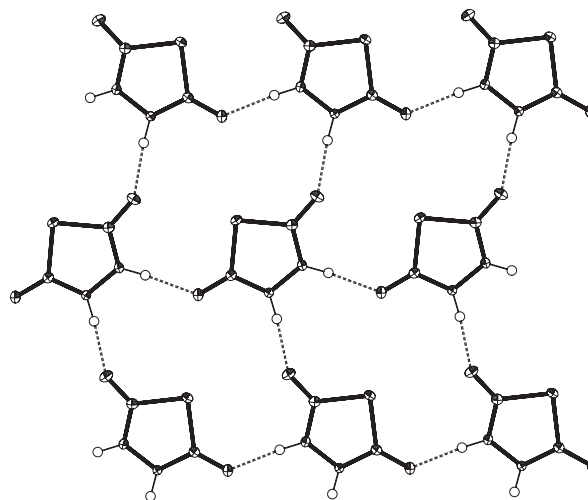


Figure 5. Hydrogen bond pattern in solid **1**.

the aromaticity of cyclic π -electron systems such as **1**, as it gives extended information on the electronic structure. One simple way of doing this is with the nucleus-independent chemical shifts (NICS) criterion of aromaticity [9] where the magnetic shielding in the ring center is calculated with *ab initio* or DFT methods. The shielding was originally probed in the plane of the ring, NICS(0), but has later more frequently been probed 1 Å above the ring center, NICS(1), [10,11] as this tends to give more reliable results. However, as this still not always gives conclusive results, a method called aromatic ring current shieldings (ARCS) has been developed [12] where the shielding is calculated in several distances above the ring center and fitted to a theoretical model. Inspired by this approach, we have calculated the chemical shifts at different distances (*r*) above the ring center (*z*-direction); and by plotting the isotropic chemical shift, the chemical shift in the *z*-direction and the in plane chemical shift versus *r*, we obtain some very characteristic graphs, in which it is easy to distinguish aromatic, antiaromatic, and non-aromatic systems. Figure 6 shows these plots for **1** and three reference compounds: 1,2-diazolidine-3,5-dione as a non-aromatic reference, thiophene as an aromatic reference, and the cyclopentadienyl cation as an antiaromatic reference. Compound **1** is clearly seen to be non-aromatic with the pattern closely resembling that of

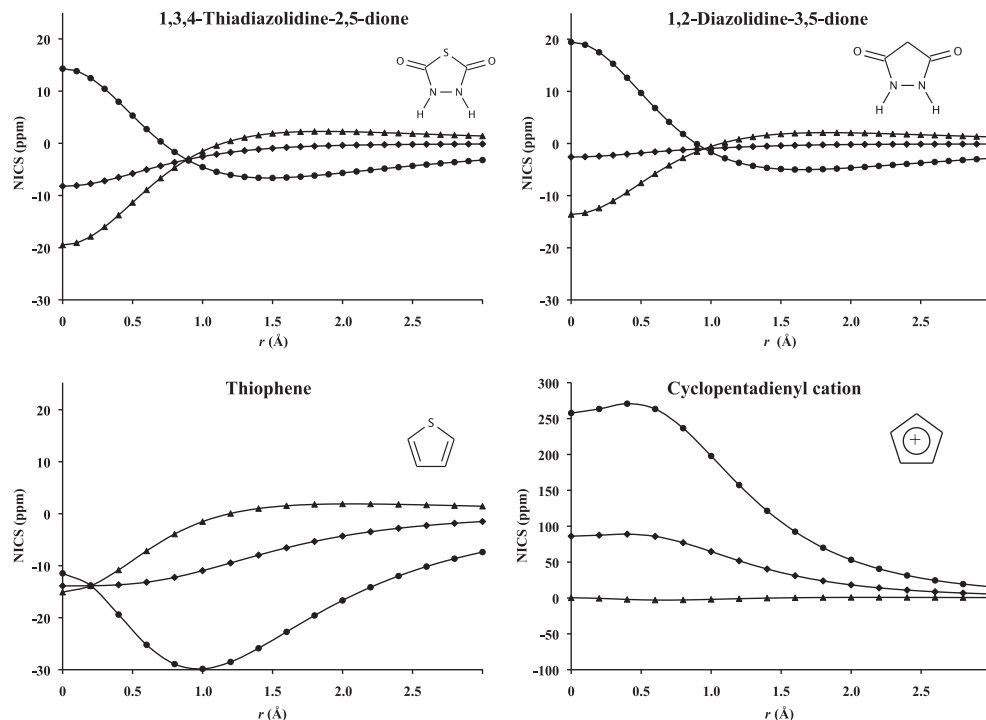


Figure 6. Extended nucleus-independent chemical shifts (NICS) plots for **1** and reference compounds. The graphs display the isotropic chemical shift (\blacklozenge), the chemical shift in the z -direction (\bullet), and the in plane chemical shift (\blacktriangle) versus the distance (r) above the ring center. The graph for **1** was obtained from calculations on the X-ray geometry, the graph for 1,2-diazolidine-3,5-dione from the same X-ray geometry, with the sulfur atom exchanged with a CH_2 group and the graphs for thiophene and the cyclopentadienyl cation from optimized geometries at the 6-311G(2df,p)/B3LYP level.

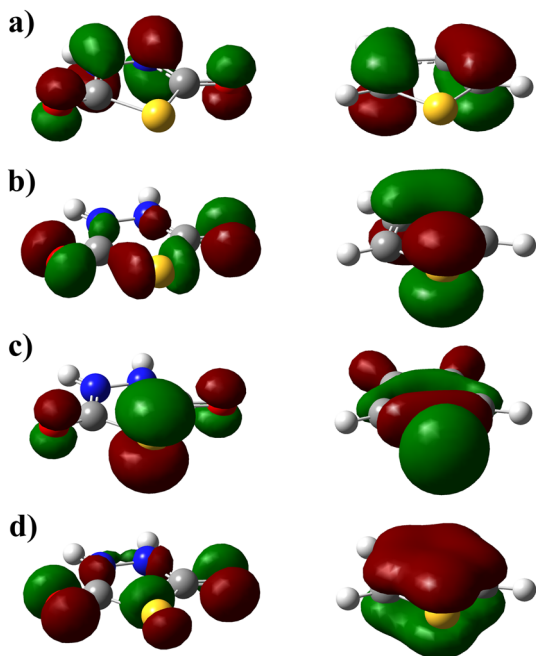


Figure 7. Comparison of the four highest occupied molecular orbitals of **1** (left) and thiophene (right) calculated at the 6-311G(2df,p)/B3LYP level. (a) HOMO, (b) HOMO-1, (c) HOMO-2, (d) HOMO-3. Isosurface values are 0.05. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the non-aromatic reference 1,2-diazolidine-3,5-dione and differing greatly from the aromatic and antiaromatic references. Furthermore, we note, that the use of NICS(0) or NICS(1) would have been inconclusive here, illustrating the need of a more detailed picture such as the one given in Figure 6. More information can be obtained from looking at the orbital plot comparison between **1** and thiophene in Figure 7. In both, the HOMO is a π -type orbital, in **1** involving out-of-plane orbitals of the oxygen and nitrogen atoms but not of the carbon atoms. For **1**, the HOMO-1 is mainly an oxygen in-plane lone-pair orbital, whereas for thiophene, it is a π -orbital involving orbitals of the carbon atoms (primarily C3 and C4) and the sulfur lone-pair orbital. In **1**, the sulfur lone-pair orbital contributes to HOMO-2 and it should be noted that the orbitals of the other atoms in the ring do not contribute to the HOMO-2 as they do in the HOMO-1 in thiophene. This implies that the sulfur p-lone-pair (the other lone-pair is in an s-type orbital) does not participate in the π -conjugation in the ring, and therefore renders **1** non-aromatic.

Actinometry. The UV spectrum of **1** in methanol consists of a band with a maximum at $\lambda=237$ nm ($\epsilon=3.08 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). In the actinometry studies of

the photolysis of **1** (Figure 1) at $\lambda=254$ nm ($\epsilon=1.42 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), a value of $\Phi=0.076(7)$ mol/Einstein was found in methanol at room temperature. Methanol was chosen as the solvent because of the high solubility of **1** in this solvent. The absorbance decreases in the whole UV range during the photolysis. The high value of Φ makes **1** a convenient source of diazene through photolysis in the studies of its solution chemistry. Furthermore, by use of flash photolysis, the dynamics of diazene in solution can be studied.

EXPERIMENTAL

The starting material hydrazinecarbothioic acid *O*-methyl ester was prepared according to the method of Rüfenacht [4]. Triphosgene was purchased from Aldrich in Copenhagen. *Caution!* Upon contact with water or other nucleophiles, triphosgene releases phosgene, which is extremely toxic. A well-ventilated fume hood should be used when handling triphosgene.

Synthesis of 5-methoxy-3*H*-1,3,4-thiadiazole-2-one. A total of 48.2 g of hydrazinecarbothioic acid *O*-methyl ester (0.454 mol) was dissolved in 150 mL of water and 50 mL of conc. hydrochloric acid. A total of 38.6 g of triphosgene (0.130 mol) was suspended in the solution and the container purged with nitrogen. The reaction was stirred vigorously for 48 h, and exhaust gas from the reaction was led through a solution of conc. sodium hydroxide. The solution was cooled to 0°C, and the precipitate was filtered off. The precipitate was extracted twice with hot (75°C) ethyl acetate leaving some white powder on the filter, and the filtrate was evaporated to dryness to give the raw product. It was then recrystallized from a 2:1 methanol/water (V:V) mixture yielding 22.3 g (43%) of a product showing no signal from triphosgene in ¹³C NMR (deuteriochloroform): δ 57.40, 160.15, and 170.00 ppm. *Anal.* Calcd for C₃H₅O₂N₂S: C, 27.27; H, 3.05; N, 21.22. Found: C, 27.18, H, 3.01; N, 21.53. The side product left on the filter when washing with ethylacetate was found to be carbonyl-bis(methoxy thiocarbonylhydrazide) as described by Rüfenacht [4]: *Anal.* Calcd for C₅H₁₀O₃N₄S₂: C, 25.21; H, 4.23; N, 23.53. Found: C, 25.33, H, 3.81; N, 23.31.

Synthesis of 1,3,4-thiadiazolidine-2,5-dione. A total of 5.16 g of 5-methoxy-3*H*-1,3,4-thiadiazole-2-one (0.0391 mol) was suspended in 200 mL of 2.2 M hydroiodic acid, and the solution was stirred for 5–6 h at 60°C. The solution was evaporated to dryness on a rotary evaporator at 60°C, and 50 mL of water was added and evaporated again. This was repeated 4–5 times until the precipitate was almost colorless, and the product was then recrystallized from methanol. Yield: 3.75 g (81%). *Anal.* Calcd for C₂H₂O₂N₂S: C, 20.34; H, 1.71; N, 23.72. Found: C, 20.29; H, 1.48; N, 23.58.

X-ray crystal structure of 1. A crystal of **1** suitable for X-ray crystallography was mounted, and intensity data was collected at 123(2) K on an Enraf-Nonius KappaCCD area detector using ω and θ scans with a scan width of 1.0° and 40 s exposure times. The crystal to detector distance was 35.0 mm. The program EVALCCD (Bruker Nonius) [13] was used for data reduction, and the data were corrected for absorption by integration [14]. The structure was solved with direct methods utilizing SHELXS [15] and refined by

Table 2
Crystal data and structure refinement for **1**.

Compound	1
Formula	C ₂ H ₂ O ₂ N ₂ S
Formula weight (g mol ⁻¹)	118.12
Crystal size (mm ³)	0.142 × 0.106 × 0.065
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
<i>a</i> (Å)	11.427(2)
<i>b</i> (Å)	6.1769(14)
<i>c</i> (Å)	5.879(2)
α (°)	90
β (°)	90
γ (°)	90
<i>V</i> (Å ³)	414.92(19)
<i>Z</i>	4
<i>D_x</i> (g cm ⁻³)	1.891
<i>T</i> (K)	123(2)
μ	0.637
No. measured/observed	11909/784
Parameters refined	43
Final <i>R</i> ₁	0.0254
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0687
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0282, 0.0706
<i>S</i> (GoF)	1.108

least-squares methods using SHELXL97 [16]. All non-hydrogen atoms were refined using anisotropic displacement parameters. All hydrogen atoms were included and the positions refined with isotropical factors of 1.2 *U*_{eq} of the parent atom. Crystallographic data are given in Table 2. Crystallographic data for the structure analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 908634 for **1**. Copies of these information can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 01223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

DFT calculations. All calculations were carried out in Gaussian09 [17] with the B3LYP functional [18–20] and the 6-311G(2df,p) one electron basis set [21,22]. The NMR shielding tensors were calculated using established methods [23–26] using the Gauge-Independent Atomic Orbital method [27–30].

Other physical measurements. Elemental analyses (C, H, N) were carried out at the Microanalytical Laboratory at our Department of Chemistry. Absorption spectra were recorded on a Perkin-Elmer Lambda 40 UV–vis spectrophotometer. Continuous photolysis was carried out on stirred solutions (*V* = 3.00 mL) in a square quartz cuvette with 1.000 cm path-length on an optical train using collimated light ($\lambda=254$ nm) from a 200 W Hg lamp and the appropriate interference filters for wave-length isolation. Chemical actinometry was performed with the use of K₃[Fe(C₂O₄)₃] solutions [31,32]. Perchloric acid was used instead of sulfuric acid in order to avoid the presence of the UV-absorbing hydrogensulfate ions. The intensity of absorbed light was in the range 6.2–8.4 × 10⁻⁸ Einstein s⁻¹ L⁻¹, and typical concentrations of **1** were around 7 × 10⁻⁴ M in methanol. The quantum yields were found by extrapolation a plot of Φ versus *t* to *t* = 0 s.

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