

Michael E. Sitzmann\* and Magdy Bichay

Indian Head Division, Naval Surface Warfare Center  
Indian Head, MD 20640, USA

John W. Fronabarger,\* Michael D. Williams and William B. Sanborn

Pacific Scientific Energetic Materials Co.  
Chandler, AZ 85226, USA

Richard Gilardi\*

Laboratory for the Structure of Matter, Naval Research Laboratory  
Washington, DC 20375, USA  
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The synthesis and properties of hydroxynitrobenzodifuroxan (5-nitro[1,2,5]oxadiazolo[3,4-*e*][2,1,3]benzoxadiazol-4-ol-3,8-dioxide) (**1**) and its salts (four metal and three amine salts) are described. Crystal structure analyses indicate that the hydroxynitrobenzodifuroxan materials can exist in two forms. One form is the isomer in which the oxy and nitro group are in positions *ortho* to each other. In the other form, these groups are *para* to each other.

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## Introduction.

Due to environmental concerns, there is considerable interest in replacing initiating explosives such as lead azide and lead styphnate with new non-heavy metal initiating materials. Preferably, these new materials will have an auto-ignition temperature in the vicinity of 200 °C or above, in addition to having sensitivity and output properties similar to lead azide or lead styphnate. The furoxan ring is a sensitizing group for initiating materials and certain dinitrobenzofuroxans such as the potassium hydroxide-4,6-dinitrobenzofuroxan adduct (KDNBF) [1] and 7-hydroxy-4,6-dinitrobenzofuroxan, potassium salt [2] are currently used or under consideration for use as initiating explosives. Our interest in hydroxynitrobenzodifuroxan was based on the proposition that non-heavy metal salts of this material would be improved lead azide/lead styphnate replacements, the rationale being: (1) that an oxy salt would raise the melting point/ignition temperature and; (2) that the combination of the oxy salt, the two furoxan rings and the nitro group would provide very high sensitivity to initiation [3]. Thus, in this report, we describe our investigation concerning the synthesis and properties of hydroxynitrobenzodifuroxan salts, including four metal and three amine salts.

## Results and Discussion.

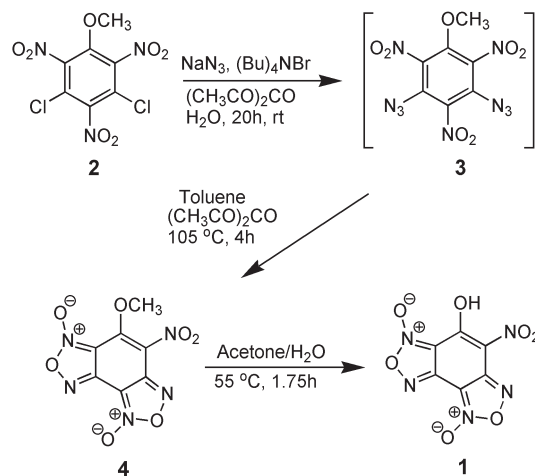
### Synthesis.

A common procedure for the preparation of benzofuroxans involves thermolysis of a benzene compound containing adjacent azido and nitro groups [4]. Thus, in our approach to the synthesis of hydroxynitrobenzodifuroxan (5-nitro[1,2,5]oxadiazolo[3,4-*e*][2,1,3]benzoxadiazol-4-ol-3,8-dioxide) (**1**), we centered on the formation of a

diazido-trinitrobenzene intermediate that also contains a hydrolysable group (such as the methoxy group in **3** in Scheme 1) [5]. Having the intermediate **3**, we could produce the furoxan rings by thermolysis, after which the hydrolysable group would be utilized to yield the desired hydroxynitrobenzodifuroxan **1**.

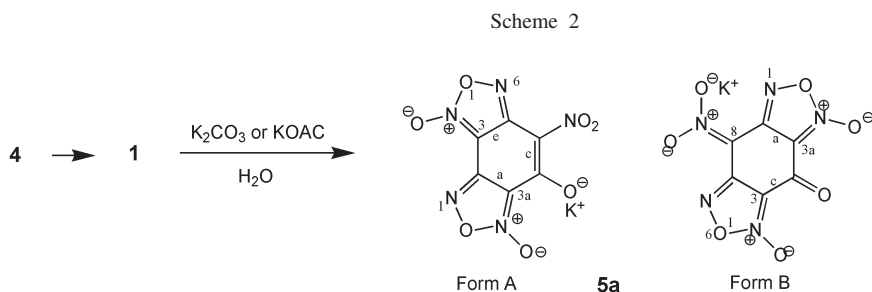
The commercially available starting material for our synthesis of **1** was 3,5-dichloroanisole which was converted to 3,5-dichloro-2,4,6-trinitroanisole (**2**) in high yield (98%) *via* the nitration method of Ott and Benziger [6]. As shown in Scheme 1, the hydrolysable intermediate diazidotrinitroanisole (**3**) was formed from **2** using sodium azide in water/dimethyl carbonate under phase transfer conditions (yield approximately 95%). Intermediate **3** is a

Scheme 1



sensitive explosive and generally was kept in dimethyl carbonate solution, which was combined with toluene before the thermolysis reaction that produces methoxynitrobenzodifuroxan (**4**), the immediate precursor to **1**. The isolated yield of crystalline **4**, calculated on the basis of starting **2**, was generally in the 55-60% range. Compound **4** is readily hydrolyzed under mild conditions [7] to form the desired hydroxynitrobenzodifuroxan **1**.

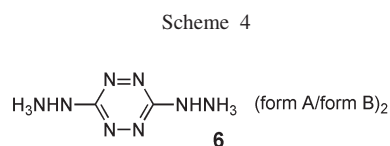
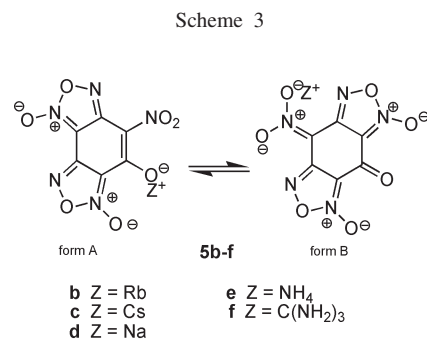
Compound **1** was only minimally characterized. Crude **1** (from hydrolysis of **4** and removal of the acetone/water solvent) has melting point 95 °C (dec) and appears to be a hydrate. The main characterization of **1** was *via* its salts, with the potassium salt (**5a**) being the first salt prepared. The salt **5a** was prepared from the methoxynitrobenzodifuroxan **4** (as outlined in Scheme 2), with the yields of **5a**, based on the amount of starting **4**, on the order of 65%. X-ray crystal structure analysis as well as <sup>13</sup>C nmr demonstrated that **5a** exists in two forms (isomers) (see Scheme 2 and Crystal Structure Analyses section below). Form A is the isomer in which the oxy and nitro group are in positions *ortho* to each other. In form B, these groups are *para* to each other. The transformation between forms A and B is an example of the Boulton-Katritzky rearrangement [4,8,9] and in this case an example of an adjacent nitro group and two furoxan rings. Previously reported examples include nitro group-furoxan [8] and furoxan-furazan combinations [9]. In some cases, equilibrium parameters and coexistence of isomers have been reported.



Other metal salts prepared by neutralization of **1** include the rubidium and the sodium salts (**5b** and **5d**, shown in Scheme 3). The sodium salt **5d** forms a monohydrate (as indicated by its ir spectrum and confirmed by C,H,N elemental analysis). The cesium salt **5c** can be prepared by neutralization, but it is also conveniently prepared by metal ion exchange of the potassium salt **5a** with cesium iodide in water.

Amine bases, such as ammonium hydroxide and guanidine carbonate, were also used to neutralize **1** and form new salts (**5e** and **5f**, respectively). When the amine base 3,6-dihydrazino-1,2,4,5-tetrazine (Scheme 4) [10] was combined with **1** in equimolar amounts, the product iso-

lated was not the mono-salt, but was the di-salt **6** (as shown by C,H,N elemental analysis).



All of the salts of **1** prepared in this study have red-brown color with the exception of the guanidinium salt **5f**, which is light yellow. This is consistent with the fact that crystalline **5f** tends to be only form A, in contrast to all the other salts which either contain some form B or tend to be

only form B. The type of crystal (form A and/or form B) favored in a particular salt was determined by X-ray crystal structure and/or ir spectral analysis (see Sections below). Our overall results suggest that the red-brown color is due to form B and is supported by the fact that when yellow crystals of **5f** are dissolved in dimethyl sulfoxide-d<sub>6</sub> for nmr analysis, the color of the solution obtained is red-brown, the same color as for the other salts. In addition, the <sup>13</sup>C nmr spectrum of **5f** in dimethyl sulfoxide-d<sub>6</sub> exhibits 10 peaks (excluding the guanidinium carbon peak), further indicating the presence of both forms (A and B) in the solution [11]. When the solvent was removed from the red-brown nmr solution (under reduced

pressure), the residue was light yellow **5f**. Crystal structure analysis of **5f** (see below) shows that hydrogen bonding of the guanidinium ion with the nitro and oxy group locks it into form A. In DMSO solution, the guanidinium ion hydrogen bonds with solvent, and the result is an equilibrium mixture of forms A and B.

#### Crystal Structure Analyses.

The crystal structure analyses described in this section identify whether form A or form B, or both, were found in the crystals that were used for X-ray analyses. We have assigned systematic names to the forms of the compound that were identified. However, compound **1** and its salts will often not be isolable as pure form A and/or pure form B from the experimental procedures.

Good crystals, suitable for X-ray structure analyses, were obtained from the potassium salt (thin red plates), the rubidium salt (dark red hexagonal prisms), and the guanidinium salt (light yellow-brown rods). Brief descriptions of the structures are provided here in Figures 1-6 and in Tables 1-3; more complete details have been deposited in the Cambridge structural database [12]. The X-ray analysis of the potassium salt was complicated by a disorder. A single model could not explain the density map, for atomic peaks were present at impossibly close distances. To explain this, each of two individual anions was extracted from the electron density map by modeling the image as a sum of two parts. It then was recognized that two isomeric ring systems, form A and form B of Scheme 3, had co-crystallized and their shapes were seen superimposed (Figures 1 and 2).

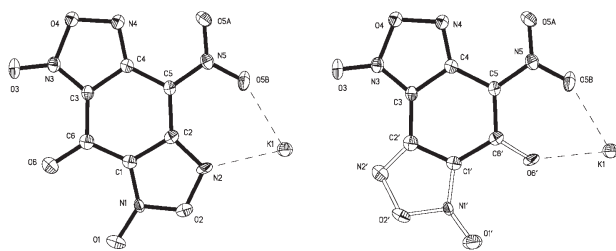


Figure 1 (a) and (b). Views of the two isomers of hydroxynitrobenzodifuroxan indicated by the X-ray analysis of its potassium salt

This dual model agrees very well with the X-ray data and gives fair geometries for the two forms (although bond distance and angle precision is low in cases of disorder) and relative occupancies for forms A and B of 48.6 and 51.4%, respectively, with an esd of 0.6%. It is unusual for two different isomers to pack so equally well that they intermingle in a co-crystal. However, Figure 2 shows the cationic environment of the two anions, and both anions present electronegative N or O atoms near each close cation. Thus, the energetic equivalence of the two different forms seems plau-

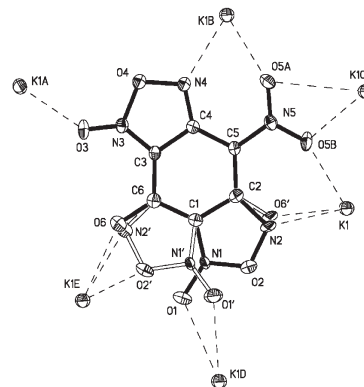


Figure 2. A view of the superposition of the two models shown in Figure 1, illustrating how two isomer images (one with solid black bonds, one with empty bonds) are present in the disordered image that emerges from the X-ray analysis.

sible in this packing scheme (see also Figure 3). In this analysis of the potassium salt, a number of potential errors (including twinning, misassignment of the space group, and misidentification of the lengths of the unit cell axes) were considered and were determined not to be factors.

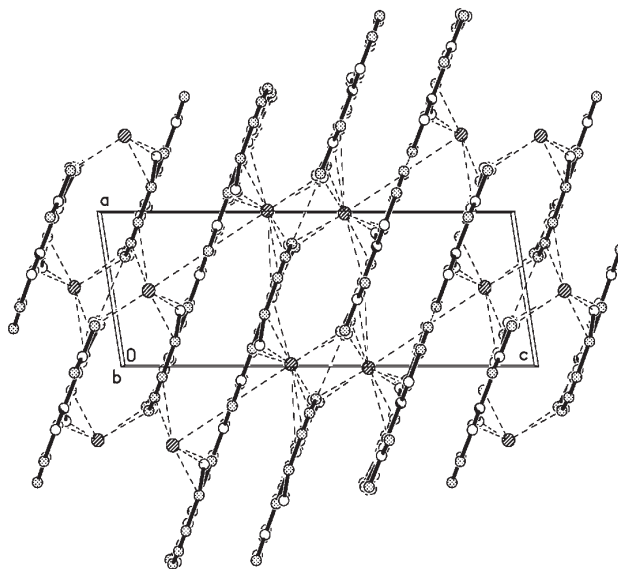


Figure 3. Packing in the crystal of the potassium salt. All anions are planar and parallel; their stacks are linked together by off-planar potassium ions which link simultaneously to several anions in adjacent planar layers.

In the rubidium salt crystal, there is no evidence of disorder in the X-ray analysis result (Figure 4). The packing scheme is a herringbone (inclined) arrangement of planes, and is quite different from that of the potassium salt, in which all planes are essentially parallel (Figure 3). It is quite likely that both forms exist in solution, but only one,

form B, packs into this crystal scheme better, and thus the equilibrium shifts over to this form.

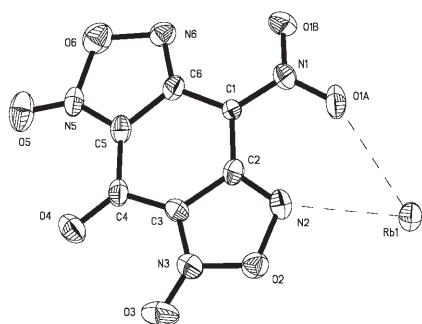


Figure 4. A drawing of the crystal asymmetric unit for the rubidium salt of **1**, showing the labeling scheme and the atomic displacement ellipsoids at the 25% level.

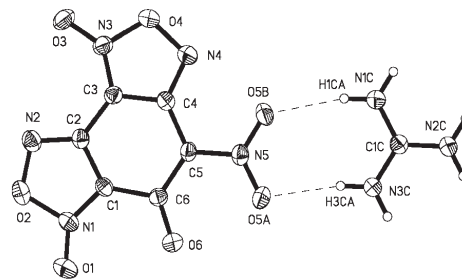


Figure 5. A drawing of the crystal asymmetric unit for the guanidinium salt of **1**, showing the labeling scheme and the atomic displacement ellipsoids at the 25% level.

$\text{cm}^{-1}$ ,  $\text{C}=\text{O}$ , is more pronounced for the rubidium salt than for the potassium salt. However, the reverse is true of the band at  $1237 \text{ cm}^{-1}$ ,  $\text{C}-\text{O}$  (see Figure 7 below). X-ray crystallography has shown the rubidium salt to be

Table 1  
Crystal Data and Structure Refinements for K, Rb, and Guanidinium Salts of **1**

Cation	K <sup>+</sup>	Rb <sup>+</sup>	$\text{CH}_6\text{N}_3^+$
Empirical formula (sum)	$\text{C}_6 \text{K N}_5 \text{O}_7$	$\text{C}_6 \text{N}_5 \text{O}_7 \text{Rb}$	$\text{C}_7 \text{H}_6 \text{N}_8 \text{O}_7$
Formula weight	293.21	339.58	314.20
Wavelength (Å)	0.71073	1.54178	1.54178
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P 2_1/n$	$P 2_1 2_1 2_1$	$P 2_1/n$
Unit cell dimensions			
a (Å)	5.8884(5)	6.232(3)	11.1514(6)
b (Å)	9.7608(8)	9.703(5)	5.2587(3)
c (Å)	16.2956(13)	15.551(7)	19.9837(18)
$\beta$ (degrees)	99.188(2)	90.00	93.369(6)
Volume (Å <sup>3</sup> )	924.58(13)	940.3(8)	1169.86(14)
Z	4	4	4
Density (X-ray, calc) (mg/mm <sup>3</sup> )	2.106	2.399	1.784
Absorption coeff (mm <sup>-1</sup> )	0.625	7.798	1.417
Crystal size (mm)	0.38 x 0.25 x 0.006	0.09 x 0.11 x 0.45	0.55 x 0.14 x 0.12
Theta range for data collection	2.44 to $25.02^\circ$	5.37 to $67.09^\circ$	4.43 to $69.09^\circ$
Reflections collected	5781	4451	4355
Reflections 'observed' [ $I > 2\sigma(I)$ ]	1141	1160	1702
Independent reflections	1623 [R(int) = 0.0343]	1640 [R(int) = 0.1222]	2179 [R(int) = 0.0289]
Data / restraints / parameters	1623 / 25 / 200	1640 / 0 / 173	2179 / 13 / 200
Final std R indices [ $I > 2\sigma(I)$ ]	R1 = 0.0407,	R1 = 0.0703	R1 = 0.0484
Final weighted R indices	wR2 = 0.1080	wR2 = 0.1782	wR2 = 0.1361

Likewise, in the X-ray analysis of the guanidinium salt, only one anion isomer was found, but in this case form A was found (Figure 5). The adjacent nitro and oxy substituents of form A seem to complement the adjacent amines of the guanidinium perfectly; Figure 6 illustrates a cluster of two anions and two cations that are bound together with ten strong H-bonds.

#### Infrared Spectral Data.

There are regions in the infrared spectra that suggest some correlation with forms A and B. The band at  $1700 \text{ cm}^{-1}$

predominately in the B form while the potassium salt is more equally distributed in A and B. Form A is assumed to be more enolate in character while B is more keto in nature. The fairly broad  $\text{C}=\text{NH}_2^+$  for the guanidinium salt, which is nearly pure form A, obscures the region from  $1600 \text{ cm}^{-1}$  to  $1700 \text{ cm}^{-1}$  for this salt. The region around  $1650 \text{ cm}^{-1}$  should be the  $\text{C}=\text{N}$  band arising from the furoxan rings and appears to be more prominent in form A. Strong absorptions are noted in all samples around  $1290 \text{ cm}^{-1}$  and have been assigned to the N-oxide in the furoxan rings. The medium intensity bands in the  $1330\text{-}1370 \text{ cm}^{-1}$  and  $1540\text{-}1580 \text{ cm}^{-1}$

Table 2  
Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for the  $\text{K}^+$  Salt of **1**;  $U(\text{eq})$  is Defined as One Third of the Trace of the Orthogonalized  $U_{ij}$  Tensor

Potassium salt of <b>1</b>	x	y	z	$U(\text{eq})$
K(1)	9898(2)	1742(1)	5928(1)	51(1)
C(3)	1178(5)	3083(3)	3221(2)	31(1)
N(3)	-907(5)	2832(3)	2816(2)	35(1)
O(3)	-2545(4)	3518(3)	2512(2)	49(1)
C(4)	2279(5)	1803(3)	3445(2)	30(1)
N(4)	921(4)	779(3)	3184(2)	37(1)
O(4)	-1130(4)	1374(2)	2778(2)	43(1)
C(5)	4584(5)	1763(3)	3912(2)	31(1)
N(5)	5644(5)	522(3)	4104(2)	36(1)
O(5A)	4622(4)	-550(2)	3862(2)	50(1)
O(5B)	7630(4)	499(3)	4512(2)	51(1)
C(1)	4493(5)	4292(3)	3870(2)	32(1)
N(1)	5868(19)	5319(8)	4129(11)	31(2)
O(1)	5694(12)	6610(5)	4082(4)	51(2)
C(2)	5740(6)	3028(3)	4134(2)	33(1)
N(2)	7900(50)	3380(19)	4500(20)	36(2)
O(2)	7909(8)	4771(5)	4544(3)	44(2)
C(6)	2192(5)	4391(3)	3434(2)	36(1)
O(6)	1165(15)	5549(7)	3194(9)	42(2)
C(1')	4493(5)	4292(3)	3870(2)	32(1)
N(1')	5250(15)	5554(6)	4009(12)	31(2)
O(1')	7011(10)	6085(6)	4340(4)	57(2)
C(2')	2192(5)	4391(3)	3434(2)	36(1)
N(2')	1389(14)	5634(7)	3411(14)	42(2)
O(2')	3386(8)	6416(4)	3637(3)	48(2)
C(6')	5740(6)	3028(3)	4134(2)	33(1)
O(6')	7630(40)	3091(15)	4569(19)	36(2)

\*N.B.: The first 11 atoms listed occur for both isomers at the same location in the crystal; the next 8 atoms occur only in form B, and the last 8 primed atoms occur only in form A. Forms A and B are present in 48.6% and 51.4% (esd 0.6%) of the sites, respectively, according to a refinement based on the X-ray data.

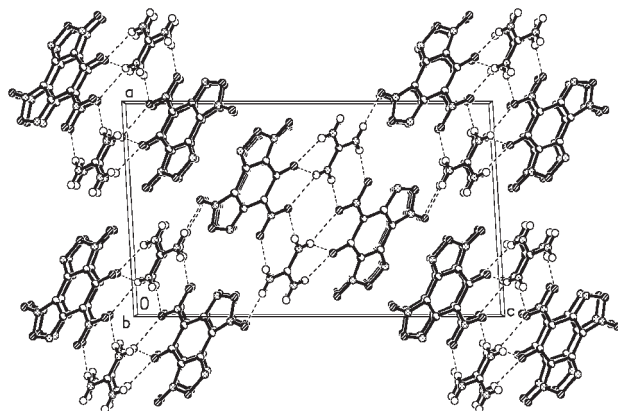


Figure 6. A drawing of the packing in the guanidinium salt viewed down the  $b$  axis of the unit cell. Ten cooperative hydrogen bonds link two ion pairs together into the dimeric unit seen at the center of the cell. A few peripheral H-bonds link these stacks of dimers together in the crystal.

Table 3  
Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for Two Other Salts of **1**;  $U(\text{eq})$  is Defined as One Third of the Trace of the Orthogonalized  $U_{ij}$  Tensor

Rubidium salt of <b>1</b>	x	y	z	$U(\text{eq})$
Rb(1)	2036(2)	-2461(1)	4133(1)	65(1)
C(1)	6445(18)	3918(10)	3858(7)	41(3)
N(1)	7265(17)	5137(10)	4154(7)	55(2)
O(1A)	6201(18)	6235(7)	4054(7)	78(3)
O(1B)	8988(16)	5148(10)	4549(6)	72(2)
C(2)	4430(20)	3888(11)	3419(8)	47(3)
N(2)	3190(20)	4905(9)	3193(6)	61(3)
O(2)	1354(14)	4262(9)	2773(5)	65(2)
C(3)	3463(15)	2563(14)	3186(6)	50(2)
N(3)	1619(16)	2801(10)	2785(6)	60(3)
O(3)	240(15)	2082(12)	2467(6)	92(3)
C(4)	4280(20)	1239(11)	3392(9)	57(3)
O(4)	3321(19)	126(10)	3254(6)	77(3)
C(5)	6320(20)	1364(11)	3817(8)	55(3)
N(5)	7429(18)	307(9)	4082(7)	58(3)
O(5)	7340(20)	-912(9)	4069(7)	93(4)
C(6)	7422(15)	2618(11)	4048(6)	52(2)
N(6)	9216(14)	2427(13)	4443(5)	61(2)
O(6)	9387(18)	920(11)	4471(7)	85(3)
Guanidinium salt of <b>1</b>				
C(1)	7217(2)	8823(5)	3808(1)	45(1)
N(1)	8265(2)	9664(5)	4055(1)	53(1)
O(1)	8992(2)	9086(5)	4490(1)	75(1)
C(2)	6870(2)	10405(5)	3267(1)	47(1)
N(2)	7637(2)	12231(5)	3157(1)	60(1)
O(2)	8550(2)	11895(4)	3641(1)	65(1)
C(3)	5744(2)	9780(5)	2924(1)	46(1)
N(3)	5195(2)	10843(4)	2397(1)	56(1)
O(3)	5421(2)	12637(4)	2024(1)	74(1)
C(4)	5036(2)	7719(5)	3128(1)	46(1)
N(4)	4046(2)	7535(5)	2733(1)	61(1)
O(4)	4111(2)	9485(4)	2262(1)	66(1)
C(5)	5434(2)	6141(4)	3691(1)	46(1)
N(5)	4717(2)	4086(4)	3856(1)	52(1)
O(5A)	5043(2)	2624(4)	4320(1)	67(1)
O(5B)	3759(2)	3748(4)	3522(1)	69(1)
C(6)	6552(2)	6624(5)	4058(1)	47(1)
O(6)	6997(2)	5434(4)	4544(1)	65(1)
C(1C)	2143(2)	-1674(5)	4213(1)	49(1)
N(1C)	1795(2)	-64(5)	3738(1)	65(1)
N(2C)	1458(2)	-3633(4)	4354(1)	60(1)
N(3C)	3180(2)	-1332(4)	4552(1)	55(1)

N.B.: Atoms labeled with a final C belong to the guanidinium cation. Only one anionic form was observed in each of these salts (see text).



regions should be the symmetric and asymmetric stretches for the lone nitro group.

the same tga response. These analyses indicate that it is currently not possible to determine the relative stabilities of

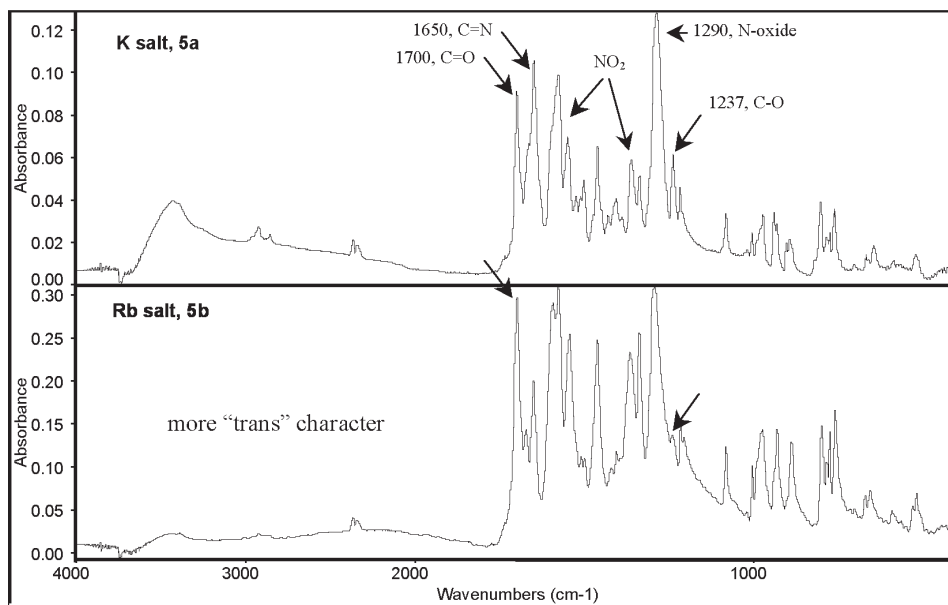


Figure 7.

#### Thermal Analyses.

As described above, salt **5a** tends to exist as a mixture of form A and form B while **5b** tends toward form B and **5f** toward form A. Experiments employing thermogravimetric analysis (tga) were conducted to determine if there are differences in the thermal stabilities of these salts that can be attributed to their crystal forms. Initial thermal analysis of a 10.49 mg sample of **5a** at 100 °C indicated the material was thermally stable at that temperature, with only 0.6% weight loss after 9000 minutes. We attributed this weight loss to hydration. However, at 120 °C, an 8.87 mg sample of **5a** lost 2.73% by weight after 1073 minutes and 34.70% after 5400 minutes. Differential scanning calorimetry (dsc) of the residual material indicated that **5a** had degraded and the material exhibited no thermal response corresponding to the original material. The rubidium salt (**5b**, 9.91 mg) demonstrated a similar response at 120 °C, with loss of 25.74% by weight after 1073 minutes and loss of 30.48% after 5400 minutes. The increased rate of decomposition of the rubidium salt (**5b**) over that of the potassium salt may indicate that the B form (the major form of **5b**) is less stable towards thermal degradation than the corresponding A form. However, thermal analysis of the guanidinium salt (**5f**, 7.48 mg) showed a loss of 22.37% by weight after 1073 minutes and 34.41% after 5400 minutes. A sample of **5f** which was aged for 33 days at 25 °C to allow for complete conversion to the A form (determined by ir) demonstrated

the A and B forms of salts of **1**, possibly due to facile inter-conversion at elevated temperatures. Thermal analysis of these materials at reduced temperature ( $\leq 100^\circ\text{C}$ ) may be informative.

#### EXPERIMENTAL

##### General.

**Caution !!** The compounds described herein are sensitive explosives and should be handled appropriately. The K, Rb and Cs salts (**5a-c**) are especially sensitive and will explode when heated too strongly. Amounts of 0.2 mg (or less) of these materials were used for the differential scanning calorimetry (dsc) experiments.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Combustion analyses (C,H,N) could not be obtained for metal salts **5a-c** because they undergo explosive decomposition when heated to elevated temperatures (approximately 180° and above). Thus, only elemental analyses for metal content, which could be performed without heating, were obtained for **5a-c**. Nmr spectra were recorded using either Varian 300 MHz Mercury Plus system or a Varian Inova system equipped with a 5 mm triple resonance triaxial PFG probe at 500 MHz for  $^1\text{H}$  and 125 MHz for  $^{13}\text{C}$ . Due to the long relaxation times of the carbons involved, nominal  $^{13}\text{C}$  spectra were acquired using a 45° pulse and a 20 sec. pulse delay. The  $^1\text{H}$  nmr and  $^{13}\text{C}$  nmr spectra were referenced to residual solvent signals. The ir spectra were recorded *via* attenuated total reflectance (atr) on a ThermoNicolet Avatar 370 FT-IR Spectrometer.

In general, salts of 1 that have relatively low solubility in water (5a-c, 5f) can be prepared essentially pure by just neutralizing crude 1 obtained from hydrolysis of 4 (using a procedure similar to the preparation of 5a). However, the sodium and ammonium salts (5d, 5e) are very water-soluble and for these salts it is best to use purified 1 for the neutralization. Purified 1, needed for the purposes of this report, was obtained by passing 5a through a column containing H ion exchange resin. A typical preparation of purified 1: Compound 5a (0.73 g, 2.49 mmol) was dissolved in 70 mL of distilled water by heating to 65-70°. The solution was cooled to 35-40° before it was passed through a column of water-washed Dowex 50x2-100 ion-exchange resin (Dowex-50W-hydrogen) (6 g of resin in a column approximately 1.2 cm diameter and 18 cm high). The column was washed with water; then the water was removed under reduced pressure to give 0.74 g of 1 as a reddish brown solid. To ensure that no potassium ion remained, the solid was dissolved in 5 mL of distilled water at room temperature and passed through another 4 g of the H ion-exchange resin. The final volume of water including washings was adjusted to 40 mL [assumed to contain about 0.62 mmol (0.16 g) of purified 1 per 10 mL for use in several of the procedures described below].

5-Methoxy-4-nitro[1,2,5]oxadiazolo[3,4-*e*][2,1,3]benzoxadiazole-3,8-dioxide (4) *via* 3,5-Diazido-2,4,6-trinitroanisole (3).

To a solution of 7.5 g (24 mmol) of 3,5-dichloro-2,4,6-trinitroanisole [6] in 75 mL of dimethyl carbonate was added a solution of tetrabutylammonium bromide (0.22 g, 0.68 mmol) in 22 mL of water. A solution containing 4.5 g (69 mmol) of sodium azide in 90 mL of water was then added and the mixture was stirred vigorously in a closed flask at room temperature (*ca.* 23°) for 20 hours. At that point, tlc of the lower yellow layer indicated essentially pure 3 with no starting material remaining [tlc conditions: silica gel (254) plates; toluene/heptane (50/50 v/v) as developer;  $R_F$  for 3 = 0.46] [ $^1\text{H}$  nmr of 3 (300MHz, acetone- $d_6$ ): 4.11 (s)]. The lower yellow layer was separated and combined with dimethyl carbonate washings (3 x 10 mL) of the upper layer. Solvent was cautiously removed under reduced pressure (without heating above 25°) until the volume remaining was 50 mL. Toluene (200 mL) was added and the solution was dried with sodium sulfate/magnesium sulfate overnight. The mixture was filtered and the filter pad was washed well with toluene (5 x 10 mL) until the washings contained little or no yellow color. The filtrate was heated (Drierite drying tube attached) at slow reflux (102-103°) for 4 hours (tlc of a sample after 3 hours indicated only a very small amount of 3 remains) [tlc conditions: silica gel (254) plates; toluene as developer;  $R_F$  for 4 = 0.64 with trailing back to origin (hydrolysis)]. The reddish solution was allowed to cool and stand at room temperature overnight before it was decanted from a small amount of insoluble solid (0.08 g). The solvent was removed under reduced pressure to give 6.73 g of brownish semisolid that was stirred with 45 mL of chloroform for 30 minutes. The mixture was cooled to -15° for 1 hour before it was filtered and the insoluble crystals were washed with a small amount of cold chloroform. The yield was 3.48 g (54%) of 4, mp 150-152° dec;  $^1\text{H}$  nmr (300MHz, acetone- $d_6$ ):  $\delta$  4.28 (s), 4.59 (s), 4.63 (s) [integration for peaks varies over time; addition of water eventually produces peaks only at 3.47 (broad) and at 3.30 (methanol)];  $^1\text{H}$  nmr (300MHz, dimethyl sulfoxide- $d_6$ ):  $\delta$  3.99 (s), 4.19 (s), 4.49 (s), 4.54 (s) [integration for peaks varies over time and after 22 hours only the peak at 3.99 remains (also large

broad peak at 4.89)]; ir (atr): 1684, 1607, 1581, 1525, 1504, 1350, 1297, 1087, 996, 828, 791, 769  $\text{cm}^{-1}$ . The analytical sample was prepared by an additional treatment with chloroform.

*Anal.* Calcd. for  $\text{C}_7\text{H}_3\text{N}_5\text{O}_7$ : C, 31.24; H, 1.12; N, 26.02. Found: C, 31.03; H, 1.13; N, 25.85.

Additional 4 can be recovered from the filtrate above by further work-up, but it is more efficient to convert the 4 in the filtrate to 5a [by removing the volatiles from the filtrate, heating the residue in acetone/water (as in the preparation of 5a below), again removing volatiles, extracting the 1 in the residue into water, then neutralizing with potassium carbonate].

5-Nitro[1,2,5]oxadiazolo[3,4-*e*][2,1,3]benzoxadiazol-4-ol-3,8-dioxide (1) and Potassium 5-Nitro[1,2,5]oxadiazolo[3,4-*e*][2,1,3]benzoxadiazol-4-olate-3,8-dioxide, Mixture of Forms A and B (5a).

To a stirred solution of 4 (1.62 g, 6.0 mmol) in 50 mL of acetone was added 10 mL of water. The mixture was heated at 53-55° for 1.75 hours before the volatiles were removed under reduced pressure to give 1.8 g of 1 as a red-brown solid, mp 95° (dec). The product 1 was stirred with 15 mL of water and the insoluble solid (very small amount) was removed by filtration. The flask was washed with 3 x 3 mL of water. To the stirred filtrate (volume about 24 mL) was added 0.6 g (4.3 mmol) of potassium carbonate in small portions to give a precipitate of red-brown crystals. The mixture was cooled at 5° for 1 hour before the crystals were removed by filtration and washed with 3 x 3 mL of ice-cold water. The damp crystals were stirred with 15 mL of acetone, then were removed by filtration and air-dried to give 1.11 g (63%) of 5a, dsc (20°/minute): onset-203°, peak-209°;  $^{13}\text{C}$  nmr (recrystallized sample, 125 MHz, dimethyl sulfoxide- $d_6$ ):  $\delta$  161.87 (form B, C-4), 159.63 (form A, C-4), 151.20 (form A, C-8b), 150.26 (form B, C-7a, 8a) 140.40 (form A, C-5), 115.21 (form B, C-8), 110.11 (form B, C-3a, 4a), 106.03 (form A, C-3a), 101.86 (form A, C-8a) and 97.35 (form A, C-4) ppm; ir (atr): 1699, 1649, 1574, 1550, 1461, 1360, 1282, 1238, 1217, 971, 939, 801, 773  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_6\text{N}_5\text{O}_7\text{K}$ : K, 13.34. Found: K, 13.02.

Rubidium 8-Aci-nitro[1,2,5]oxadiazolo[3,4-*d*][2,1,3]benzoxadiazol-4-one-3,5-dioxide, Mostly Form B (5b).

A dilute solution of rubidium hydroxide was prepared by adding water (20 mL) to 0.88 g of 50% rubidium hydroxide/water. Part (2.9 mL) of this solution (contains 0.064 g, 0.62 mmol of rubidium hydroxide) was added slowly dropwise to 10 mL of the aqueous solution of purified 1 [13] stirred in an ice bath. After an additional 30 minutes in the ice bath, the dark red-brown crystals were removed and washed with cold water to give 0.12 g (57%) of 5b; dsc (20°/minute): onset-189°, peak-192°; ir (atr): 1697, 1591, 1576, 1544, 1460, 1356, 1337, 1290, 1216, 978, 929, 887, 797, 773, 757  $\text{cm}^{-1}$  (another sample of 5b showed 1299 instead of 1290  $\text{cm}^{-1}$  and an even smaller peak at 1650  $\text{cm}^{-1}$ , presumably indicating that this sample was essentially only form B).

*Anal.* Calcd. for  $\text{C}_6\text{N}_5\text{O}_7\text{Rb}$ : Rb, 25.17. Found: Rb, 24.76.

Cesium 5-Nitro[1,2,5]oxadiazolo[3,4-*e*][2,1,3]benzoxadiazol-4-olate-3,8-dioxide, Form A and/or B Not Established (5c).

Potassium salt 5a (90 mg, 0.31 mmol) was dissolved in 20 mL of water by heating at 65-70°. A solution containing 310 mg (1.2 mmol) of cesium iodide in 4 mL of water was added and the

resulting solution was allowed to cool to 25°. After 30 minutes, the dark crystals were removed and washed with 4 x 1 mL of cold water to give 75 mg (63%) of 5c; dsc (20°/minute): onset-194°, peak-195°; ir (atr): 1698, 1595, 1575, 1542, 1462, 1364, 1336, 1297, 1214, 1083, 971, 929, 884, 794, 773, 757 cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>6</sub>N<sub>5</sub>O<sub>7</sub>Cs: Cs, 34.34. Found: Cs, 33.83.

Sodium 5-Nitro[1,2,5]oxadiazolo[3,4-*e*][2,1,3]benzoxadiazol-4-olate-3,8-dioxide, Form A and/or B Not Established (5d).

A dilute solution of sodium hydroxide was prepared by adding water (40 mL) to 0.48 g of sodium hydroxide pellets. Part (2.1 mL) of this solution (contains 0.025 g, 0.62 mmol of sodium hydroxide) was added slowly dropwise to 10 mL of the aqueous solution of purified 1 [13] stirred in an ice bath. The water was removed under reduced pressure to give a red solid (0.18 g) that was dissolved in 10 mL of acetone at 25°. The solution was filtered to remove a small amount of insoluble solid and the filtrate was concentrated under reduced pressure to a volume of 1-2 mL before dichloromethane (7 mL) was slowly added to give 0.10 g (56%) of 5d as the monohydrate; dsc (20°/minute): onset-149°, peak-160°; ir (atr): 3516, 1698, 1652 (this peak is somewhat larger than usual for crystals that also exhibit the 1299 peak), 1602, 1578, 1548, 1468, 1384, 1338, 1299, 976, 931, 804, 763, 773 cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>6</sub>N<sub>5</sub>O<sub>7</sub>Na(H<sub>2</sub>O): C, 24.42; H, 0.68; N, 23.73. Found: C, 24.13; H, 0.96; N, 23.19.

In another experiment performed in the same manner as above, the crude 5d (obtained by removal of water from the reaction solution) was dissolved in methanol and then filtered to remove a small amount of insoluble material. Removal of the methanol gave 5d with a significantly different ir spectrum than the spectrum given above (*e.g.*, there are major peaks at 1645 and 1296 cm<sup>-1</sup>). However, the ir of this same sample, taken months later, was identical to the one above.

Ammonium 5-Nitro[1,2,5]oxadiazolo[3,4-*e*][2,1,3]benzoxadiazol-4-olate-3,8-dioxide, Form A and/or B Not Established (5e).

A dilute solution of ammonium hydroxide was prepared by adding water (5 mL) to 0.75 g of 29% ammonium hydroxide. Part (approximately 0.5 mL) of this solution was added slowly dropwise to 10 mL of the aqueous solution of purified 1 [13] until the pH reached 7-8 (by pH paper). The water was removed under reduced pressure to give a residue (0.14 g) that was a mixture of darker and lighter colored crystals. The residue was stirred with 2 mL of methanol at 25° and the mixture was filtered to give 0.04 g (24%) of insoluble red-brown crystals of 5e; dsc (20°/minute): onset-185°, peak-192°; <sup>1</sup>H nmr (300MHz, dimethyl sulfoxide-*d*<sub>6</sub>): δ 7.1 (broad s); ir (atr): 3188, 1693, 1595, 1548, 1474, 1423, 1372, 1332, 1299, 1201, 1083, 1003, 976, 931, 892, 801, 781, 772, 760 cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>6</sub>H<sub>4</sub>N<sub>6</sub>O<sub>7</sub>: C, 26.48; H, 1.48; N, 30.88. Found: C, 26.58; H, 1.67; N, 30.23.

When the methanol solvent was removed from the filtrate above, the crystals obtained are a mixture of both forms as indicated by the ir spectrum which shows a reasonably strong peak at 1649 cm<sup>-1</sup> and peaks at 1299 and 1281 cm<sup>-1</sup> of about equal intensities.

Guanidinium 5-Nitro[1,2,5]oxadiazolo[3,4-*e*][2,1,3]benzoxadiazol-4-olate-3,8-dioxide, Mostly Form A (5f).

A dilute solution of guanidine carbonate was prepared by adding water (5 mL) to 0.28 g of guanidine carbonate. Part (1 mL) of this solution (contains 0.056 g, 0.62 equivalents of guanidine carbon-

ate) was added slowly dropwise to 10 mL of the aqueous solution of purified 1 [13]. A very light reddish precipitate formed and the pH was 7-8 (by pH paper). The mixture was cooled to 5° for 1 hour before the crystals were removed by filtration and washed with 3 x 2 mL of cold water. The light reddish crystals were air-dried overnight to give 0.12 g of light yellow crystals of 5f. A second crop of 5f (0.02 g obtained by removal of water from the filtrate and re-adding a small amount of water) brought the total yield to 0.14 g (74%); dsc (20°/minute): onset-187°, peak-190°; <sup>1</sup>H nmr (300 MHz, dimethyl sulfoxide-*d*<sub>6</sub>): δ 6.88 (s); <sup>13</sup>C nmr (75 MHz, dimethyl sulfoxide-*d*<sub>6</sub>): δ 160.9, 158.5, 156.6 (guanidinium C), 150.3, 149.4, 139.6, 114.4, 109.5, 105.4, 101.4, 96.8 (the nmr solution is red-brown in color; removing the dimethylsulfoxide-*d*<sub>6</sub> under reduced pressure gave 5f as a yellow solid); ir (atr): 3490, 3374, 1646 (strong), 1571, 1558, 1418, 1289, 1247, 1083, 973, 939, 802, 787, 777, 761 cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>7</sub>H<sub>6</sub>N<sub>8</sub>O<sub>7</sub>: C, 26.76; H, 1.92; N, 35.67. Found: C, 26.91; H, 1.85; N, 35.52.

3,6-Dihydrazino-1,2,4,5-tetrazine, bis(5-nitro[1,2,5]oxadiazolo[3,4-*e*][2,1,3]benzoxadiazol-4-ol-3,8-dioxide) Salt (6).

Purified 1 was prepared from 0.25 g (0.85 mmol) of 5a in similar fashion to the procedure given in the general experimental section above. To the solution of purified 1 in water (50 mL) was added 0.12 g (0.85 mmol) of 3,6-dihydrazino-1,2,4,5-tetrazine [10]. The mixture was stirred for 30 minutes until all material was dissolved. The water was removed under reduced pressure to give 0.32 g of red-brown solid that was stirred with 25 mL of isopropanol at 25° for 1 hour. The insoluble material (0.28 g) was removed by filtration and stirred with 30 mL of isopropanol at 25° for 1 hour to give 0.24 g (86%) of 6 as a red-brown solid; dsc (20°/minute): onset-148°, peak-169°; <sup>1</sup>H nmr (300MHz, dimethyl sulfoxide-*d*<sub>6</sub>): δ 10.54 (s); ir (atr): 3150 and 2900 region (broad peaks), 1702, 1592, 1547, 1477, 1385, 1361, 1339, 1303, 1205, 1083, 1000, 929, 893, 800, 772, 761 cm<sup>-1</sup> [14].

*Anal.* Calcd. for C<sub>14</sub>H<sub>8</sub>N<sub>18</sub>O<sub>14</sub>: C, 25.78; H, 1.24; N, 38.65. Found: C, 25.85; H, 1.65; N, 37.15.

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#### REFERENCES AND NOTES

\* Authors to whom correspondence should be addressed. Regarding synthesis/ properties: MES/JWF; Regarding crystal structures: RDG.

[1] R. J. Spear and W. P. Norris, *Propellants, Explosives, Pyrotechnics*, **8**, 85 (1983).

[2] W. P. Norris, A. Chafin, R. J. Spear and R. W. Read, *Heterocycles*, **22**, 8 (1984).

[3] By J. W. Fronabarger. In U. S. Patent application: John W. Fronabarger and Michael E. Sitzmann, "Nitrobenzodifuroxan Compounds, Including Their Salts, and Methods Thereof", 13 Aug 2003.

[4] P. N. Preston and G. Tennant, *Chem. Rev.*, **72**, 650 (1972).

[5] Our initial attempt to prepare such a hydrolyzable intermediate (namely, 3,5-diazido-2,4,6-trinitrochlorobenzene), by treating 1,3,5-trichloro-2,4,6-trinitrobenzene with two equivalents of sodium azide was



unsuccessful, the idea being to replace two of the chloro groups with azide and use the remaining chloro group as the hydrolysable moiety. The reaction furnished instead primarily a mixture of starting material and 1,3,5-triazido-2,4,6-trinitrobenzene. Thus, it would appear that azide replacement of chloride in trichlorotrinitrobenzene activates the remaining chloro groups toward further displacement by azide, thereby favoring formation of the triazido compound.

[6] D. G. Ott and T. M. Benziger, U. S. Patent 4,952,733 (1990); *Chem. Abstr.*, **114**, 142852a (1991).

[7] Even small amounts of water present in the acetone- $d_6$  and DMSO- $d_6$  nmr solvents were sufficient to cause some hydrolysis of **4** and generate a peak for methanol (see Experimental Section).

[8] A. J. Boulton and A. R. Katritzky, *Proc. Chem. Soc., London*, 257 (1962).

[9] A. J. Boulton, A. C. Gripper-Grey, and A. R. Katritzky, *J. Chem. Soc.*, 5958 (1965).

[10] Dihyrazinotetrazine is available *via* a simplified method recently reported. See D. E. Chavez and M. A. Hiskey, *J. Heterocyclic Chem.*, **35**, 1329 (1998).

[11] Form B and form A would be expected to produce 4 and 6 peaks, respectively.

[12] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-256738 for the potassium salt of **1**, CCDC-256737 for the rubidium salt, and CCDC-256736 for the guanidinium salt. Copies of the data can be obtained freely on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (UK); Tel.: (+44) 1223-336-408, Fax: (+44) 1223-336-033, and E-mail: deposit@ccdc.cam.ac.uk

[13] For the preparation of the solution containing purified **1**, see general experimental section.

[14] 3,6-Hydrazino-1,2,4,5-tetrazine; ir (atr): 3294, 3218, 3026, 1637, 1537, 1453, 1052, 1005, 940  $\text{cm}^{-1}$ .