

# **A New Method for the Synthesis of Dinitrogen Tetroxide Impregnated On Charcoal (N<sub>2</sub>O<sub>4</sub>/Charcoal) and It's Application as Selective Oxidant of Thiols to Disulfides Organic Compounds**

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**(NJC)**

**(Received on 7/3 /2011 )**

**(Accepted for publication 27/9 /2011)**

## **Abstract**

A new laboratory method was investigated to prepare a liquid dinitrogen tetroxide (purity, 99%) from nitric acid and Al-Zahdi date. N<sub>2</sub>O<sub>4</sub> was easily impregnated on charcoal to give a stable homogeneous reagent N<sub>2</sub>O<sub>4</sub> / charcoal. A fast and efficient method for the chemoselective oxidative coupling of heterocyclic thiols to afford their corresponding heterocyclic disulfides using liquid dinitrogen tetroxide (N<sub>2</sub>O<sub>4</sub>) as the reagent in CH<sub>2</sub>Cl<sub>2</sub> at room temperature is described. The stability, easy preparation, high selectivity of the reagent and high percent of products make this method as a useful procedure. The purity of liquid N<sub>2</sub>O<sub>4</sub> was determined by titration method. The chemical structure and purity of the disulfide products were proved by using melting point measurement, elemental analysis, and FTIR spectroscopy.

(99%)

(N<sub>2</sub>O<sub>4</sub>)

N<sub>2</sub>O<sub>4</sub>

(N<sub>2</sub>O<sub>4</sub>/Charcoal)



## Introduction

Dinitrogen tetroxide ( $\text{N}_2\text{O}_4$ ) is the chemical compound that forms an equilibrium mixture with nitrogen dioxide ( $\text{N}_2\text{O}_4 \leftrightarrow 2\text{NO}_2$ ). It is a powerful oxidizer and hypergolic with various forms of hydrazine compounds<sup>(1)</sup>.  $\text{NO}_2$  gas is made by the catalytic oxidation of ammonia as industrial Haber process<sup>(2)</sup>. On laboratory scale, a pure and dried lead nitrate at  $500^\circ\text{C}$  in steel vessel<sup>(3)</sup>, heating reaction of 100%  $\text{HNO}_3$  and 98%  $\text{H}_2\text{SO}_4$  in the presence of Arsenic oxide<sup>(4)</sup>, and reaction of  $\text{NaNO}_2$  with 98%  $\text{H}_2\text{SO}_4$  in the presence of oxygen<sup>(5)</sup>, provides one of the source of  $\text{N}_2\text{O}_4$  gas.

$\text{N}_2\text{O}_4$  and its complexes have found wide application in organic transformation, they have been used as nitrating agent<sup>(6-9)</sup>, oxidizing agent<sup>(10,11)</sup>. In order to reduce of high reactivity, corrosive nature, and handling problems,  $\text{N}_2\text{O}_4$  was used as complexes with organic polymeric compounds<sup>(12,13)</sup>, Dioxane- $\text{NO}_2$  (prepared from  $\text{N}_2\text{O}_4$  and dioxane)<sup>(14)</sup>, complexation of  $\text{N}_2\text{O}_4$  with 18-crown-6<sup>(15)</sup> and  $\text{N}_2\text{O}_4$  has been supported on polyvinyl pyrrolidone ( $\text{PVP-N}_2\text{O}_4$ )<sup>(16)</sup>

$\text{N}_2\text{O}_4$  reacts also with some metals to form a good, stable, and highly efficient reagents [ $\text{Fe}(\text{NO}_3)_3 \cdot 1.5\text{N}_2\text{O}_4$  and  $\text{Cu}(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$ ] which were used also to transformate the sulfides to sulfoxides<sup>(17)</sup>. Recently,  $\text{N}_2\text{O}_4$  was impregnated on silica gel or activated charcoal to give stable heterogeneous reagents, which were employed in chemoselective deprotection of trimethylsilyl ether to corresponding alcohols<sup>(18)</sup>, oxidation of thiol<sup>(19)</sup> sulfides and disulfides<sup>(20)</sup>, N-nitrosation of amines amides and urea's<sup>(21)</sup>. Disulfides are important organosulfur compounds possessing unique and diverse chemistry in the synthetic and biochemical area<sup>(22)</sup>. Numerous methods have been reported for the selective oxidative coupling of thiols<sup>(23)</sup>, but most of them suffer from one or more disadvantages such as commercial unavailability, toxicity or high cost of the required reagent, long reaction times. In this work we presented a new laboratory method for preparation of liquid  $\text{N}_2\text{O}_4$  and  $\text{N}_2\text{O}_4$ /charcoal system from nitric acid and AL-Zahdi date in simple and efficient procedure. We were also employed the

prepared  $N_2O_4$  /charcoal reagent for oxidation of some heterocyclic thiols to new corresponding heterocyclic disulfides. High yield and rates have been obtained.

## Experimental

Al-Zahdi date was obtained from locally market. Thiols and other chemicals were purchased from Fluka and Aldrich. The reactions were monitored by T.L.C (silica-gel 60 F<sub>254</sub>, n-hexane, ethyl acetate). The products were purified by flash chromatography on  $SiO_2$  (Eluent:  $CH_2Cl_2$ ) and identified by infrared spectra (KBr) which were recorded on a Shimadzu 8261 Pc Spectrometer. Elemental analysis (C, H, N) was performed on a Perkin 240C Elemental Analyzer. Melting point were obtained on a Gallen Kamp point apparatus are uncorrected. Evaporation was carried out with Bunchier RE 120 rotary evaporator under reduced pressure. The oxidizing agent employed in the oxidizing tower was prepared by dissolved 5 g of  $CrO_3$  in 5ml water then 95 g of quartz sand (20-30 mesh) was added. The mixture was stirred thoroughly for 5 minutes and then dried at  $120^\circ C$  to give the quartz sand carrying chromium trioxide.

## Preparation of liquid $N_2O_4$ :

A three-neck round-bottom flask (1 L) was fitted with, condenser for cooling, oxygen inlet and the third for date feeding. It was constructed with drying tower, oxidizing tower and condenser (Figure 1). 0.5 L of nitric acid (65-98%) was added in the reaction flask, and then 150 g of sliced date (AL-Zahdi) was added gradually along the time of reaction. After 5 minutes a brown gases was evolved, and blown by a stream of oxygen through condenser into a drying tower (packed with nearly 80 g of the mixture of phosphorus pentoxide and quartz sand,  $P_2O_5:SiO_2$ , 1 : 1 in wt), then through an oxidizing tower (packed with Ca.100 g of oxidizing agent). Dimerzation of  $NO_2$  to  $N_2O_4$  and liquidified was completely in the (cooled,  $-15^\circ C$ ) condenser, then dropped into the receiver as yellow to brown liquid of  $N_2O_4$  (yield was 70% wt/wt of  $HNO_3$ ).

## Preparation of Charcoal-Supported $N_2O_4$ :

In 250 ml round bottom flask, 20 g of activated charcoal and 50 ml of dry dichloromethane were mixed and cooled to the temperature at  $-10^\circ C$ . A 20 ml of liquid  $N_2O_4$  was added slowly with continuous gently stirring. After 4h of standing in the refrigerator, the mixture was flashed with  $N_2$  gas until removed the excess of  $N_2O_4$ . The solvent was evaporated under reduced

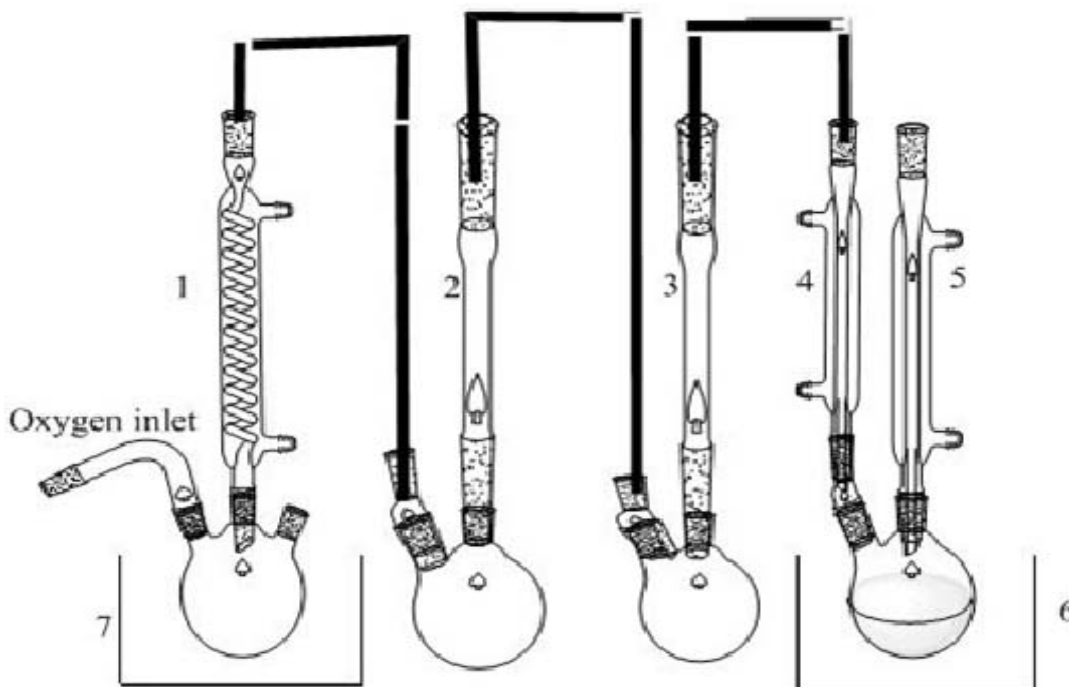
pressure with rotary evaporator to give 34 g of  $N_2O_4$  / Charcoal reagent. Each 1g of  $N_2O_4$ /Charcoal contains 0.4117g of  $N_2O_4$ .

General procedure for the preparation of disulfide:

To a solution of thiol compound (5 mmol) in  $CH_2Cl_2$  (25 ml), a 0.575 g of ( $N_2O_4$  /Charcoal) reagent was added gradually with continuous gently agitation for appropriate time at room temperature. The reaction was monitored by TLC, using n-hexane: ethyl acetate (40: 60) as eluent. After completion of the reaction, the mixture was filtered and the filtrate was

washed with cooled water. The organic layer was dried on  $Na_2SO_4$  then Passed through silica gel column using a mixture of ethyl acetate and methylene chloride as eluent to afford the pure disulfide compound after evaporation of the solvent on rotary evaporator under reduced pressure. The melting point, reaction time, yield percent and characteristic infrared spectrum bands values are shown in Table1.

Exemplary FTIR spectrum of 2, 2'-dithio bis- benzothiazole is shown in figure 2.



**Figure 1. Apparatus sitting for preparation of liquid dinitrogen tetroxide: 1) Condenser (10° C), 2) Drying Tower (packed with nearly 80 g of the mixture of phosphorus pentoxide and quartz sand,  $P_2O_5$ :  $SiO_2$ , 1: 1 in wt), 3) Oxidizing Tower (packed with Ca.100 g of oxidizing agent), 4&5) Condensers (-15° C), 6&7) Cooling Vessel (-5° C & 25° C).**

**Table1. Oxidative Coupling of Heterocyclic Thiols to Disulfide Compounds by N<sub>2</sub>O<sub>4</sub>/Charcoal in CH<sub>2</sub>Cl<sub>2</sub>.**

Entry	Thiol	Disulfide	Time (min.)	Yield %	m.p °C (ref.)	Infrared vibrations (cm <sup>-1</sup> )
1	2-Mercapto - benzothiazole	2,2'-Dithio-bis(benzothiazole)	10	91	178-180 (178-179) <sup>25a</sup>	3059 (ν, C-H, aromatic), 1558 (ν, C=N), 1465, 1429 (ν, C=C, aromatic), 1311, 1238, 1006, and 758 (ν, C-s-s-C), 725 (ortho disub.), 669 (ν, C-s-C)
2	4-Mercapto - pyridine	4,4'-Dithio-bis(pyridine)	5	90	76-79 (76-78) <sup>25a</sup>	3081 (ν, C-H, aromatic), 1600, 1570, 1547, 1498, 1485 (ν, C=N, C=C, aromatic ring), 1183, 1010, 740, and 485 (ν, C-s-s-C)
3	2-Mercapto - pyridine	2,2'-Dithio-bis(pyridine)	5	90	57-59 (56-60) <sup>25a</sup>	3076, 3010 (ν, C-H, aromatic), 1603, 1563, 1552, 1501, 1483 (ν, C=N, C=C, aromatic ring), 1195, 1015, 750, 710, and 490 (ν, C-s-s-C)
4	2-Mercapto - thiazole	2,2'-Dithio-bis(thiazole)	5	95	106-109 new	3030 (ν, C-H, aromatic), 1607, 1573, 1498, 691 (ν, C=N, C=C, and C-s-C, thiazole ring), 1177, 1011, and 482 (ν, C-s-s-C)
5	2-Mercapto -5 - methoxy-benzoimidazole	2,2'-Dithio-bis(5-methoxy-benzoimidazole)	8	90	165-168 new	3205 (ν, N-H), 3070 (ν, C-H, aromatic), 2956 (ν, CH <sub>3</sub> ), 1610, 1580, 1550, 1490 (ν, C=N, C=C, aromatic benzoimidazol ring), 1260, 1190, 487 (ν, C-s-s-C), 840, 770 (subs. ring)
6	2-Mercapto - benzoxazole	2,2'-Dithio-bis(benzoxazole)	8	90	90-94 (92-94) <sup>25b</sup>	3100 (ν, C-H aromatic), 1617, 1605, 1467 (ν, C=N, C=C aromatic benzo-oxazol ring), 1260, 1160, 486 (ν, C-s-s-C), 744 (ortho disub.)
7	2-Mercapto -benzoimidazole	2,2'-Dithio-bis(benzoimidazole)	8	89	200-203 (202-204) <sup>25c</sup>	3198 (ν, N-H), 3085 (ν, C-H aromatic), 1618, 1585, 1560, 1493 (ν, C=N, C=C aromatic benzoimidazol ring), 1127, 1173, 480 (ν, C-s-s-C), 750 (ortho disub.)

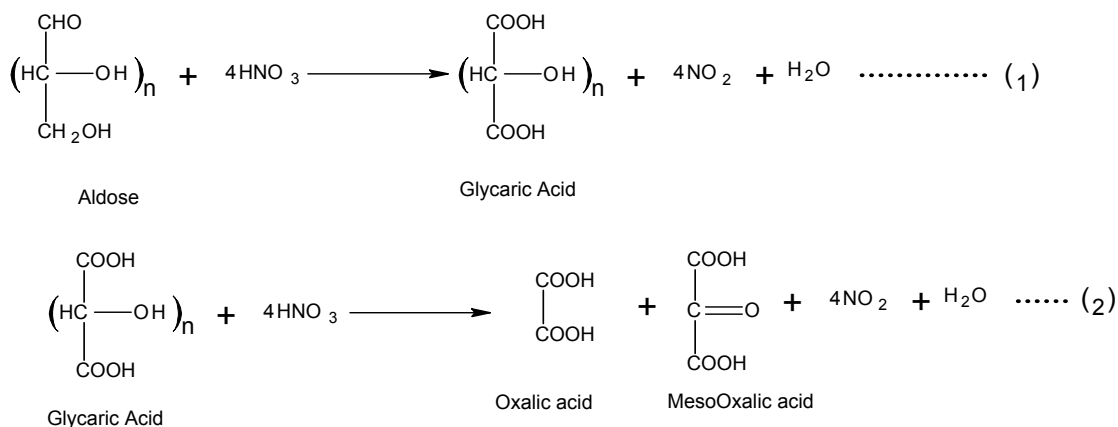
8	2-Mercapto-4-hydroxy-pyrimidine	2,2' - Dithio-bis (4-hydroxy - pyrimidine)	5	95	>300 new	3440 (ν, O-H), 3050 (ν, C-H aromatic), 1614, 1566, 1477, 1340 (ν, C=N, C=C aromatic), 1180, 1020, 488 (ν, C-s-s-C), 810, 750 (subs. ring)
9	2-Mercapto-5-amino - thiadiazole	2,2' - Dithio-bis(5-amino - thiadiazole)	10	90	233-236 new	3430, 3388 (ν, NH <sub>2</sub> ) 1637, 1593, 1488, 1340, 690 ((ν, C=N, C-s-C, thiadiazol ring), 1190, 1007, 490 (ν, C-s-s-C)
10	3-Mercapto-5-amino-1,2,4 - triazole	2,2' - Dithio-bis(5-amino-1,3,4-triazole)	8	92	>300 new	3440, 3378 (ν, NH <sub>2</sub> ), 3100 (ν, N-H), 1619, 1590, 1512, 1480 (ν, C=N, C-N, triazol ring), 1177, 1014, 488, 490 (ν, C-s-s-C)
11	2-Mercapto-4-amino purine	2,2' - Dithio - bis(5-minopurine)	8	90	>300 new	3490, 3385 (ν, NH <sub>2</sub> ), 3180 (ν, N-H), 1620, 1599, 1530, 1489 (ν, C=N, C=C aromatic purine ring), 1188, 1012, 487 (ν, C-s-s-C), 770, 654

## Results and Discussion

A liquid dinitrogen tetroxide with high purity (99%) was prepared from nitric acid and Al-Zahdi date. The purity was determined by titration method, by using KMnO<sub>4</sub> solution in the presence of conc. H<sub>2</sub>SO<sub>4</sub> and ferric ammonium sulfate as titrant<sup>(24)</sup>. The percentage yield of liquid N<sub>2</sub>O<sub>4</sub> was depended on the nitric acid concentration, but in generally, method can be employed on a range of 65-98%

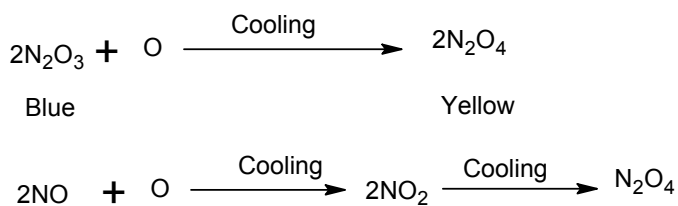
nitric acid. The reaction was occurred spontaneously and without any catalyst, moreover it was exothermic reaction so, cooling with water is necessary to keep the temperature of reaction flask not elevated.

The principle idea for N<sub>2</sub>O<sub>4</sub> formation is built on oxidation reduction between the aldoses sugar in date as reducer and nitric acid as oxidizer<sup>(25, 26)</sup>. The aldoses consist of a good moderate reducing agent, aldehyde and hydroxyl groups (**Scheme 1**).

**Scheme 1**

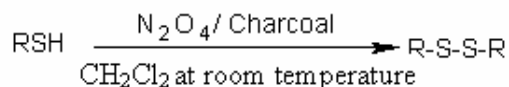
The residual by product gave a dicarboxylic acid (mainly oxalic acid) when it was left in the refrigerator. Oxygen current was used during the

reaction to convert the other nitrogen oxides (NO and N<sub>2</sub>O<sub>3</sub>) to N<sub>2</sub>O<sub>4</sub> <sup>(27, 28)</sup> (**Scheme2**).

**Scheme 2**

N<sub>2</sub>O<sub>4</sub>/Charcoal reagent was prepared according to the reported procedure<sup>(20)</sup> from liquid N<sub>2</sub>O<sub>4</sub> and activated charcoal at -10°C. Reagent is stable up to 60°C, and can be stored at room temperature in a capped bottle for months without any loss of activity.

Oxidative coupling of heterocyclic thiols by treatment of N<sub>2</sub>O<sub>4</sub> supported on charcoal proceeds readily in CH<sub>2</sub>Cl<sub>2</sub> at room temperature (**Scheme 3**). The reaction times are usually between 5-10 minutes as shown in Table 1.

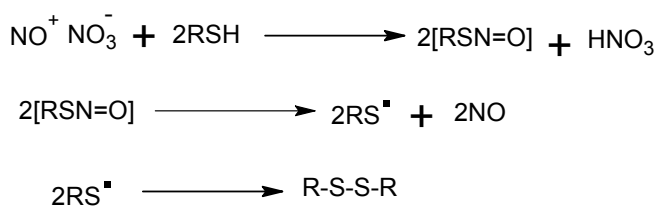


R = heterocyclic ring or substituted heterocyclic ring

### Scheme 3

Several molar ratios of  $\text{N}_2\text{O}_4$  to heterocyclic thiol were tried (1:1, 1:2, 1:3 and 1:4) to optimize the oxidation process. We were found that 1:2 molar ratio was established as other ratios. It is reasonable to assume that 1 mole of  $\text{N}_2\text{O}_4$  reacts with 2 moles of thioheterocyclic compounds to produce 1 mole of the corresponding disulfide and 1 mole of  $\text{HNO}_3$  (Scheme 4).

$\text{N}_2\text{O}_4$  is known to be in equilibrium with  $\text{NO}^+$  and  $\text{NO}_3^-$  in solution by its self ionization and degree of ionization



### Scheme 4

Since charcoal is insoluble in the organic solvent, the products were easily isolated by washing the reaction mixture with suitable solvent as dichloromethane evaporation of the filtrate under vacuum, followed by flash chromatography. Often produced

increases with dielectric constant of the solvent<sup>(14)</sup>. Thiols can be readily converted to their corresponding thionitrites with a  $\text{N}_2\text{O}_4$  in dichloromethane at room temperature. Disulfides result from the hemolytic cleavage of the sulfur–nitrogen bond of the unstable thionitrites and subsequent coupling of the resultant thiyl radicals<sup>(23d)</sup>.

pure disulfide heterocyclic compounds in high yield.

As may be seen, the method offers a simple, mild and efficient reagent for the oxidation of variety of heterocyclic thiols to corresponding disulfides. The chemical structure and purity of the disulfide products were proved by



using melting point measurement, elemental analysis, and FTIR spectroscopy. The measured results in elemental analyses closely corresponded to the calculated ones (see table 2), demonstrating that the expected compound was obtained. Figure 2 displays FTIR spectrum of 2, 2'-Dithio bis (benzothiazole ) as exemplary FTIR spectrum .It showed a sharp peaks between 1311, and 1006

$\text{cm}^{-1}$ , in addition to a sharp peak at  $758 \text{ cm}^{-1}$  which assigned to characteristic vibration of C-S-S-C bonds. The infrared spectra of the disulfide products as shown in the table 1, confirmed the presence of C-S-S-C bonds. The spectra also approved that, there was no weak band at (2500-2600)  $\text{cm}^{-1}$  region related to S-H group.

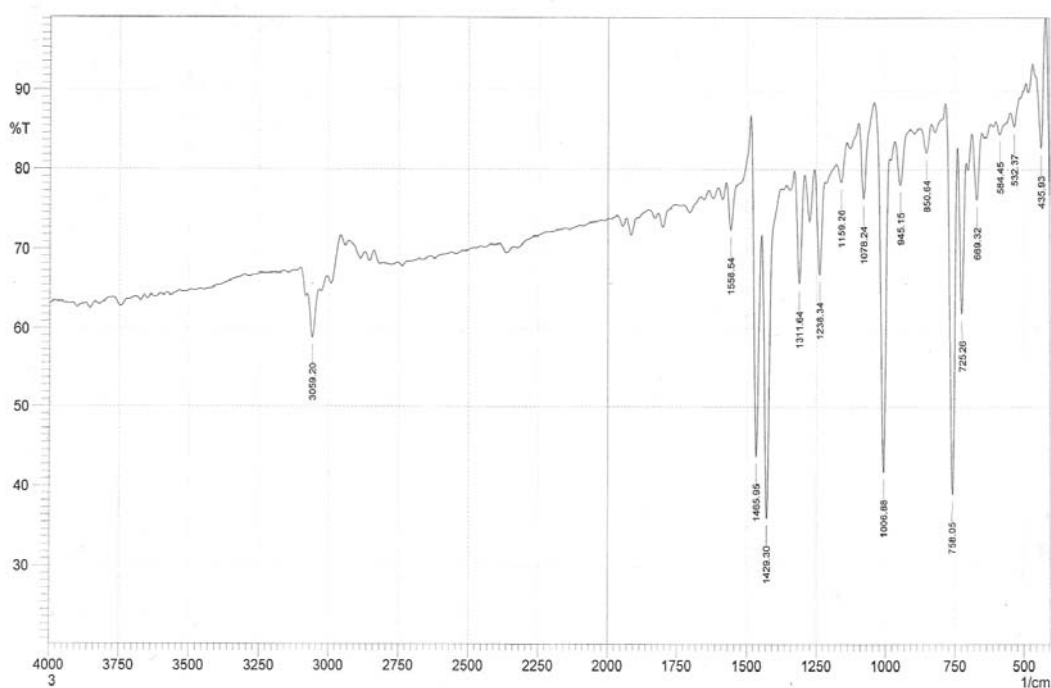


Figure 2. FTIR spectrum of 2, 2'-dithio bis(benzothiazole).

**Table 2. Elemental Analysis of Disulfide Compounds**

Disulfide	Formula	Mol.wt	Found (required) (%)		
			C	H	N
2,2'-Dithio - bis(benzothiazole)	C <sub>14</sub> H <sub>8</sub> N <sub>2</sub> S <sub>4</sub>	332	50.95 (50.60)	2.50 (2.40)	8.22 (8.43)
4,4' - Dithio - bis(pyridine)	C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> S <sub>2</sub>	220	54.60 (54.54)	3.44 (3.63)	13.00 (12.72)
2,2' - Dithio - bis(pyridine)	C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> S <sub>2</sub>	220	55.00 (54.54)	3.42 (3.63)	12.55 (12.72)
2,2' - Dithio - bis(thiazole)	C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> S <sub>4</sub>	232	30.94 (31.03)	1.80 (1.72)	12.11 (12.06)
2,2' - Dithio - bis(5-methoxy - benzoimidazole)	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub> S <sub>2</sub>	358	52.99 (53.63)	3.66 (3.91)	15.22 (15.64)
2,2'-Dithio - bis(benzoxazole)	C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub>	300	55.87 (56.00)	2.45 (2.66)	9.50 (9.33)
2,2' - Dithio - bis(benzoimidazole)	C <sub>14</sub> H <sub>4</sub> N <sub>4</sub> S <sub>2</sub>	298	57.00 (56.37)	3.70 (3.35)	18.82 (18.79)
2,2' - Dithio - bis(4 -hydroxy - pyrmidine )	C <sub>8</sub> H <sub>6</sub> N <sub>4</sub> S <sub>2</sub>	222	43.11 (43.24)	2.66 (2.70)	25.43 (25.22)
2,2' - Dithio - bis(5 - amino- thiadiazole)	C <sub>4</sub> H <sub>4</sub> N <sub>6</sub> S <sub>4</sub>	264	18.50 (18.18)	1.48 (1.51)	31.22 (31.81)
2,2 - Dithio - bis(5 - amino - 1,3,4 - triazole)	C <sub>4</sub> H <sub>6</sub> N <sub>8</sub> S <sub>2</sub>	230	21.00 (20.86)	2.51 (2.60)	49.00 (48.69)
2,2' - Dthio - bis(5 - amino - purine)	C <sub>10</sub> H <sub>8</sub> N <sub>10</sub> S <sub>2</sub>	332	35.95 (36.14)	2.44 (2.41)	41.89 (42.16)

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