

Annexure III: Synthesis of strong electron acceptor compounds

Synthesis of electron acceptor compounds 2, 3, 5, 6-tetracyanodithadiene and 2, 3, 4, 5- tetracyano thiophene

III.1 Introduction:

An electron acceptor molecule (EA) is a chemical entity that accepts electrons transferred to it from another compound, ideally electron donor (ED) molecule. EA can be considered as an oxidizing agent, by virtue of its accepting electron and consequently self reduction.

The reactivity of the bis (benzene) vanadium with poly-nitrile compounds is an active subject of research since the discovery of the exceptional room-temperature magnet $V(\text{TCNE})_x$, prepared from $V(\text{C}_6\text{H}_6)_2$ and TCNE in dichloromethane, by Miller et al. [1]. This lead to investigation of variety of nitrile based compounds as EA and their reactions with various transition metals and/or ED molecules.

Significantly less is known about complimentary poly-nitrile dithiin and thiophene consisting of electron acceptor molecules. To extend the scope of this reaction, the reactivity of bis (toluene) vanadium [$V(\text{C}_7\text{H}_9)_2$] with thio based poly-nitrile compounds is planned. Here, we present synthesis and characterization of 2, 3, 5, 6-tetracyanodithadiene (TCTD) and 2, 3, 4, 5- tetracyano thiophene (TCTP).

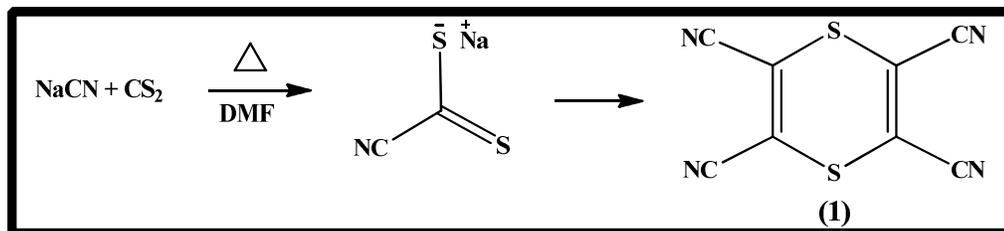
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III.2 Experimental

III. 2.1 Syntheses of Compounds:

A general methodology of TCTD[2] and TCTP [3] preparation/syntheses is mentioned in Scheme III.1 and Scheme III.2.

Scheme: III.1

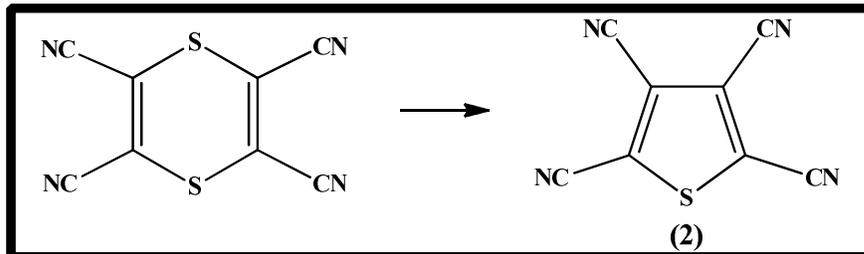


In reaction, carbon disulfide (0.1 mmol) was added dropwise over a period of 20-25 minute into DMF solution (9mL) containing sodium cyanide (0.1 mmol) with continuous stirring. The temperature was held at 35-40C with external cooling during the addition period. The resulting dark-yellowish brown colour solution was then heated for 30 minutes at 60C. After 30 minutes reaction mixture was cool down to room temperature and left to stand overnight (10-12 hrs) at room temperature. Dark shiny yellow brown prismatic shaped crystals of sodium cyanodithioformate were obtained. These formed crystals were solubilised by addition of cold 20 ml water into the flask and stirred well. After one hours sulphur was precipitate as by-product which was filtered through Celite bed. Iodine balls were added into the clear solution and stirred well gives expected tetracyano-1, 4-Dithhin product as precipitate. The product was filtered and further purified by acetone-water mixture.

Yield: 42%.

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Scheme III.2:

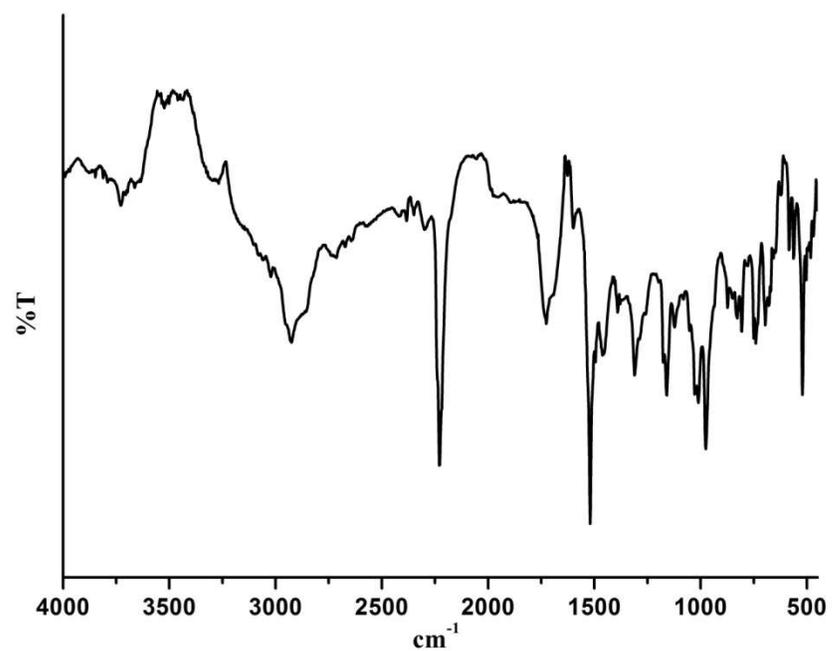


Cesium fluoride (32 mmol) was added over a period of 1 h to a solution of **1** (23 mmol) in diglyme at 60 °C and then warmed to 90 °C for 1 h. The mixture was cooled, diluted with an equal volume of water, and filtered. The water-insoluble material was crystallized from benzene to give of tetracyanothiophene (mp 198 °C).

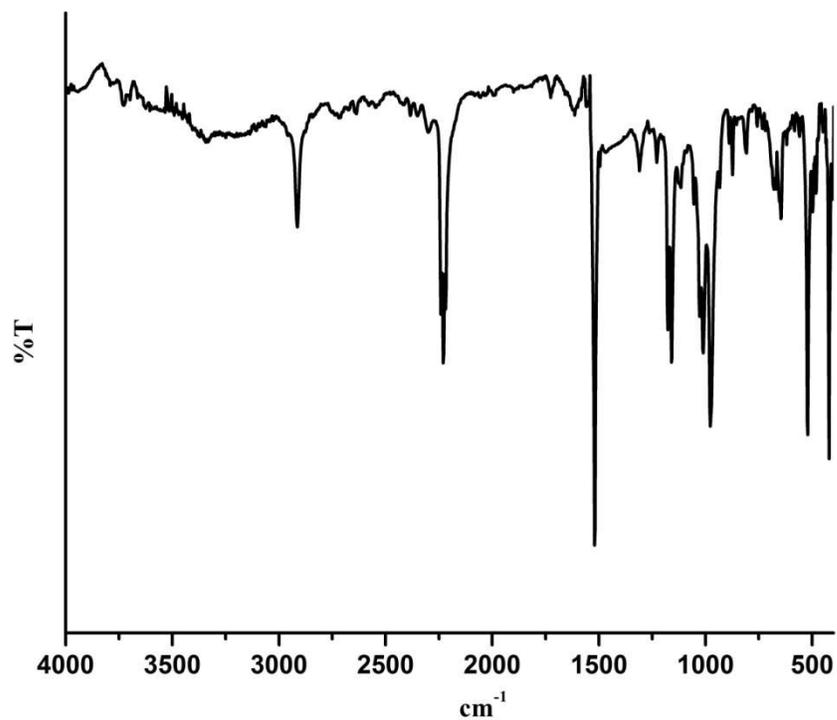
Yield: 40%

III.3 Result and Discussions

III.3.1 FT-IR



(a)



(b)

Fig. III.1: FT-IR spectra of compound 1 (a) and compound 2(b)

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Table III.1: Wave-numbers (cm⁻¹) of the bands observed in the powder FT-IR spectra of compound 1 and 2

1-Tetracyanodithiadene[4]	2-Tetracyanothiophene [5]
2929s	2913vs
2231s	2242s
2222s	2229vs
1556m	2218v
1505m	2224s
1505vs	2196sh
1528s	1695w
1495m	1519vs
1385w	1495m
1372m	1310m
1340m	1178s
1310w	1158vs
1176s	983s
1154s	977sh
1164m	916m
1124sh	896m
1112m	874m
1088w	859w
1051m	820w
1023s	796m
1001vs	770m
978vs	703m
994s	530s
984s	524sh
872m	504w
690m	487vs
524s	481s
430s	464s
418w	436s

vs- very strong, s- strong, m- medium, w- weak, sh- shoulder

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III.3.2 Elemental analyses:

The calculated and observed elemental analyses were consistent with the formulae $C_8N_4S_x$.

Compound 1: Anal. Calc. for $C_8N_4S_2$: C, 44.43; N, 25.91; S, 29.66%. Found: C, 44.51; N, 25.87; S, 29.89 %.

Compound 2: Anal. Calc. for C_8N_4S : C, 52.17; N, 30.42; S, 17.41%. Found: C, 52.09; N, 30.15; S, 17.83 %.

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III.3.3 ^{13}C NMR spectra

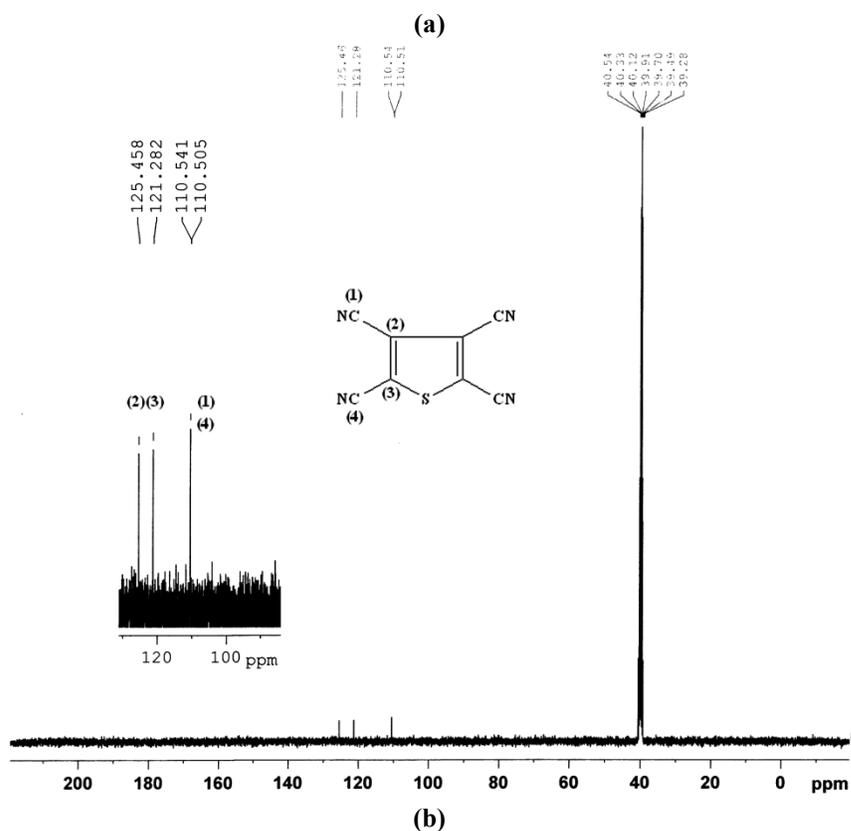
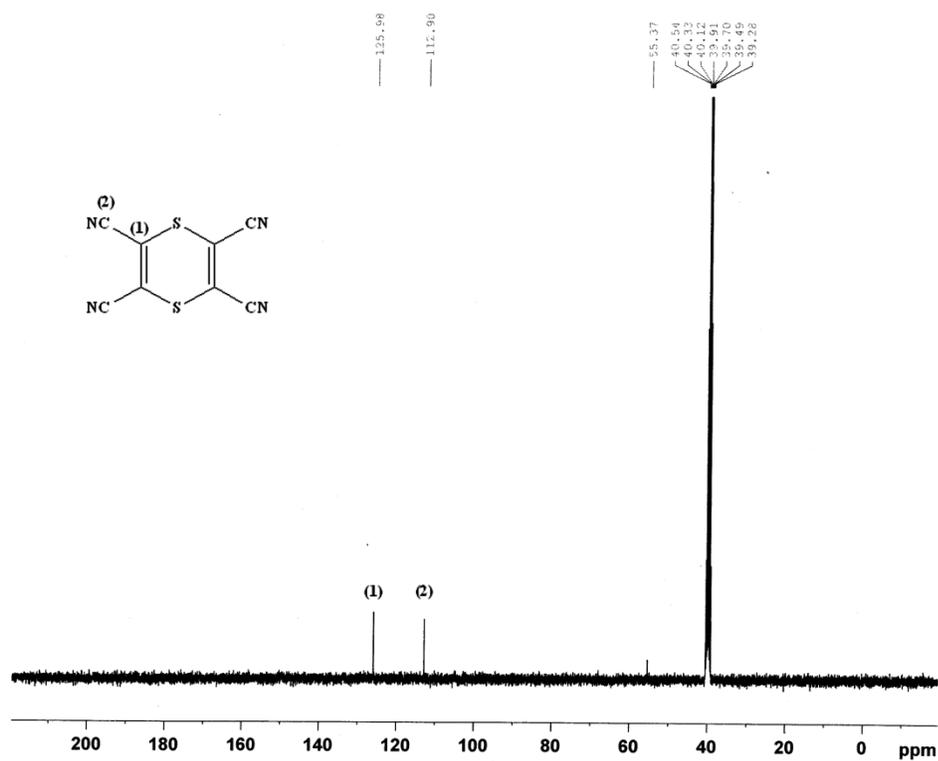


Fig. III.2: ^{13}C NMR spectra of compound 1 (a) and compound 2(b)

III.4 References

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