

Synthesis of Three New Donor- Acceptor [4] Dendralenes

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Summary: Three new donor - acceptor [4] dendralene compounds have been synthesized. Wittig reaction was used for the preparation of first two compounds and third one by Knoevenagel condensation. Their mass was calculated by APCI mass spectra which are in good agreement with theoretical data. UV-Vis data indicate the cross- conjugation in these systems due to the push-pull intra molecular charge transfer (CIT) sequence from electron donor to acceptor group. The ¹H-NMR signals appear in aromatic region confirming the formation of trans (having π - structures) isomers rather than cis may be due to the exposure of the compounds to ambient light. The dominating roll of electron acceptor nitro, methoxy and cyano benzene groups in conjugation is clearly shown. The ¹³C-NMR spectra which also supported the above analytical data and the number of carbons atoms obtained representing well the structures established.

Keywords: dendralene, Wittig reaction, cross- conjugation, UV-Vis, Knoevenagel condensation

Introduction

Dendralenes are polyene hydrocarbon in which carbon-carbon double bonds are aligned in cross conjugated arrangement and require the presence of at least three carbon-carbon double bonds [1]. These compounds are classified by an acyclic polyolefinic structure in which both the degree of unsaturation and level of cross conjugation are of highest order [2]. Such a cross conjugation is a commonly encountered phenomenon in natural product and dyestuff chemistry, although in a majority of cases various π -systems are polarized either by hetro atoms and / or by electron-donating or accepting substituent [3].

It has also been suggested that the presence of electron rich functionality can increase the degree of electronic communication in cross conjugated systems [4]. Dendralenes substituted with redox – active groups which readily give rise to open shell species are very rare [5]. Novel applications have been envisaged for stable cross conjugated radicals which they may form. For example they may act as soliton valves and switches in a molecular electronic devices [6]. This means that switching one source off will allow the transfer of electrons via an alternative possible root within the molecule, hence a switching device [2-3,5-6,8-19]. Other potential applications include improvement in the capability of modern computing and telecommunication technologies , optical data processing, laser scanning and new frequency generation owing to the ability of these compounds to show highly non- linear optical (NLO) effects [6]. Increasingly, organic molecules are becoming targets for these applications mainly due to their process ability and the possibility of tailoring the molecules with desired physico-chemical parameters. A lot of work has been initiated on organic compounds that exhibit conductivity of donor- acceptor type, known as the charge-transfer complexes [7]. The similarity of UV spectrum of [4] dendralene(3,4-dimethylenehexa-1,5diene) ($\lambda_{\max}$ =216.5nm) to that of butadiene ($\lambda_{\max}$ =217nm) suggest that dendralene can not exist in coplanar form [3]. Inspection of molecular models indicates that planar structures for the dendralenes would cause severe steric hindrance between the endo-hydrogen atoms. Hence, the polyenes prefer twisted conformations to avoid accumulation of substituent. Thus dendralenes substituted with donor-acceptor groups are very rare and their electronic properties are unexplored. Moreover, their nonlinear optical

studies would allow further investigation into the chemistry and nature of these compounds.

Results and Discussion

The product 1, 2 and 3 were obtained as brown, orange and brown solids in a yield 66.12%,10.8 and 26.95%, having melting points 44-46 , 192-194 and 210-212°C respectively. They are fairly good soluble in chloroform, acetone as well as in dichloromethane (DCM). The first two compounds were prepared by Wittig reaction and last one was attempted by Knoevenagel condensation.

The APCI mass spectra of the compounds are shown in Fig 1-3 respectively with the corresponding peaks [M^+] (m/z 512, calcd; 512.61), (Theory FW=637.9585, Prac FW=637,638) and (Theory FW=525.8558, Prac: FW=525,527) confirming the purity and formation of right compounds.

The UV- visible absorption spectra of compound 1, 2, 3 were recorded and data is shown in Table-1. Compound 1 and 2 have near identical spectra; they have a maximum absorbance at 395 and 394 nm respectively and shoulder 322 and 320 nm. The major absorbance can be assigned to a ‘ Push – Pull’ intramolecular charge transfer (ICT) sequence from electron donor (thiophene or bromo thiophene) to acceptor (nitrobenzene or methoxy benzene) groups, indicating no significant affect due to the presence of bromine on the transition energy.

Fig. 4-6 of ¹H-NMR spectra of compound 1, 2 and 3 show no evidence of –CH=O signal, indicating full conversion of dialdehyde to targeted compounds. Due to the highly π -conjugated structures, NMR signal must appear in the aromatic region (σ >6.0ppm). The spectra were interpreted and assignments are given as for Fig 4 σ = 8.21ppm (s, 1H), σ = 7.4ppm with the coupling constant of these protons (8.8 Hz) (s,2H), σ = 7.42 ppm (s,6H) and σ =6.95ppm (s,8H).which may be attributed to trans conformer rather than cis, may be due to the exposure to ambient light, showing lack of conjugation from electron donating (thiophene) group and dominating roll of electron acceptor (nitrobenzene) group [20]. In Fig. 7 ¹H-NMR spectrum clearly depicted the thiophene peaks in aromatic region at (6H, σ =6.85ppm, 7H,

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$\sigma=7.25\text{ppm}$), similarly the P-substituted benzene protons lie in same region at (1H, $\sigma=6.97\text{ppm}$, 2H, $\sigma=7.5\text{ppm}$) and vinyl double bond protons were at (3H, $\sigma=7.3\text{ppm}$, 4H, $\sigma=6.82\text{ppm}$, and 5H, $\sigma=6.98\text{ppm}$) confirming the π -conjugated structure of the compounds. Whereas, methoxy protons were present in aliphatic region of the spectrum matching

well with the data reported in literature [20]. The spectrum of Fig. 6 clearly implied the thiophene peaks at 3H, $\sigma=7.55\text{ppm}$ and vinyl double bonds at 1H, $\sigma=7.93\text{ppm}$, 2H, $\sigma=7.77\text{ppm}$, favoring for the formation of right compound donor –acceptor dendralene as reported in literature [20].

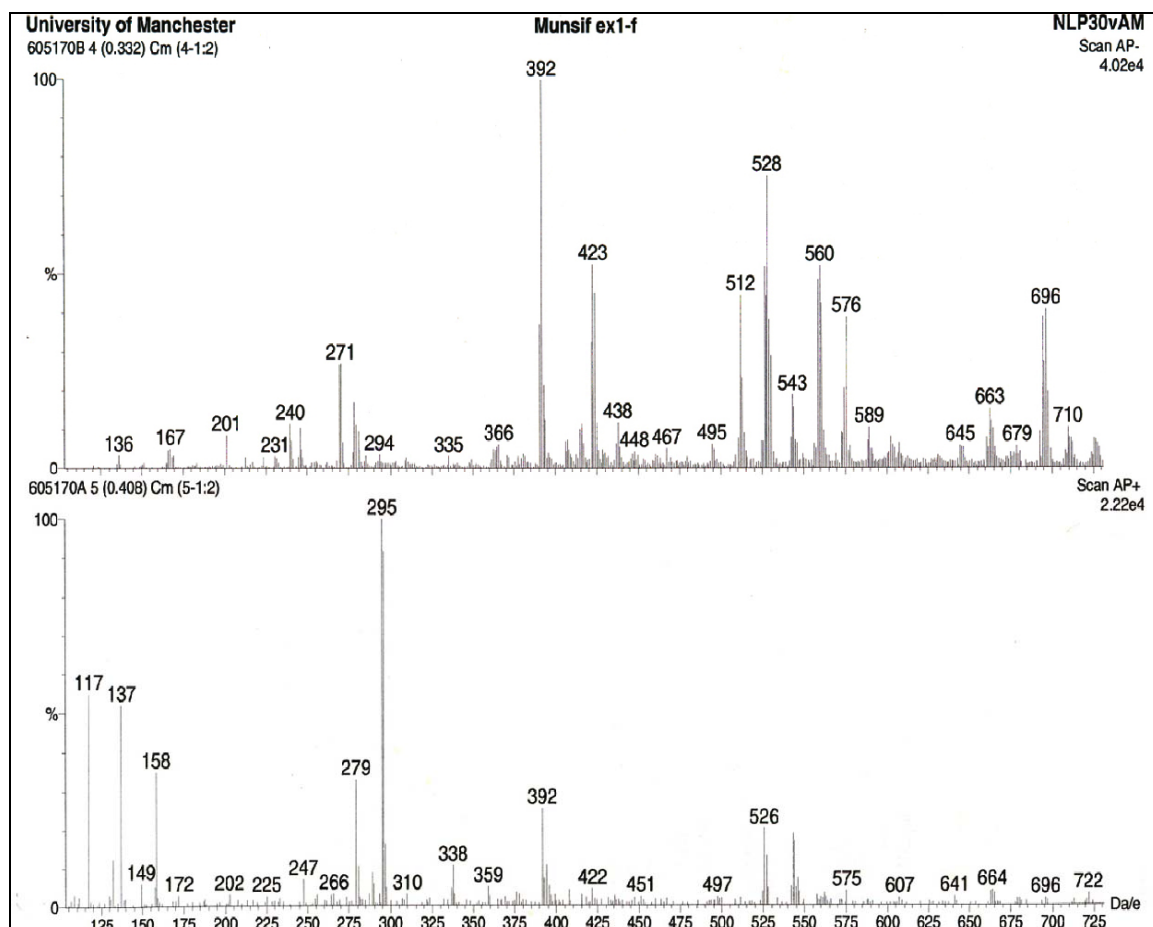


Fig. 1: APCI-Mass spectrum of compound 1.

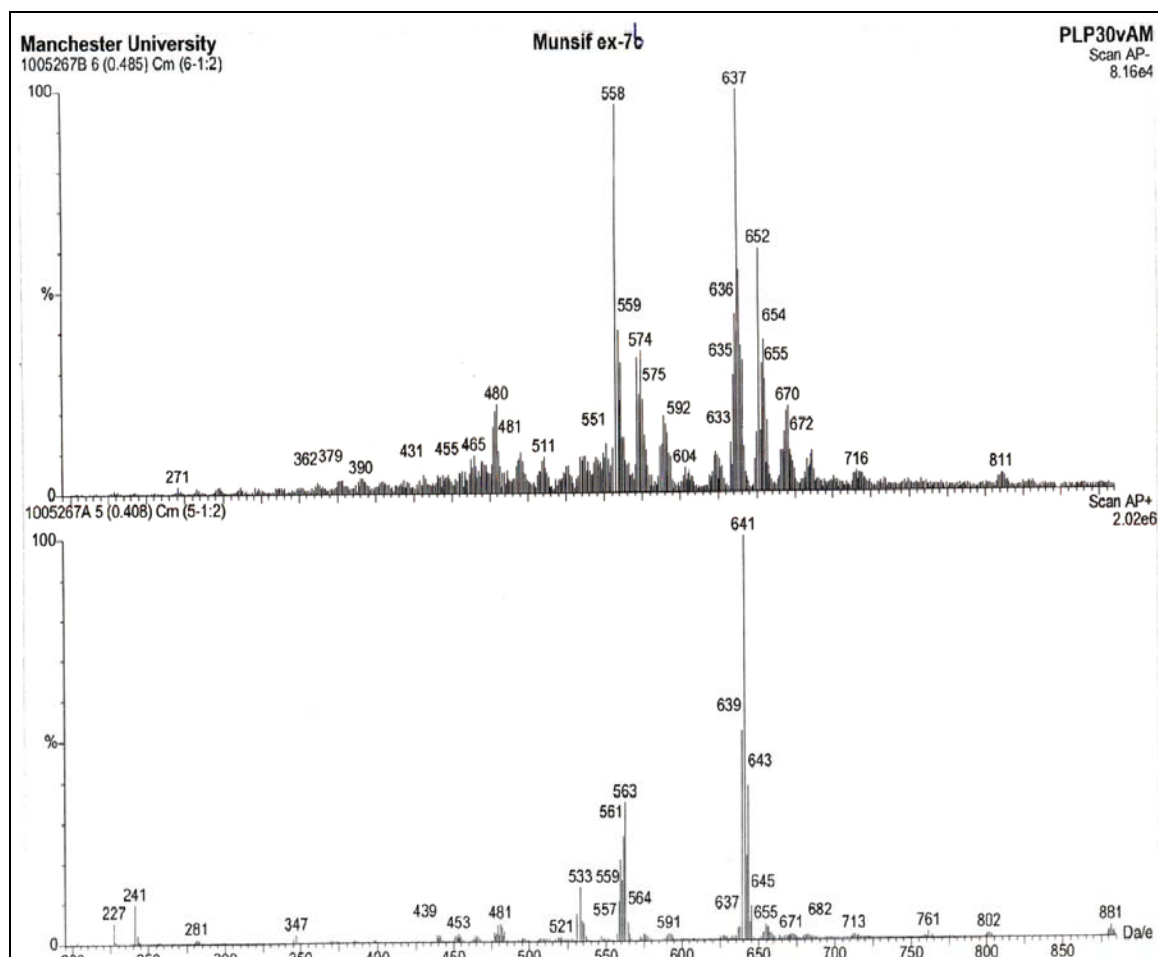


Fig. 2: Mass Spectra of [4]Dendralene compound 2.

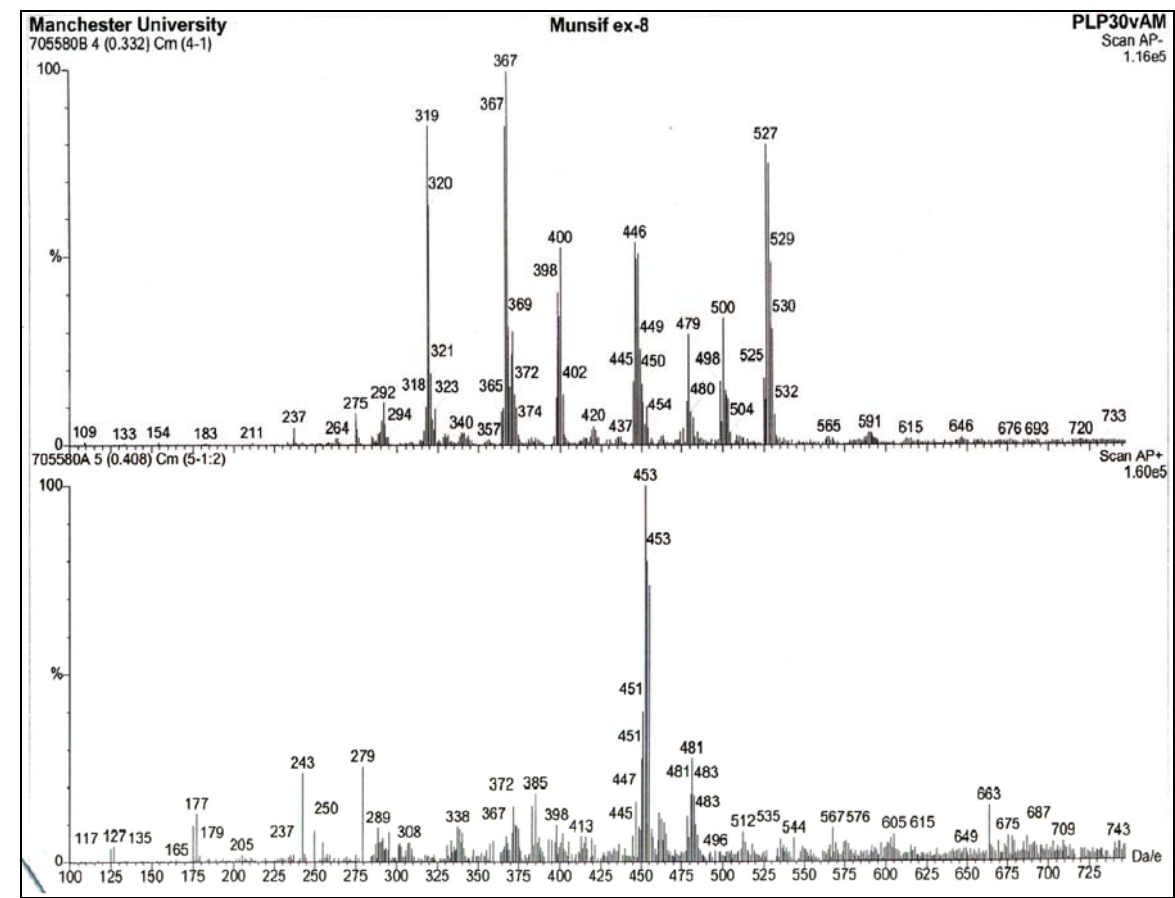


Fig. 3: Mass spectra of [4]Dendralene compound 3.

Table-1: Spectral and analytical results of [4] dendralene systems.										
Product/ Colour	R/time h	Yield %	M.P °C	M. formula	M. mass M ⁺	¹ H-NMR δ (ppm)	¹³ C-NMR δ (ppm)	E.analysis	C.V.	U.V.λ _{max} (nm)
Brown	18	66.12	44-46	C ₂₈ H ₂₀ S ₂ N ₂ O ₄	512.61-512	Noaldehyde, and thiophene peaks 6.97(o,1H),7.5(m,2H) 7.3(v,3H)6.82(v,4h) 6.98(v,5H) 6.85(thioph, 6H) 7.25(thioph, 7H)	146.57 130.28, 123.5	C=65.61.15 H=3.93, 5.05 N=5.46,9.92 S=12.51,0.45	1.70	394 (broad) 395 (weak) 320 (broad) 322 (weak)
Orange	18	10.8	192-194	C ₃₀ H ₂₄ S ₂ O ₂ Br ₂	637.958-637		-	-	-	
Brown	24	26.95	210- 2012	C ₂₀ H ₈ S ₂ N ₄ Br ₂	525.85-525	7.93(1H), 7.77(2H) 7.28(3H), 7.55 (4H)	-	C=45.67, 42.28 H=1.54, 1.99 N=10.66, 5.54 S=12193, 12.88	-	-

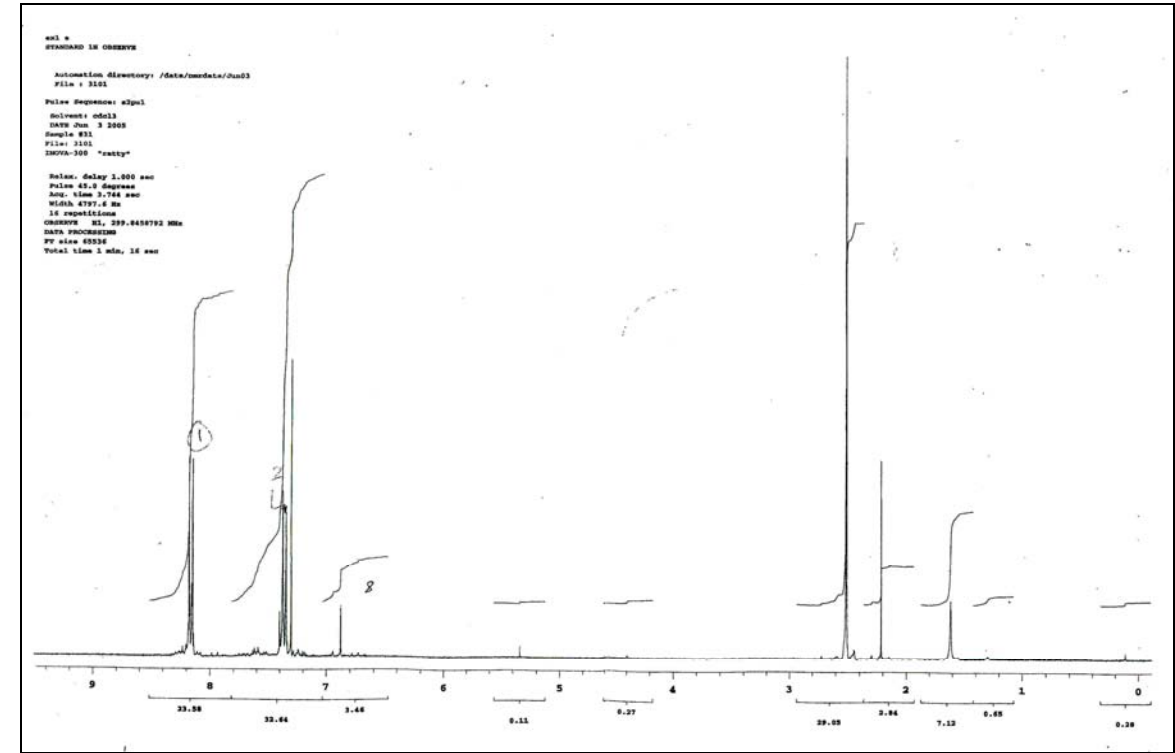
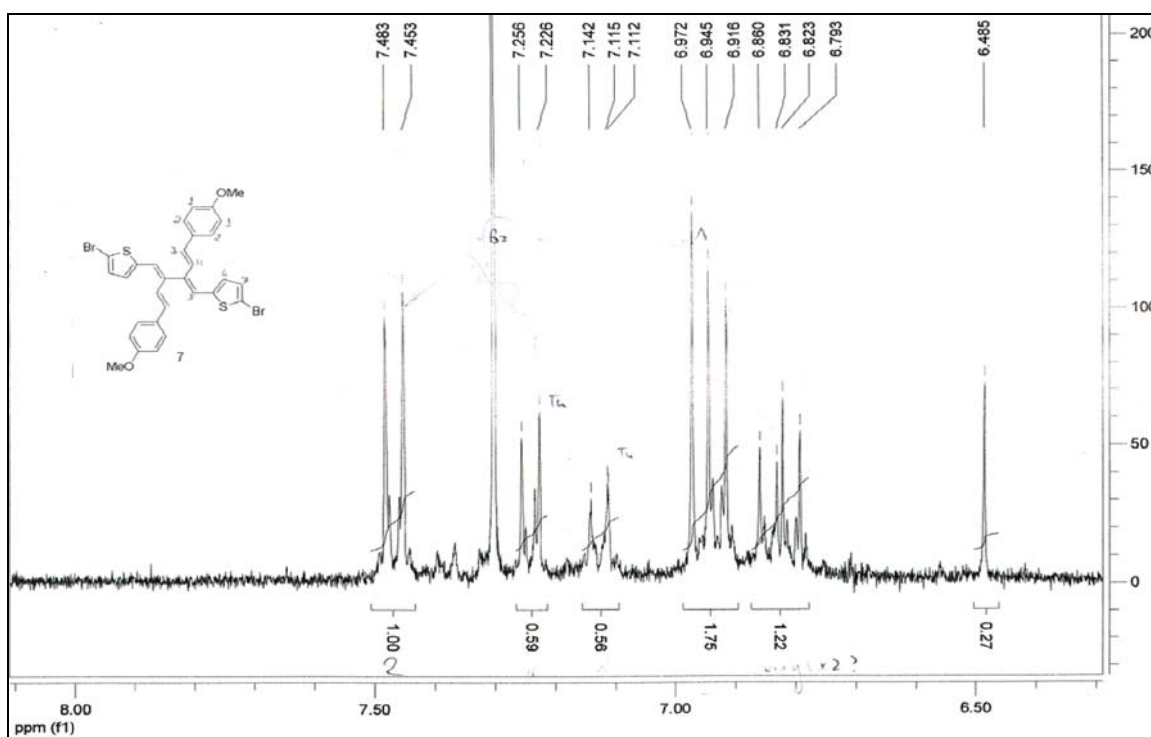
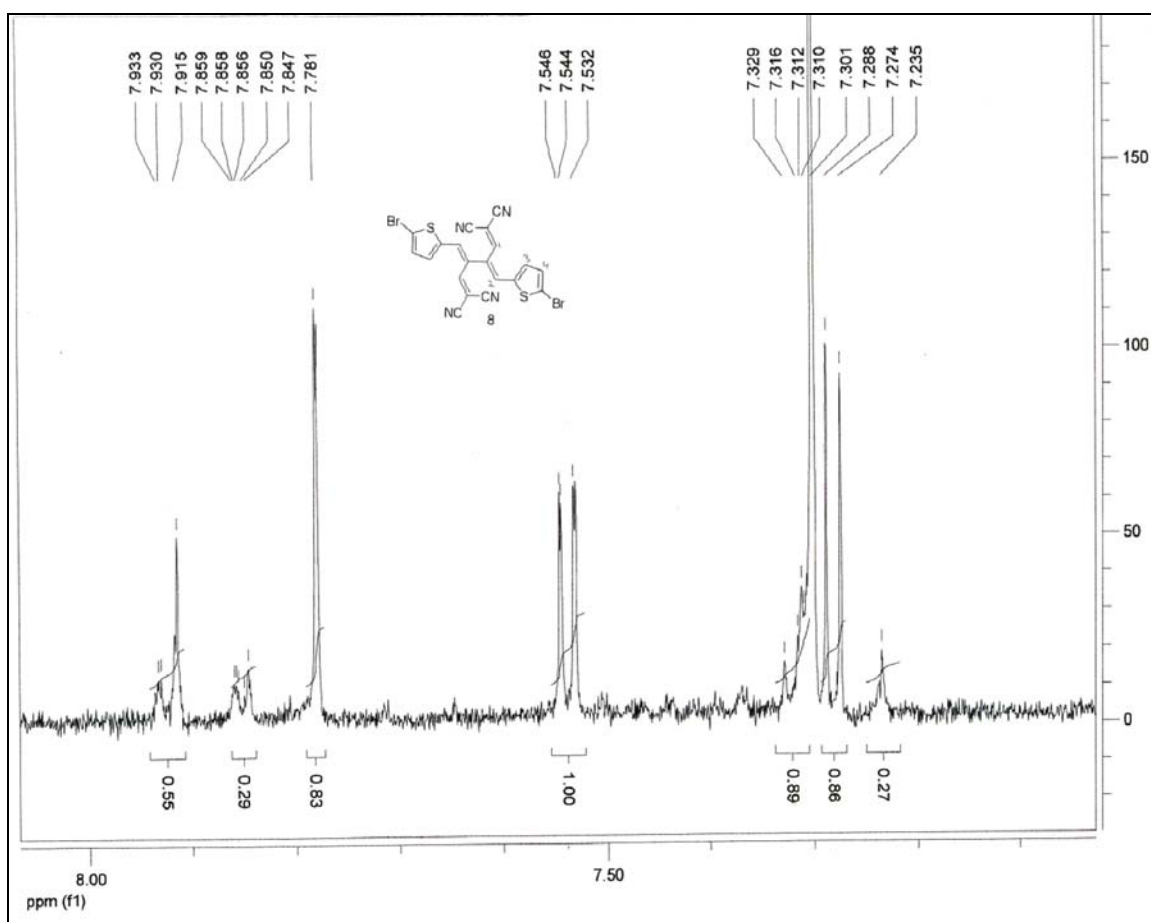


Fig.4: ¹H-NMR of [4]Dendralene compound 1.

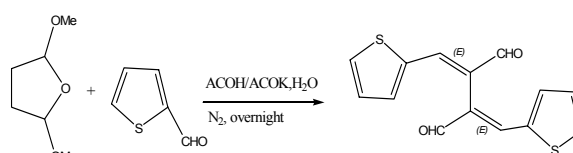
Fig. 5: ¹H-NMR spectra of Dendralene [4] compound **2**.Fig. 6: ¹H-NMR of [4] Dendralene compound **3**.

¹³C-NMR data in Table-2 and Fig. 8 indicate signals in the aromatic region especially in $\sigma=23.5$ -205.5 ppm. The spectra were bit difficult to explain however, number of carbon atoms per signals could be evaluated from the relative signals intensities and were in accordance to the structure 1, 2.

The HOMO of these compounds is localized on the donor (bis thiophene- butadiene or bisbromothiophene-butadiene) unit. The LOMO-1 is also localized over the same atoms but shows double bond character between the central carbon atoms, while LUMO +2 orbital is localized on the acceptor (nitro benzene, methoxybenzene and cyano benzene) groups. This coincides well with the experimental

lemda max of the UV-visible data i-e 395nm [20]. The other transition in tran isomer occur for the transition HOMO-2-LUMO predicted at 324 nm This is in good agreement with the higher energy band seen at 320 nm in UV-visible spectrum.

Experimental



Scheme-1: Synthesis of 1,4-dithiophene-2,3-diformyl butadiene

Table-2: Analytical data of 1,4-diaryl-2,3-diformylbutadiene.

Product	Color	R/time h	Yield %	M.P °C	M. formula	M. mass M ⁺	¹ H-NMR δ (ppm)	¹³ C-NMR δ (ppm)	E.Analysis	FT-IR (cm ⁻¹)
1,4-dithiop Hene-2,3-diformul butadiene	brown	Over night	64	78.81	C ₁₄ H ₁₀ S ₂ O ₂	274.2, 274	9.65 (s,2H), 7.86 (s,2H) 7.40 (dd4H) 7.02 (m,2H)	191.47, 146.101 37.40, 135.54 133.54, 128.131 10.00	Cal. Found C=61.3, 63.59 H=3.6, 4.07 S=23.4, 18.69	3077 (Sp2, C-H) 2818(Sp2,C-H) 1666 (Str C=O)
1,4-dibromo thiophene-2,3- diformyl butadiene	brown	Over night	22.22	192- 194	C ₁₄ H ₈ S ₂ O ₂ Br ₂	432.8,432	9.72(s,2H) 7.88(s,2H) 7.36(dd4H) 7.18(m2H)	190.64,145.23 145.20,138.65 135.93,135.86 131.36,121.93	Cal. Found C=38.92,39.25 H=1.86, 1.87 Br=36.99,36.37 S=14.84,14.57	1677 (C=O str) 1588 (C=C str) 1061 (C-Br str)

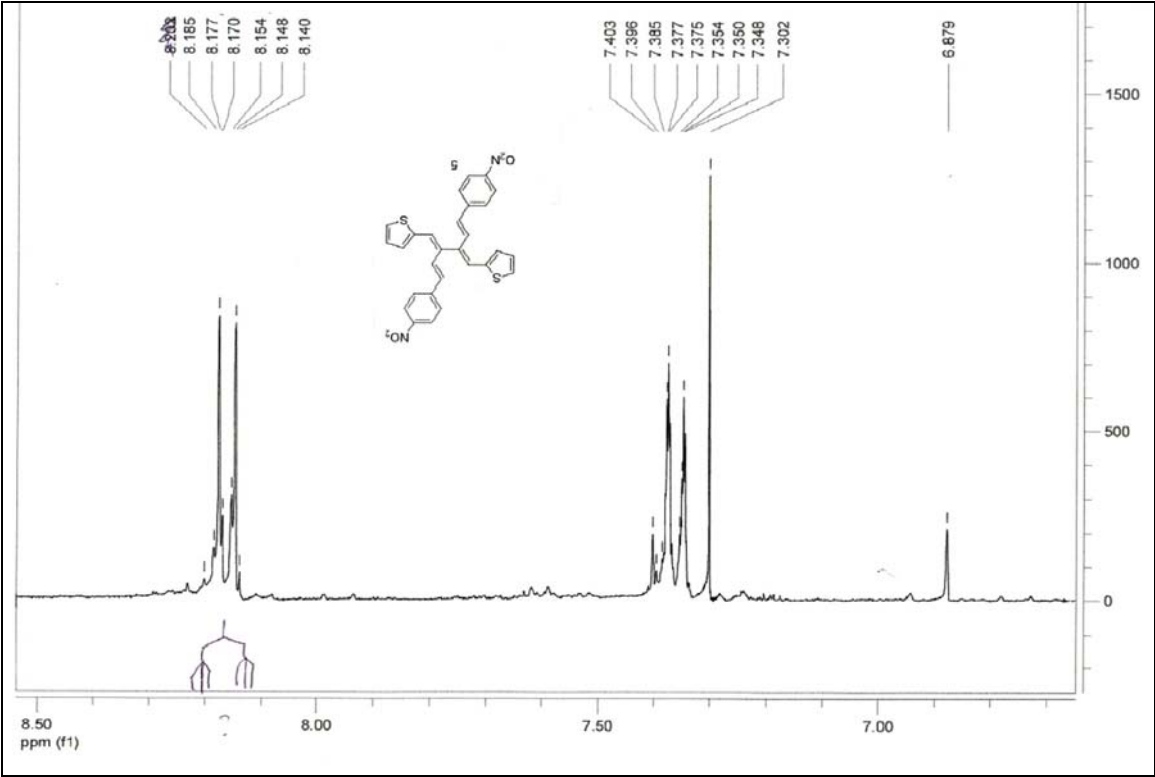


Fig. 7: Elaborated peaks of ¹H-NMR of [4]Dendralene compound 1.

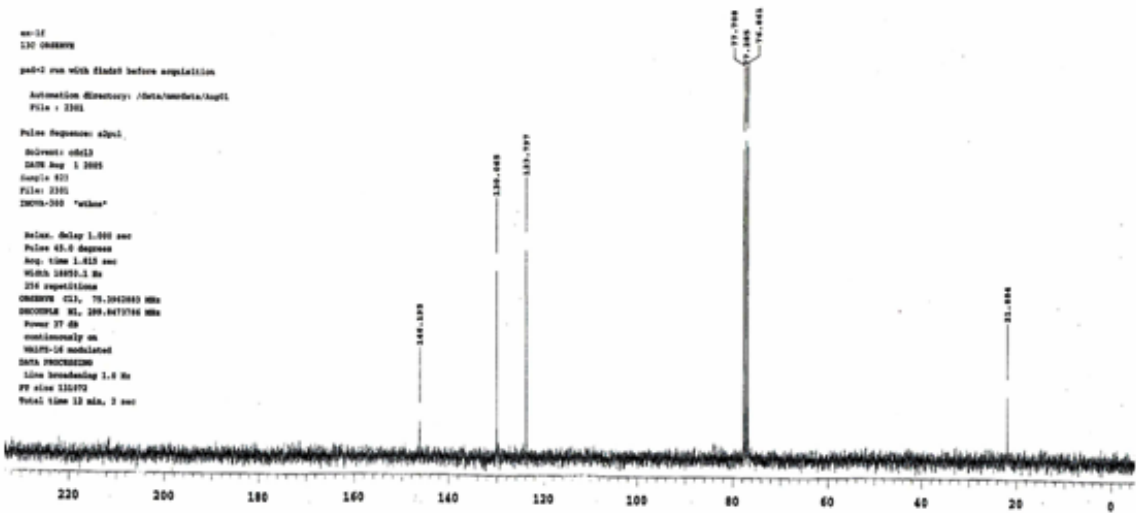
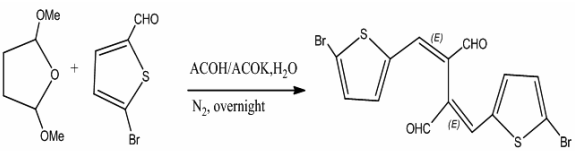


Fig. 8: ¹³C-NMR of [4]Dendralene compound 1

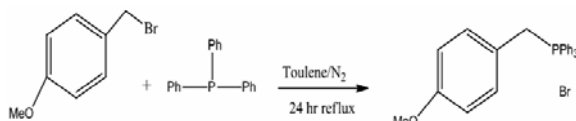
A mixture of 2,5-dimethoxytetrahydrofuran (Lancaster England, 2.0 ml, 15.0 mmol), 2-thiophenecarboxaldehyde (Lancaster England, 9.0 g, 80.2 mmol) acetic acid (Analar England, 3.0 mol), water (3.0 mol) and potassium acetate (May and Baker England, 5.0 g) in a round bottomed flask was heated in nitrogen atmosphere under reflux overnight. A heterogeneous dark brown mixture was observed after an hour and a TLC spot check suggested that some product might have been formed. Purification by silica column chromatography with 1:1.5 petroleum ether: ethyl acetate produced a brown solid which was confirmed by analysis as the product (1,4-dithiophene-2,3-diformylbutadiene). The yield obtained was 64%.The analytical data is tabulated in (Table 2).



Scheme-2: Synthesis of 1,4- dibromo dithiophene-2,3-diformylbutadiene

A mixture of 2,5-dimethoxytetrahydrofuran (Lancaster England) a colorless liquid (40.1 mmol, 5.29g,7.779ml), 5-bromothiophene-2-carboxaldehyde (Lancaster England) a red color liquid (80.2 mmol, 9.0 g, 14.25ml), glacial acetic acid (Analar England, 4.5 ml) water (4.5 ml) and potassium acetate (May and Baker England, 2.0g) in a round bottomed flask

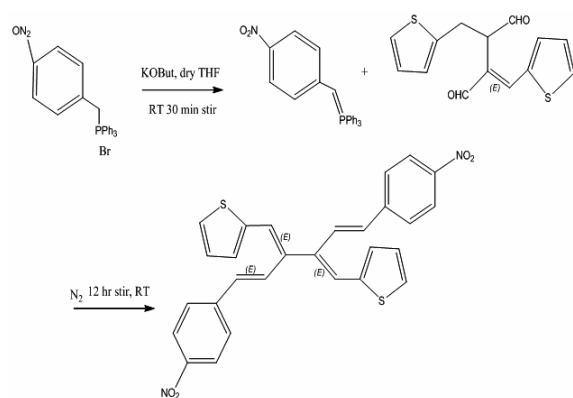
under nitrogen atmosphere was heated under reflux for overnight. During reflux the mixture changed from red to more intense brown color. After cooling the mixture was poured into water (75ml), then extracted with ethyl acetate (3×200). The organic (dark brown) layer was separated and washed with saturated sodium bicarbonate solution (200ml) and distilled water (200ml). The brown liquid was then heated for fifteen minutes with activated charcoal, dried with magnesium sulfate, filtered and left over night. Much of its part was crystallized. The liquid part was separated and concentrated up to few ml. The crystals were washed with petroleum ether in order to remove impurities. A brown colored compound was obtained. The TLC spot check in 1:1 petroleum: dichloromethane with starting material indicated that crystallized compound was the desired aldehyde. The ^1H -NMR, ^{13}C -NMR, IR and Mass spectrum (APCI) of the sample (in CDCl_3 and Acetone as solvents respectively) indicated that the compound was pure. The net weight of the compound obtained was 3.819g, 22.22%, MP = 194-196°C. The analytical data is given in (Table-2).



Scheme-3: Synthesis of 4-methoxybenzylphosphonium bromide

A mixture of 4-methoxybenzyl bromide (Aldrich USA, 4.0g, 0.0199 mol), dry toluene (50 ml), triphenyl phosphine (Aldrich, 5.21 g, 0.0199 mol) in a round bottom flask was refluxed under nitrogen for 24 hours. On cooling a white precipitate formed which was filtered on Buchner funnel. The white precipitate was washed with diethyl ether, dried to constant weight 8.195 g, 88.94%.

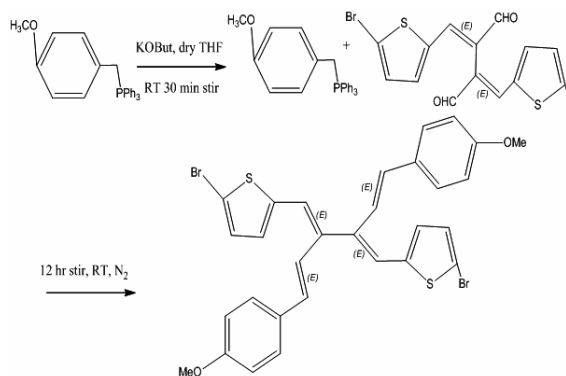
Synthesis of Dendralene



Scheme-4: Product 1.

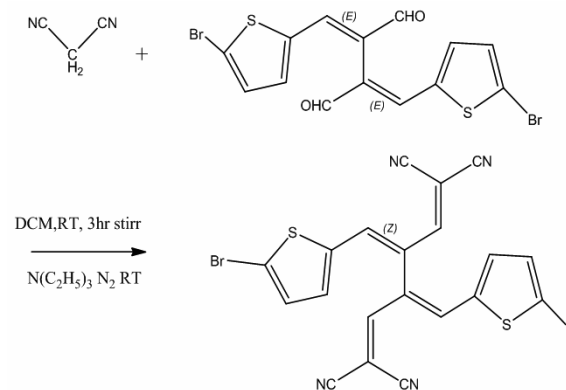
A mixture of 4-nitrobenzyltriphenylphosphonium bromide (Aldrich USA, 5.5 mmol, 2.62 g), dry tetrahydrofuran (BDH England, 100 ml) and potassium tert-butoxide (Aldrich USA, 6.56 mmol, 0.735g) was stirred together under nitrogen atmosphere at room temperature in a round bottom flask for 30 minutes. An orange suspension was obtained. At this stage 1,4-dithiophene-2,3-diformylbutadiene (1.82 mmol, 500 mg) was added and reaction was allowed to take its course for eighteen hours. A deep brown solution was observed in which all the reagents were completely dissolved. The mixture was added to water (100ml) and extracted with dichloromethane (3 × 150 ml), washed with saturated solution of sodium bicarbonate (3 × 100 ml) and distilled water (3 × 100 ml). The organic

layer was separated, treated with charcoal to decolorize it, dried over magnesium sulfate and filtered. The solvent was removed by rotary evaporator; a brown solid, compound was obtained. The fraction were differentiated by TLC spot check in dichloromethane and purified by silica column using dichloromethane as an eluent. ^1H -NMR in CDCl_3 and mass spectra (APCI) in acetone allowed identification of the desired product. 66.12%, with melting point 44-46 °C. The analytical data is placed in (Table-1).



Scheme-5: Product 2.

In a round bottomed flask 100ml of tetrahydrofuran, 4-methoxybenzylphosphonium bromide (synthesized in the lab) (3.471 mmol = 1.608 g) and potassium tert-butoxide (Aldrich USA, 4.165 mmol, 0.467 g) were added and stirred under nitrogen atmosphere at room temperature for 30 minutes. The color of the solution changed to orange. At this stage 1,4-dibromodithiophene-2,3-diformylbutadiene (1.157 mmol, 0.500 g) was added and reaction mixture was allowed to stir for more than twenty four hours under nitrogen at room temperature. The color of the reaction mixture was changed from orange to brown. The contents of the flask were poured into distilled water (40ml), extracted with dichloromethane (3×150 ml), washed with standard solution of sodium bicarbonate (3×150 ml) then with distilled water (3×100 ml). Organic layer (orange colored) was separated by separating funnel, dried over magnesium sulfate and filtered. The solvent was removed on rotary evaporator. An orange colored liquid of few ml was obtained which was allowed to crystallize overnight. The product was checked by TLC in DCM and in a mixture of dichloromethane: petroleum (2:1). The compound was purified by silica column chromatography using dichloromethane: petroleum ether (2:1) as eluent. The ^1H -NMR (in CDCl_3), mass spectra (APCI) (in acetone) data confirm the target compound. The net weight of the compound was 0.080 g and yield 10.8%. The analytical is placed in (Table-1).



Scheme-6: Product 3.

In a three necked round bottomed flask malanonitrile (Aldrich, Germany, 2.314 mmol,

0.153g) was dissolved in anhydrous chloroform (Aldrich, 20ml) under nitrogen atmosphere. Pyridine (Aldrich, 2.314 mmol, 0.187 ml) was added by syringe into the flask. The solution was stirred under nitrogen for half an hour at room temperature. This solution was added by syringe to a stirred suspension of 2,2'-dibromodithiophene-2,3-diformylbutadiene (1.157 mmol = 0.500 mg). The mixture was brought to reflux overnight for 24 hours under nitrogen. The contents of flask were then poured into distilled water (100 ml). The organic and aqueous layers were then separated by separating funnel. The organic layer was then washed with saturated solution of sodium bicarbonate (3 x 100 ml), then washed with brine (100ml) and distilled water (100ml). Organic layer was then separated, dried over magnesium sulfate, filtered and solvent was removed by rotary evaporator. A brown solid was obtained. The TLC spot check and purification by silica column was done in dichloromethane. The ¹H NMR (in CDCl₃) and mass spectra (APCI) (in acetone) data suggested that the reaction had worked well and desired compound was obtained. Yield was calculated as 26.96%. The analytical data is given in (Table-1).

Conclusion

The three new redox-active [4] dendralene compounds have been synthesized rightly. UV-Vis data indicate the poor cross- conjugation in these systems due to the push-pull intra molecular charge transfer (CIT) sequence from electron donor to acceptor group. The ¹H-NMR data resembles with trans conformers, showing dominating roll of electron acceptor nitro, methoxy and cyano benzene groups in conjugation, which is consistent with our previous studies on such a type of systems [20].

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