The synthesis and adsorption properties of some carbohydrate-terminated dendrimer wedges

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THE SYNTHESIS AND ADSORPTION PROPERTIES OF SOME CARBOHYDRATE-TERMINATED DENDRIMER WEDGES

Richard L. Ainsworth

A thesis submitted for the degree of Doctor of Philosophy at the University of Durham.

September 1997

Abstract

The Synthesis and Adsorption Properties of some Carbohydrate-Terminated Dendrimer Wedges

Richard Ainsworth PhD Thesis September 1997

A range of dendritic molecules that are designed to bind to a cotton surface has been synthesised. The architecture of the molecules allows the location of various functional, property modifying units at the focus and the attachment of recognition groups at the periphery of a dendritic molecule with wedge topology.

The synthesis and characterisation of dendrimer wedges up to the second generation using a divergent approach has been performed. These wedges are readily built up using a simple and efficient stepwise pathway from the central core, and surface recognising species are subsequently attached to the molecule utilising procedures developed in conjunction with Unilever Research Laboratories. Work has been carried out to assess their adsorption onto a cotton surface and the postulated adsorption mechanism is discussed.

Acknowledgements

There are many people I would like to thank for keeping me going during my time in Durham. Firstly, I want to take this opportunity to thank Jim Feast for his help and inspiration during the last 3 years. I must also thank my industrial supervisors Ezat Khoshdel, Andy Hopkinson and Jonathan Warr for their help and also the warm welcome I always received at Port Sunlight. I acknowledge the patience and expertise shown by Julia Say in running many of my n.m.r. spectra and the guidance that was given by Dave Hunter in the High Pressure Lab, who never panicked during meltdown. I'd also like to say cheers to Terry Harrison with his help with computers….. when he wasn't helping HMV that is.

I should also like to thank a number of people who have made my stay in Durham so enjoyable. A huge amount of respect is due to the lads of the TCE and the M-House People during undergraduate life. In no particular order: Andy Caddy, Mark Colling, Tim Roberts, AJ Pratt, Phil Birch (I thought I'd put AJ between the two of you!), Mike Calboutin and Stuart T. Perry. And cheers to Jeremy Bull for not quite managing to kill us in an RTA. There are many other people I have met and become friends with at University but space is restricted and I apologise for anyone I have not mentioned. Having been at St. Aidan's College for 6 years I wish to thank several members of staff who have made life there bearable. Kitty and Pauline get my thanks despite the inedible slop they invariably served under the guise of it being food. Also cheers to Theresa, Chris and Michelle for the craic, Mischief the Cat, the SCR drinks cabinet, and most of

the porters, even Ken. During my PhD I have had the dubious pleasure of being a member of the Senior Common Room which has been enlightening for many reasons, not least learning about the former Czechoslovakia. In particular, thanks go to the Spice Boys: Ste Coulson (Poor Spice), Jase Hall (Scoops Spice), Lee Hollingdale (Rude Spice), Dave Nettleton (Old Spice), Alan Outram (Capt. Jazz Spice), Mike Watson (Mad Spice), Phil Birch (again) (Beer'd-up Spice), Graham Glen (Tight Spice) and Mark Tookie (Greatly Exaggerated Spice)…. yeah, I've run out of ideas. Nice one, lads! Like it.

Working in the IRC has been fun for the most part and without some of the people there I doubt if I would ever have stayed sane or spud-free. Cheers to: Michael Jeschke (Pecky), our favourite Telly Tubby "Lard-Lard," for keeping the atmosphere bearable except with his feet; Rob Staples (Runner), for always being "there" when we needed him ("there" = at home having a quiet night in); Peter Dewhurst (Foggy), always up for C-Rock-ing, and for his punctuality; Andy Brown (no nickname) for losing at tennis and vying to become the new Runner/Splitter; Robin Harrison (better not, it'd only be rude) for being a bit good at chemistry; Gav Bown (Southern Puff) for his redefinition of Common English Usage and everyone else, especially those in my lab for putting up with me. Suits-you! Oooh! Cheers from Boyzone.

Lastly, I would like to thank my family for their love and support.

Rich.

Memorandum

The work reported in this thesis has been carried out at the Durham site of the Interdisciplinary Research Centre in Polymer Science and Technology between October 1994 and September 1997. This work has not been submitted for any other degree either in Durham or elsewhere and is the original work of the author except where acknowledged by means of appropriate reference.

Statement of Copyright

Financial Support

I gratefully acknowledge the funding provided by Unilever Research, Port Sunlight Laboratories, and the Interdisciplinary Research Centre in Polymer Science and Technology.

PREFACE

Preface

As the formulation technology of household detergents and personal products becomes more intricate, the development of cost effective specialised additives becomes increasingly important. Ensuring the binding of an active species to a specific surface is of prime importance as this will lead to the more efficient use of the active components of the formulation. At the moment expensive additives in detergents are not used as effectively as is desirable on the basis of technological efficiency, economic and environmental considerations. A substantial amount of agents, such as softeners and optical brighteners, are wasted as they are washed away and not deposited onto fabric surfaces where they are required. This work endeavours to begin to provide an understanding of a possible solution to this problem.

The field of dendrimer science is exploited to solve the problem. The architecture that is provided by a dendrimer wedge is used to carry both cotton-recognising end groups and a surface modifier (R-group). It is hoped that a structure of this type will adsorb onto a cellulose surface from aqueous solution (Figure I).

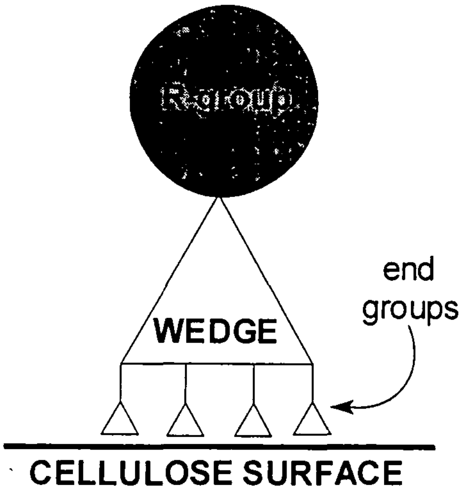
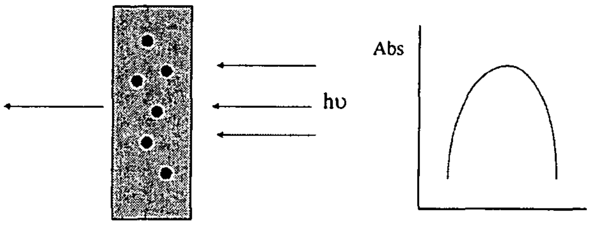
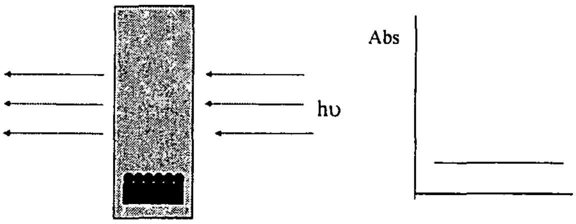


Figure I Schematic representation of the aims of the project.

The most important dendron focus described in this work is a group that absorbs in the UV region. It was hoped that there would be a detectable change in the absorption spectrum of an aqueous solution of surface active wedges carrying chromophores when some of the material was bound to a cotton surface introduced into the solution. The colour change could be monitored using a spectrophotometer, thus giving a relatively straightforward analytical probe for surface recognition. The concept is illustrated in Figure II.



No surface - material in solution
- strong absorption



Specific surface - material bound
- low absorption

Figure II Monitoring surface activity using UV-absorbing dendrimers.

The thesis begins with an introduction to the field of dendrimer science. How a dendrimer may be constructed, what properties they possess and what uses there are for such species are amongst the subjects discussed. Chapter 2 is concerned with the synthesis and characterisation of poly(propylene imine) dendrimer wedges using various core moieties. Chapter 3 discusses how these dendritic wedges may be modified to recognise a cotton surface and Chapter 4 analyses the surface activity of these species towards cotton, in water. Chapter 5 presents conclusions and offers suggestions for future work.

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CHAPTER 1

An Introduction to Dendrimers

1. An Introduction to Dendrimers

Synthetic polymers of novel topology are beginning to attract more interest from academic and industrial research groups alike as the demand for speciality materials rises, and as the control of a polymer's detailed structure and function becomes increasingly important.[1] Dendrimers, for example, have well-defined molecular weight, structure, size and organisation. This is in stark contrast to traditional polymers which display a distribution in molecular weight and structure, and whose properties are critically dependent on this distribution.

Dendrimers, from the Greek word *dendritic* = treelike, are monodisperse polymers. Typically, a dendrimer contains three basic units, the core moiety, C, the interior building blocks, B, and the terminal, or surface groups, S (Figure 1.1). The interior building blocks are arranged into layers, or *generations*, and a highly symmetrical, cascade structure results (Figure 1.2).[2] There are many examples in nature of such extensively branched species including trees, ferns and coral.

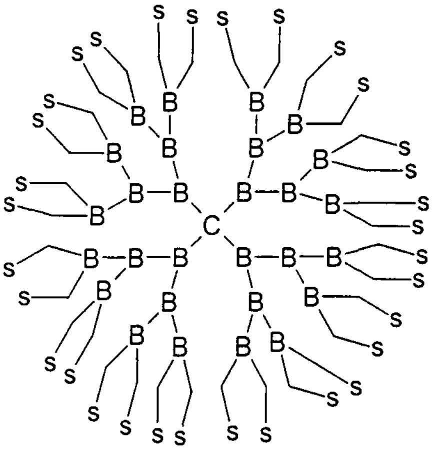


Figure 1.1 A diagram of an idealised dendrimer.

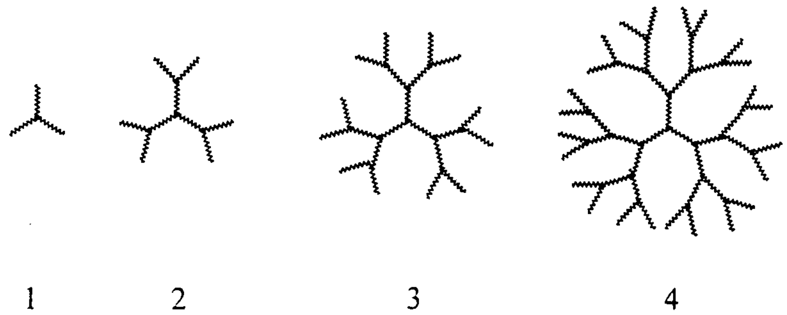


Figure 1.2 The concept of dendrimer generation.

The branching geometry of the various internal building blocks, coupled with steric constraints, means that dendrimers are three-dimensional objects rather than the two-dimensional structures shown in Figure 1.2. The dendrimer fills space adopting a globular formation and at high generations approximates to a spherical shape.

1.1 History

Current concepts in multi-branched polymeric species can be traced back to the work done by Flory.[3] In 1952 he produced a theoretical paper discussing the preparation of polymers from so-called AB_x monomers, monomers containing one type-A and two or more type-B functional groups. The A and B groups on different monomers have the ability to react with each other. Although substantially branched, such structures would not form cross-linked network systems and therefore stepwise growth could create novel branched polymeric materials (Figure 1.3).

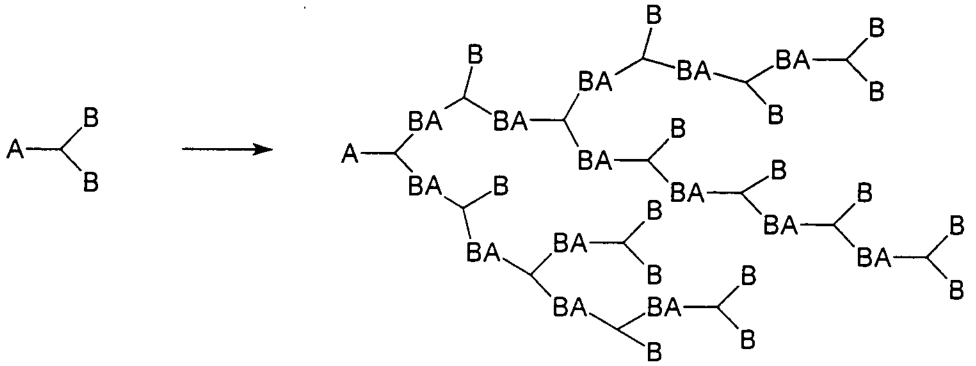


Figure 1.3 A schematic representation of an AB_2 -type polymerisation as described by Flory.[3]

In 1978, Vögtle reported the synthesis of *cascade* molecules whilst constructing compounds with large molecular cavities capable of Host-Guest interactions.[4] A monoamine was reacted with acrylonitrile producing two branches with nitrile-group termination. These were reduced to primary amines and, on repetition of the cyanoethylation and reduction steps, gave the poly(propylene imine) dendrimer wedge whose structure is shown in Figure 1.4.

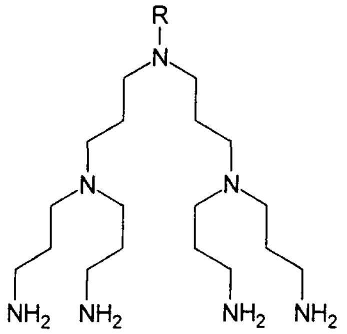


Figure 1.4 The Vögtle poly(propylene imine) dendrimer wedge.

The explosion of interest in this area of polymer chemistry began only as recently as the mid-eighties with two research groups, those of Newkome[5,6,7] and Tomalia,[8,9,10] reporting their early work. The term *dendrimer* was originally coined by Tomalia in 1985 when describing regularly branched poly(amidoamines) which are now more commonly known as Starburst™ (PAMAM) Dendrimers (Figure 1.5).

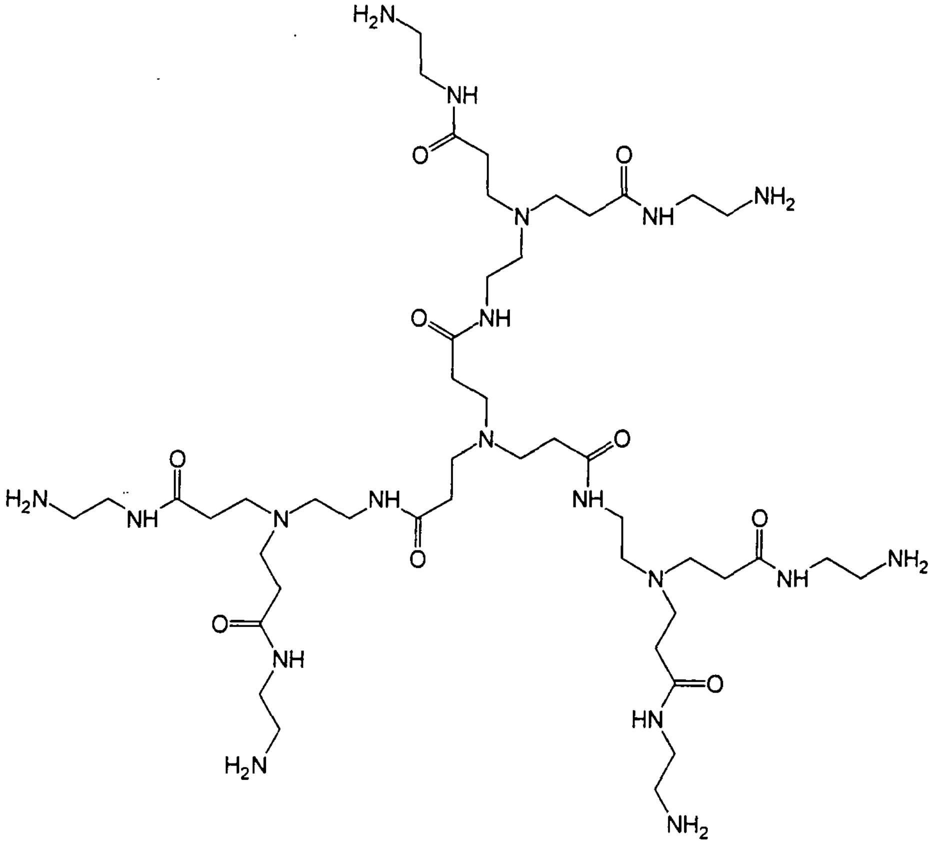


Figure 1.5 An example of Tomalia's Starburst™ (PAMAM) dendrimers.

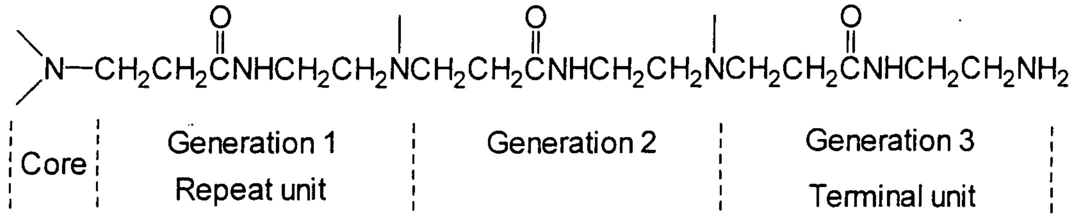
In the last ten years, the number of groups designing dendrimer syntheses, and the variety of dendrimers made, have grown immensely as their novel properties become more desirable and potential uses are found.

1.2 Nomenclature

A systematic nomenclature for dendrimers has been described by Newkome[11] who suggests that cascade polymers be described by the formula:

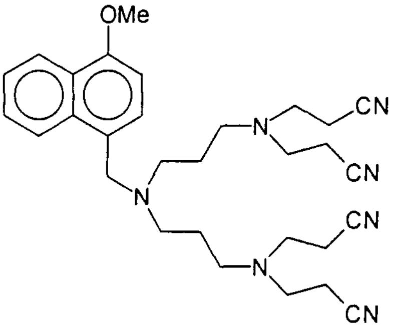
$$[\text{Core unit}][(\text{Repeat unit})^{G}_{N_b}(\text{Terminal unit})]_{N_c}$$

Where G is the number of generations, N_b is the branch multiplicity of the repeat unit (given that the same branch unit is present throughout the structure), and N_c is the multiplicity of branching from the central core referring to a dendrimer of the type:



$$\rangle N{-}CH_2CH_2\overset{O}{\overset{\|}{C}}NHCH_2CH_2\overset{|}{N}CH_2CH_2\overset{O}{\overset{\|}{C}}NHCH_2CH_2\overset{|}{N}CH_2CH_2\overset{O}{\overset{\|}{C}}NHCH_2CH_2NH_2$$

Using this notation, a dendrimer with the structure shown below is described as $[4\text{-methoxy-}C_{10}H_6CH_2N][(CH_2CH_2CH_2N)^{1}_{2}(CH_2CH_2CN)]_2$.



Tomalia[8] describes his dendrimers by the formula:

$$[\text{Core unit}]\left[(\text{Repeat unit})_{\frac{N_r^G-1}{N_r-1}}(\text{Terminal unit})_{N_r^G}\right]_{N_c}$$

Where N_c is the core multiplicity, N_r is the repeat unit multiplicity and G is the number of generations. So, for example, a fifth generation PAMAM dendrimer with an ethylenediamine core can be described as:

$$[\mathrm{NCH_2CH_2N}]\left[(\mathrm{CH_2CH_2CONHCH_2CH_2N})_{(2^5-1)}\mathrm{H}_{2^5}\right]_4$$

Clearly these proposed nomenclatures are complicated, and these notations have not been widely adopted. Thus, other authors have chosen to use various shorthand nomenclatures to describe their dendrimers. Fréchet[12] defines his polyether dendrimers as a function of the number and nature of chain ends, the generation number and the functionality of the core. Hence, a fourth generation dendrimer, consisting of four layers of ether-linked building blocks, 16 cyano terminal groups and a single hydroxy group at the focal point (Figure 1.6), is described as *polyether* $(CN)_{16}$*-[G-4]-OH.*

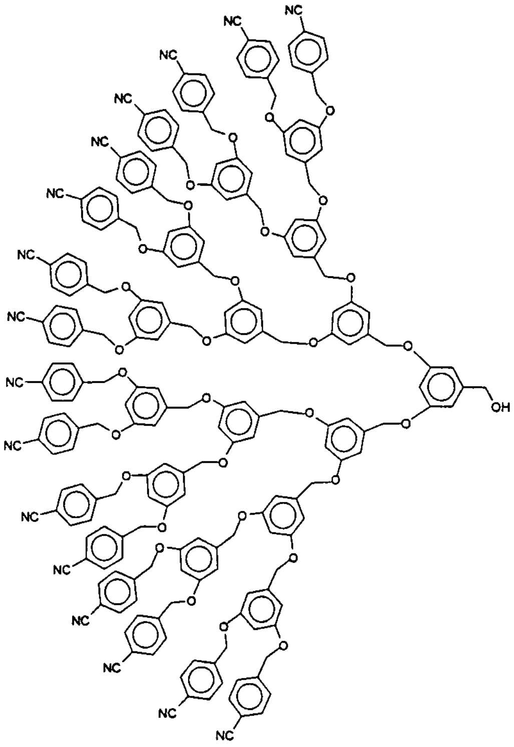


Figure 1.6 Fréchet's dendron, *polyether* $(CN)_{16}$*-[G-4]-OH.*

Meijer describes his poly(propylene imine) dendrimers in an even briefer shorthand notation. A dendrimer wedge built onto the end of a polystyrene chain[13,14] with 8 NH_2 terminal groups (Figure 1.7) is described as PS-*dendr*-$(NH_2)_8$.

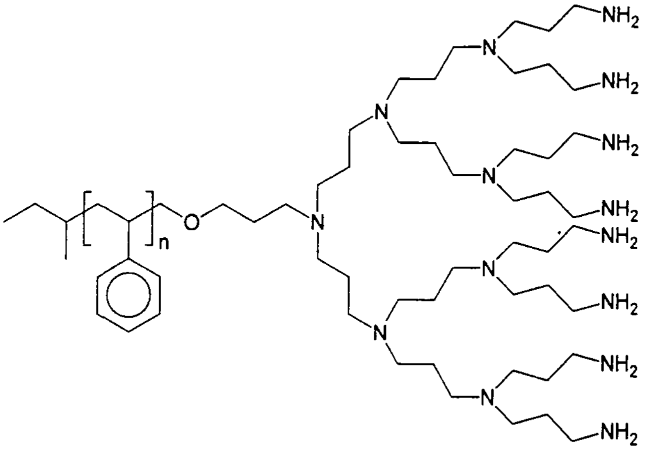
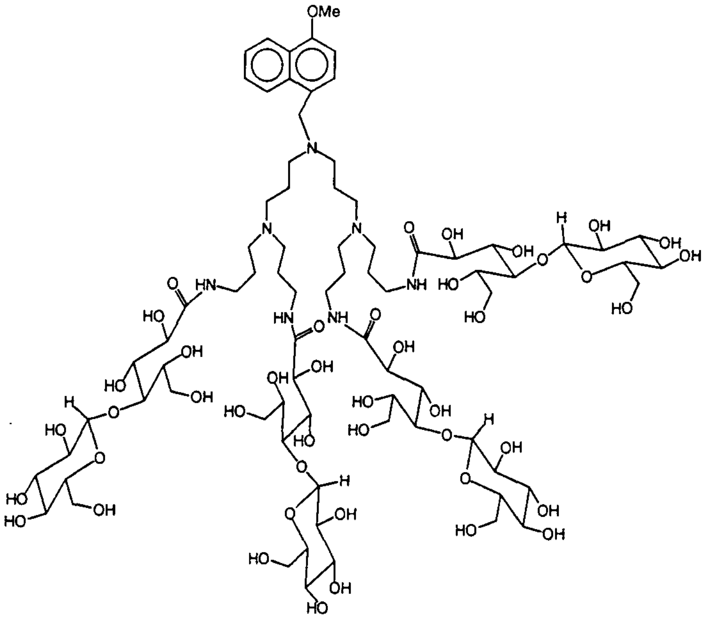
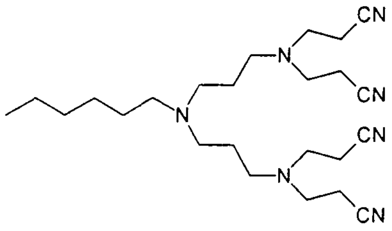


Figure 1.7 Meijer's macromolecular amphiphile, PS-*dendr*-$(NH_2)_8$.

This shorthand proves to be useful in describing the dendritic architectures in this work. Hence a poly(propylene imine) dendrimer wedge with a UV active species at the focus and 4 carbohydrate groups at the periphery is described as *UV-dendr-(carb)$_4$*, and a dendrimer wedge constructed using hexylamine as the focus with 4 cyano groups at the termini is described as *Hex-dendr-(CN)$_4$*; both these structures are shown in Figure 1.8.



UV-dendr-(carb)$_4$



Hex-dendr-(CN)$_4$

Figure 1.8 Nomenclature for dendrimers described in this work.

To avoid any ambiguity and/or difficulty, the structures are drawn out in full and labelled as they arise in the thesis, and a key in the form of a bookmark has been constructed to aid the reader.

1.3 Approaches to synthesis

There are essentially two distinct routes for making dendrimers. Tomalia[9,10,11] and Newkome[6,7,8] employed the first, a *divergent* strategy, in the mid-eighties. More recently, Hawker and Fréchet,[12,15,16] and Miller and Neenan[17,18] have devised a *convergent* strategy. The fundamental difference between these two synthetic strategies is the direction of growth. Synthesis of dendrimers via divergent routes starts at a polyfunctional core and proceeds outwards as layer, upon layer, of building blocks are attached in a protection/deprotection iterative procedure. This process leads to ever-larger dendritic molecules with increasing numbers of chain ends. In contrast, convergent growth begins at what will eventually be the outer extremity of the dendrimer and proceeds inwards via a series of *dendron wedges* of increasing size that are eventually attached to the core molecule. Each process has various advantages and disadvantages as compared to the other. However, as is the case for regular polymers, to enable uniform dendrimers to be synthesised it is essential that, for either process, reactions proceed to completion in high yields, with no side reactions.

1.3.1 Divergent approach to dendrimer synthesis

In the original method, divergent synthesis (Figure 1.9), growth starts at a central core molecule by reaction with two or more protected branching units. The protecting moieties are subsequently removed to give reactive terminal functional groups. These may be coupled to further branching units and, with repetition of these steps, regular dendrimers are prepared.

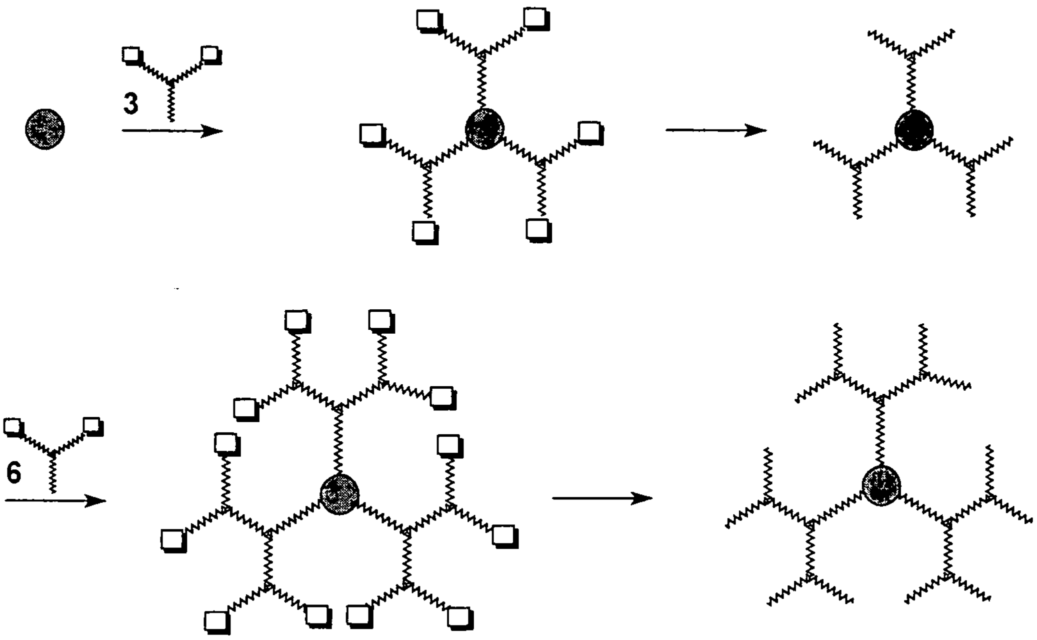


Figure 1.9 A diagrammatic representation of the divergent approach to dendrimer synthesis.

The first syntheses of dendritic macromolecules all employed the divergent route. The first reported synthesis of a dendrimer, by Vögtle,[4] utilised a divergent strategy using a series of Michael additions to acrylonitrile (A) and subsequent reduction steps (B) to build a dendrimer (Figure 1.10). In the representation of divergent growth in Figure 1.9, the nitrile-groups can be considered to be protected primary amines. The Michael reaction proceeded without too many problems, however, on reduction of the nitrile groups with cobalt (II) chloride hexahydrate and sodium borohydride, side reactions seriously affected growth.

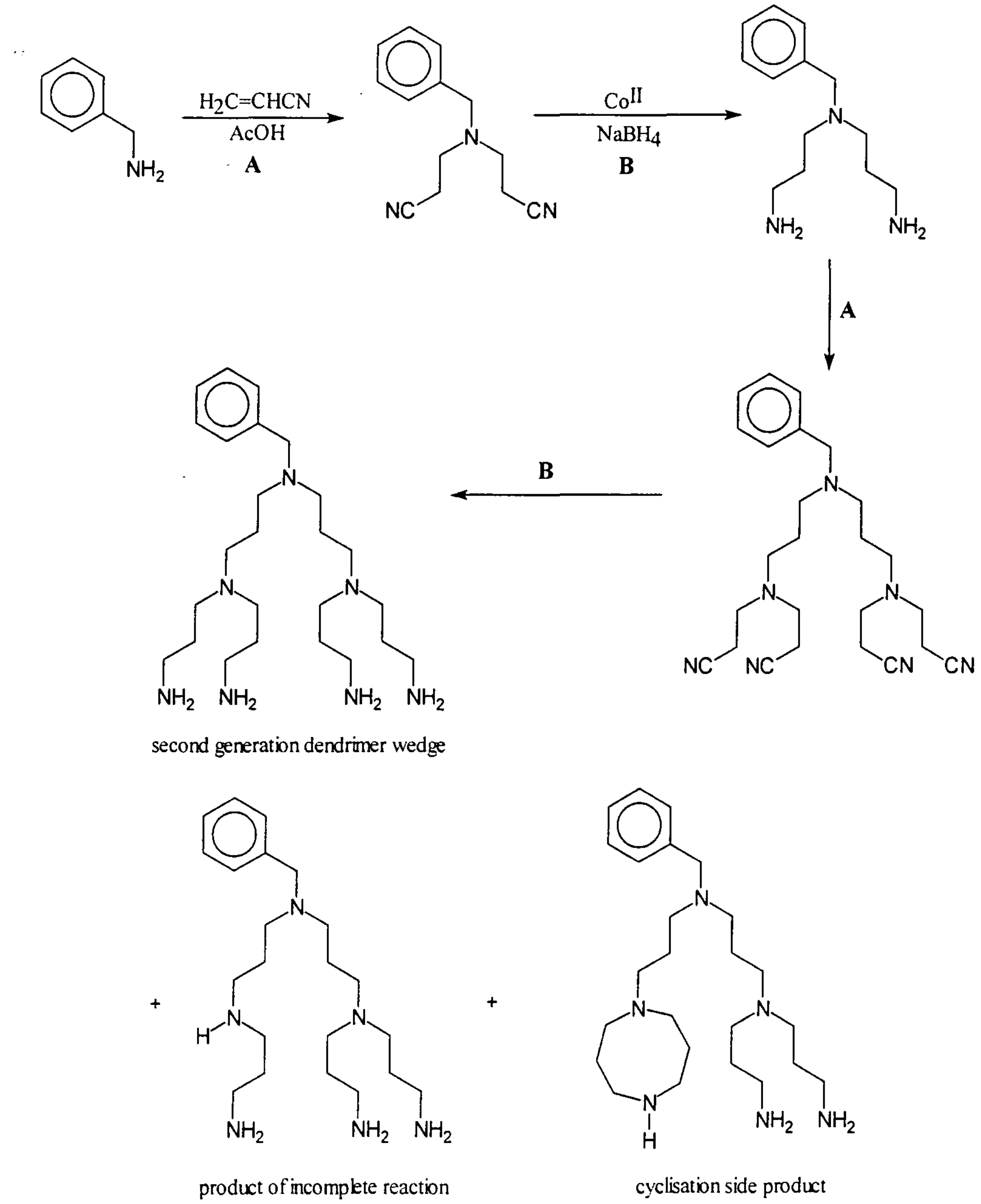


Figure 1.10 Vögtle's divergent strategy for dendrimer synthesis.

Tomalia also employed a Michael reaction in his divergent strategy when making poly(amidoamine) (Starburst™ PAMAM) dendrimers (Figure 1.11).[8,9,10] He reacted a trifunctional core molecule, ammonia, with methyl acrylate to form a triester (Step A). Regeneration of the reactive N-H groups was achieved by amidation using excess 1,2-diaminoethane (Step B). Repeating these two steps, removing the large excess of reagents at each step, larger and larger dendrimers, up to the 10th generation, could be made. Using exacting experimental and purification procedures, it is possible to synthesise dendrimers on a kilogram scale and these are now commercially available.

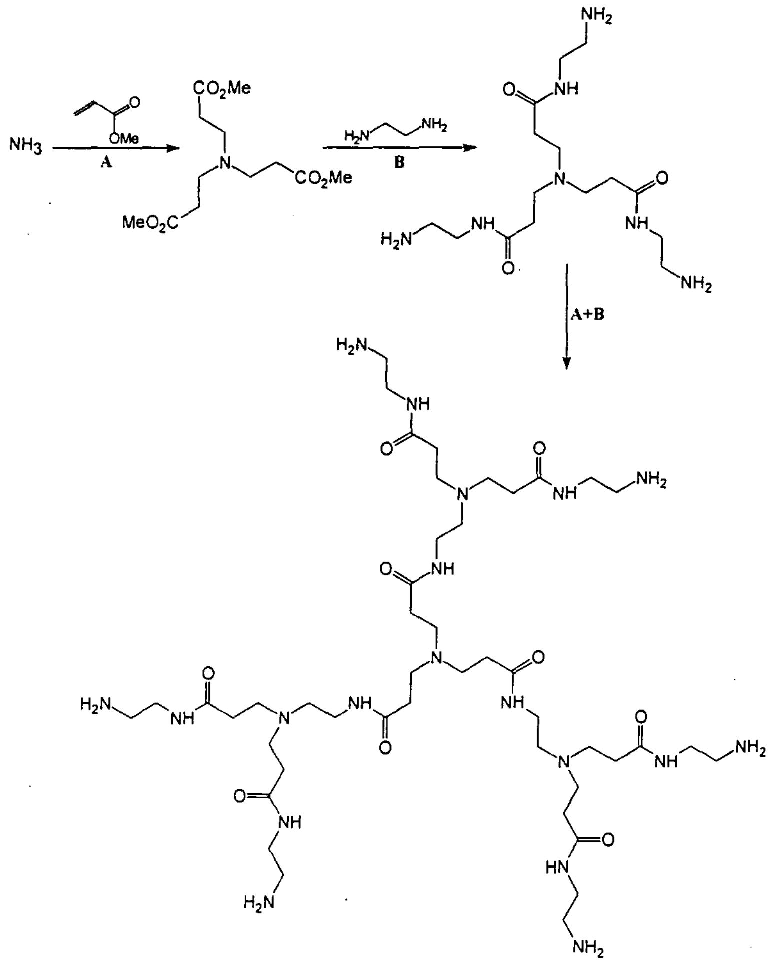


Figure 1.11 Tomalia's divergent route to Starburst™ (PAMAM) dendrimers.

Newkome also used a divergent approach when synthesising water soluble poly(ether amides) (Figure 1.12).[5,6,7] Just like Tomalia's route, growth started at a trifunctional core, however, Newkome utilised a building block with a branching factor of 3. This triples the number of end-groups after each generation and hence quickly increases the branching density. The core was reacted with chloroacetic acid and converted to the ester, followed by reduction and tosylation. The tosylate (A) was converted to an ester (B), which, on amidation with tris(hydroxymethyl)aminomethane, produced the required dendrimer (C). Newkome called these structures *arborols*.

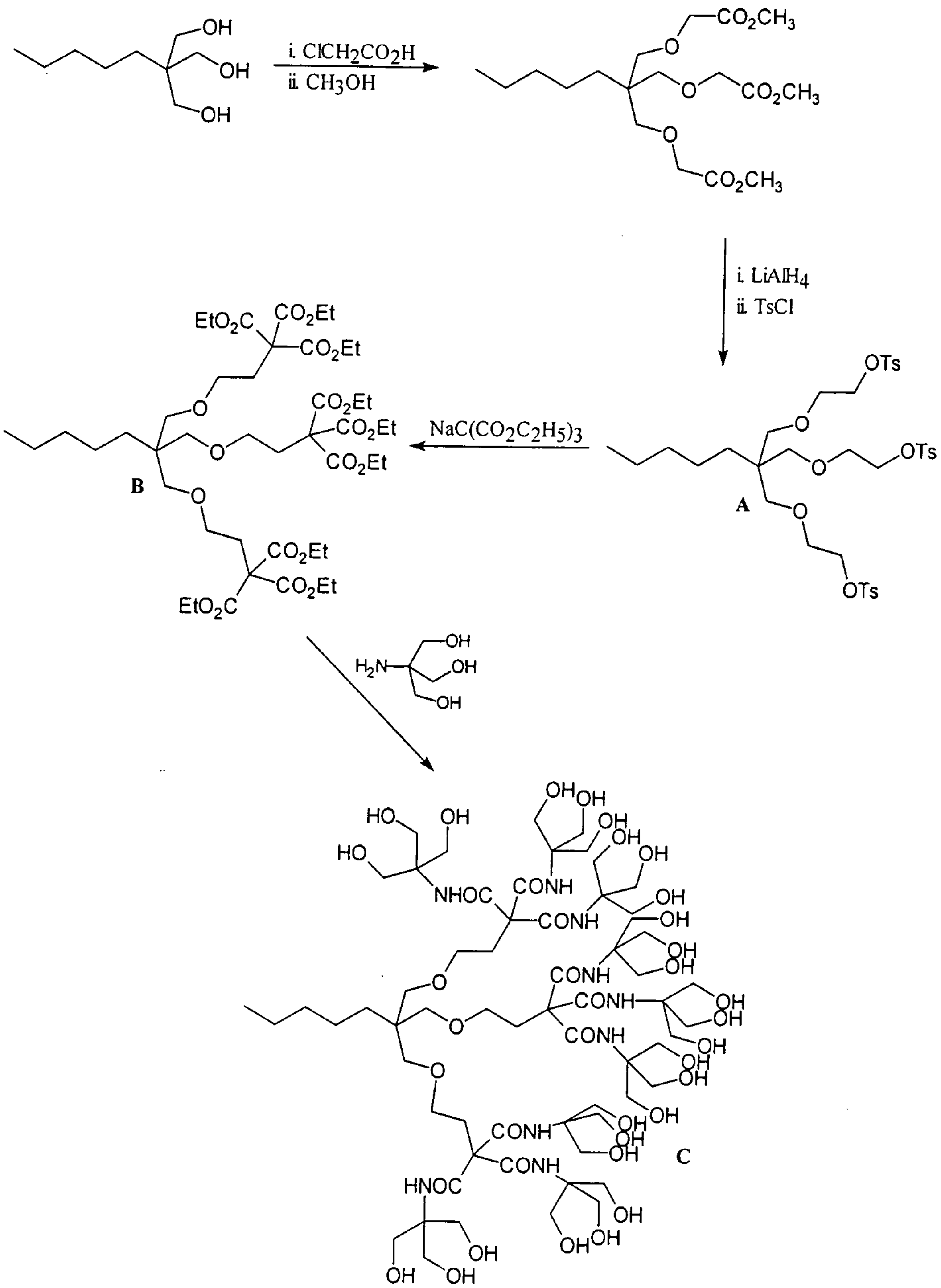
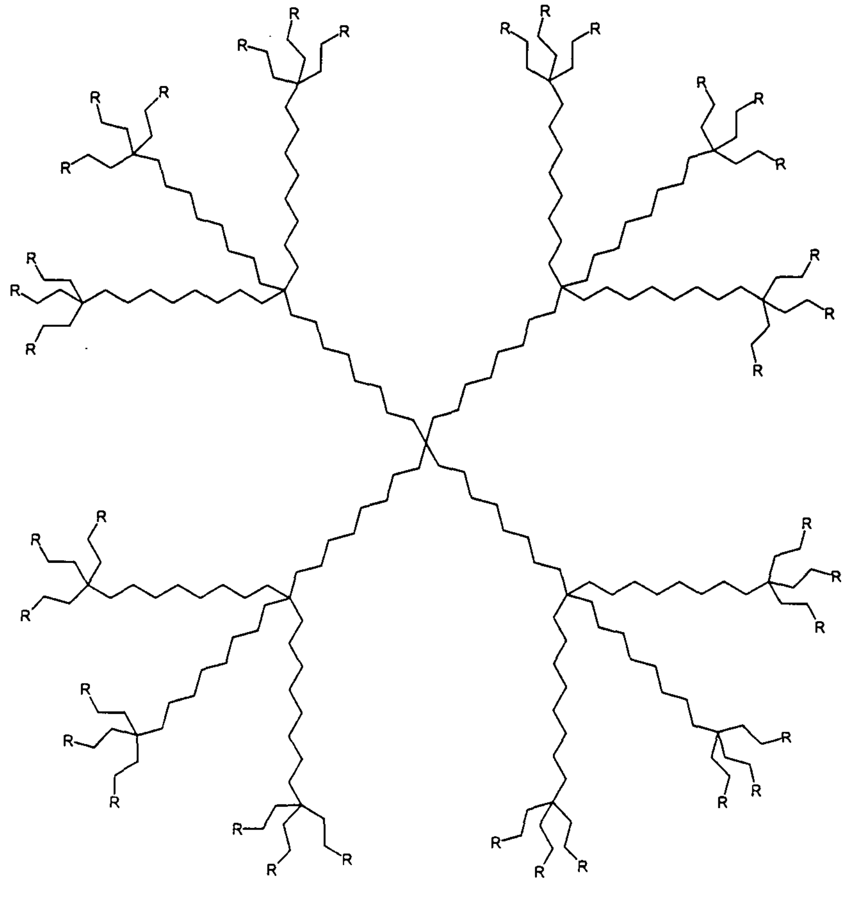


Figure 1.12 Newkome's arborol synthesis.

Using the divergent approach, a large number of dendritic structures, incorporating a variety of building blocks, have been synthesised. Newkome also prepared an alkyl carbon cascade polymer that possessed the characteristics of a globular micelle.[19] The dendrimer incorporated a branching factor of 3 and a core that had a functionality of 4 (Figure 1.13). The synthetic strategy was somewhat complicated, for example the tetra-functional core was obtained in a relatively low yield from an eight step synthesis.



R= CH_2OH or CO_2H

Figure 1.13 Newkome's alkyl carbon dendrimer.

Vögtle has continued his efforts in the field of dendrimers synthesising dendritic poly(aryl sulphones) using a variety of core moieties, most interestingly an aza-crown, hexaza-1,4,7,10,13,16-cyclooctadecane, which has a core functionality of 6 (Figure 1.14).[20,21]

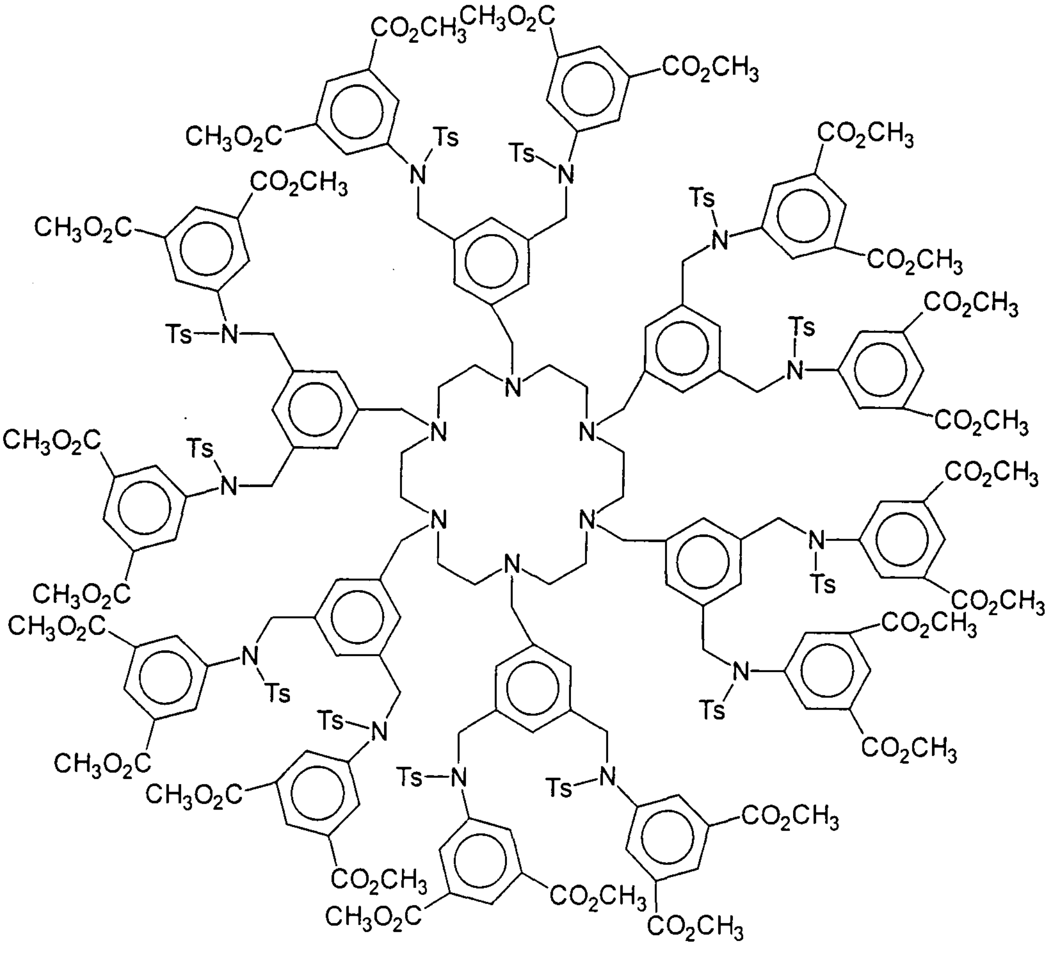


Figure 1.14 A crown as a dendritic core.

When building dendrimers via the divergent approach, it is conceded that defect structures may be apparent at large generations. However, it is also recognised that these defects will have little or no effect on the dendrimer's final properties.

1.3.2 Convergent approach to dendrimer synthesis

Although the divergent route has been utilised very successfully in the synthesis of dendrimers, it can lack versatility. For example, it is not possible to attach more than one kind of end-group to the periphery of the dendrimer. The convergent route, which was first introduced by Hawker and Fréchet,[12,15,16] overcomes such limitations. Construction begins at what will eventually be the outer surface of the dendrimer and proceeds inwards. A series of dendritic wedges, or dendrons, are constructed which are protected at the focus. With removal of this protecting group, the dendrons can be attached to a central core molecule (Figure 1.15).

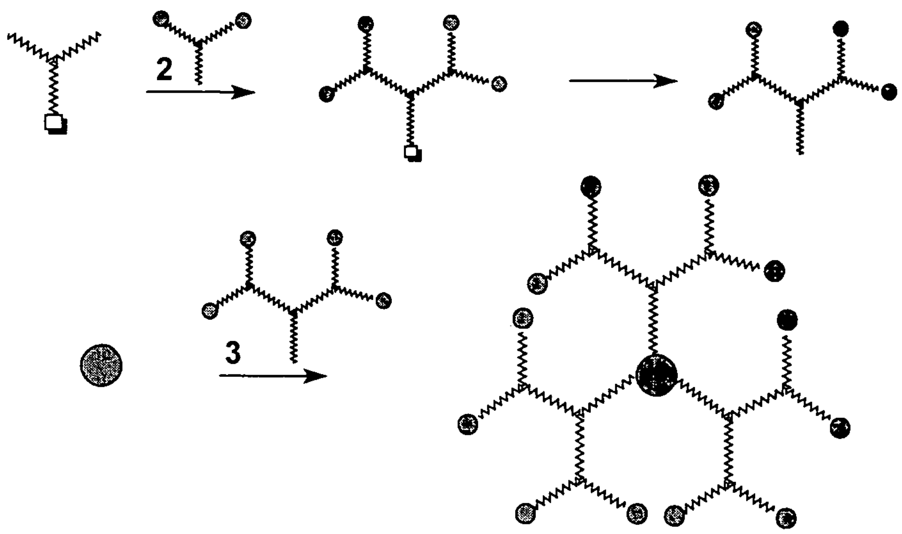


Figure 1.15 A diagrammatic representation of the convergent approach to dendrimer synthesis.

This strategy is more versatile since, with careful control of reactions, it is possible to attach different types of dendrons to the same core. These dendrons can be constructed with different building blocks, to give dendritic *block copolymers*,[22] or have different end-groups. They can also be attached to a variety of dendritic cores or cores of different functionality.

Using the convergent approach, Fréchet built polyether dendrimers with molecular weights in excess of 10,000 in excellent yields (Figure 1.16). The dendrimers were based on a 3,5-dihydroxybenzyl alcohol monomer unit, where the benzyl alcohol could be regarded as the protected focus. 3,5-Dihydroxybenzyl alcohol was refluxed in acetone for 48 hours with one equivalent of the benzylic bromide. Optimum reaction conditions required the use of potassium carbonate and 18-crown-6 (Step A). Deprotection of the dendron was carried out using carbon tertabromide and triphenylphosphine (Step B). Dendrons of this type were attached to a trifunctional core, 1,1,1-tris(4'-hydroxy-phenyl)ethane, to produce a much larger dendrimer using the same reaction conditions as those used in Step A. It is possible to have different functional groups in the para position of the outer benzene ring, such as Br and CN groups.[23] Further evidence of versatility is that these dendrons can be attached to many other core molecules, amongst them, buckminsterfullerene[24] and large phenol-terminated dendrimers,[25] known as *hypercores*.

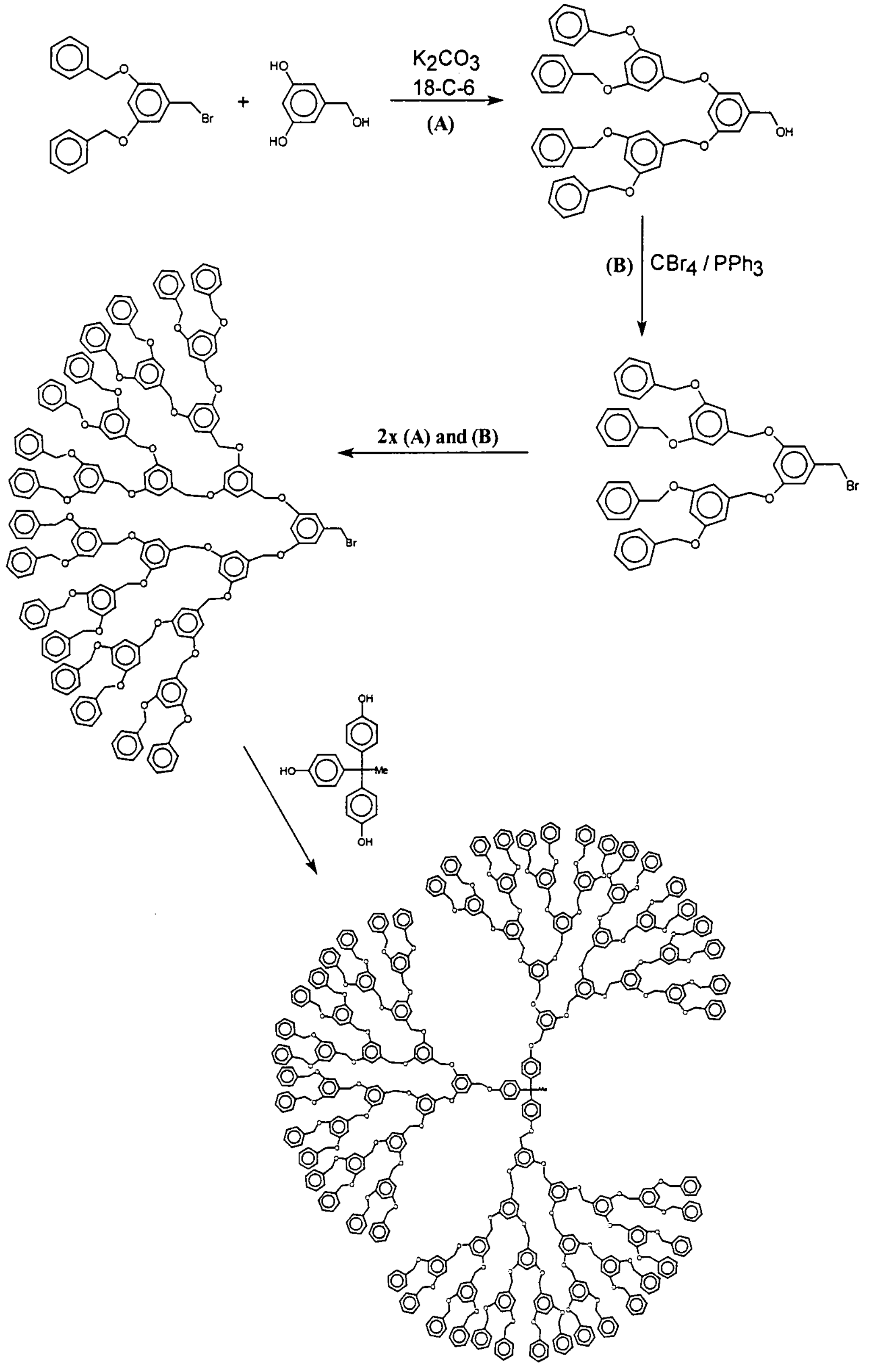


Figure 1.16 Fréchet's convergent approach to dendrimer synthesis.

Shortly after Hawker and Fréchet published their convergent strategy, Miller and Neenan reported the synthesis of an all-carbon poly(phenylene) dendrimer,[17,18] also using a convergent strategy (Figure 1.17). The strategy for linking benzene rings depended upon the Suzuki coupling of aryl boronic acids with aryl halides which was catalysed by $Pd(PPh_3)_4$ (Step A). The aryl trimethylsilane was then transformed into an arylboronic acid by treatment with BBr_3 followed by hydrolysis (Step B). The arylboronic acid dendrons were attached to a 1,3,5-tribromobenzene core using the same reaction conditions as those used in Step A and the desired product was purified by chromatography and crystallisation.

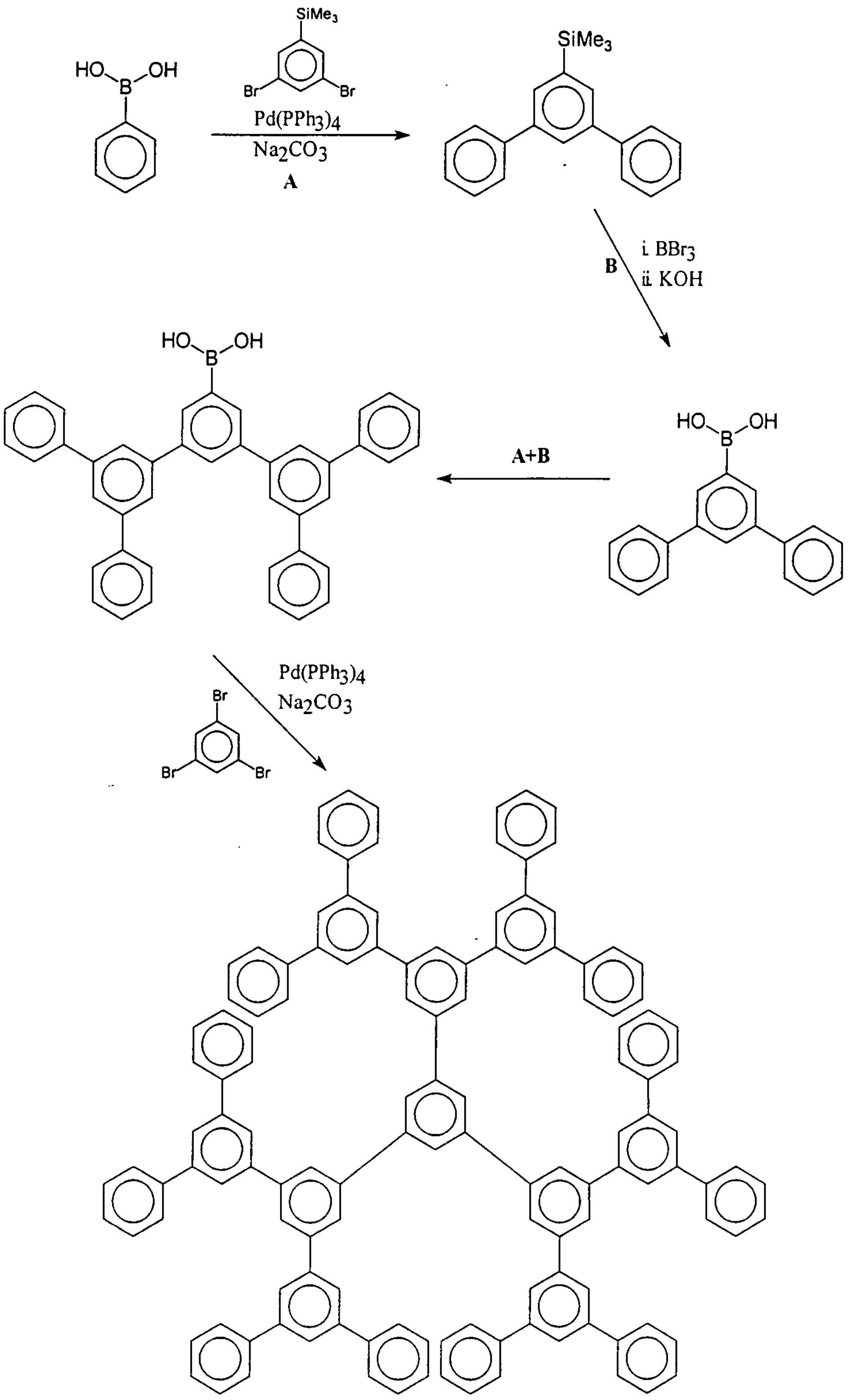
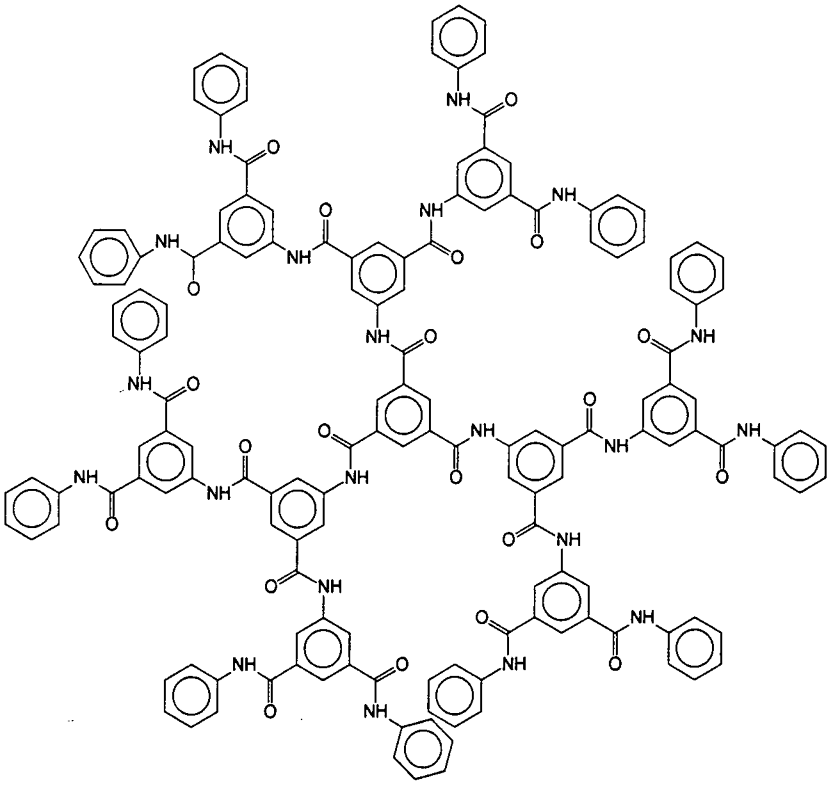
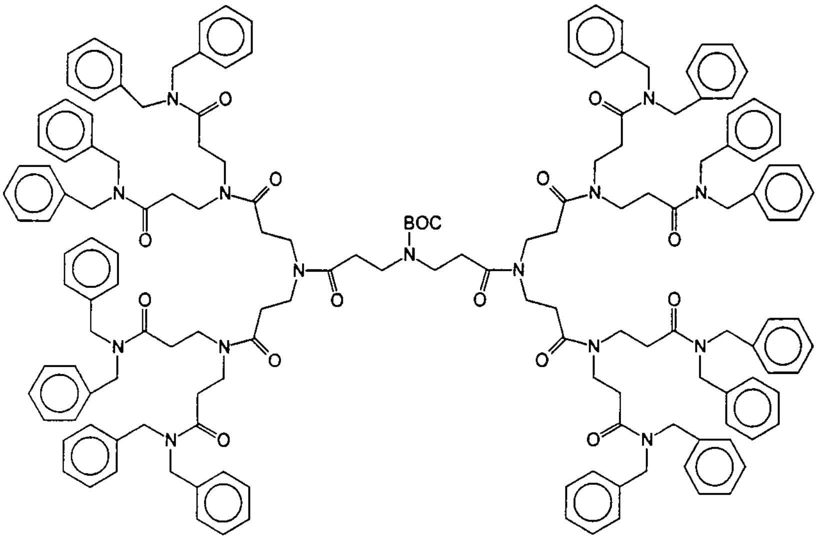


Figure 1.17 Miller and Neenan's convergent strategy to poly(phenylene) dendrimers.

Many other types of dendrimers have been built using the convergent route. Feast[26] and Fréchet[16] have reported 2 different dendritic polyamides (Figure 1.18).



A dendritic polyamide prepared by Feast



A dendritic polyamide prepared by Fréchet

Figure 1.18 Polyamide dendrimers.

Various aryl ester dendrimers have been prepared, an example of which is shown in Figure 1.19.[27,28,29]

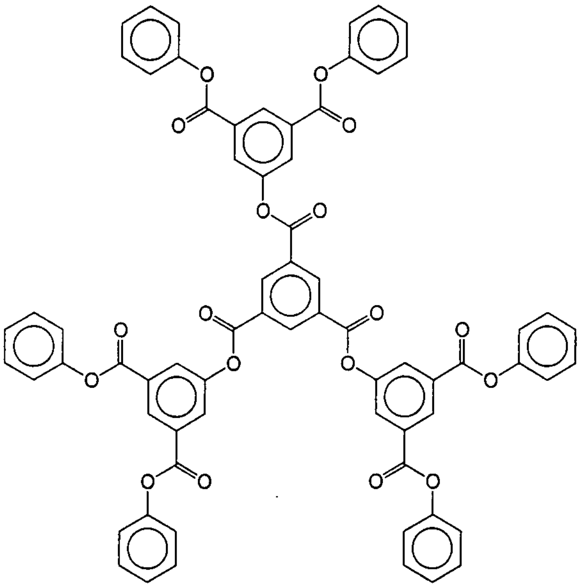


Figure 1.19 A dendritic polyester prepared using a convergent route.

Other dendrimers prepared using a convergent strategy include poly(ether ketones)[30] (Figure 1.20) and phenyl acetylenes (Figure 1.21).[31,32]

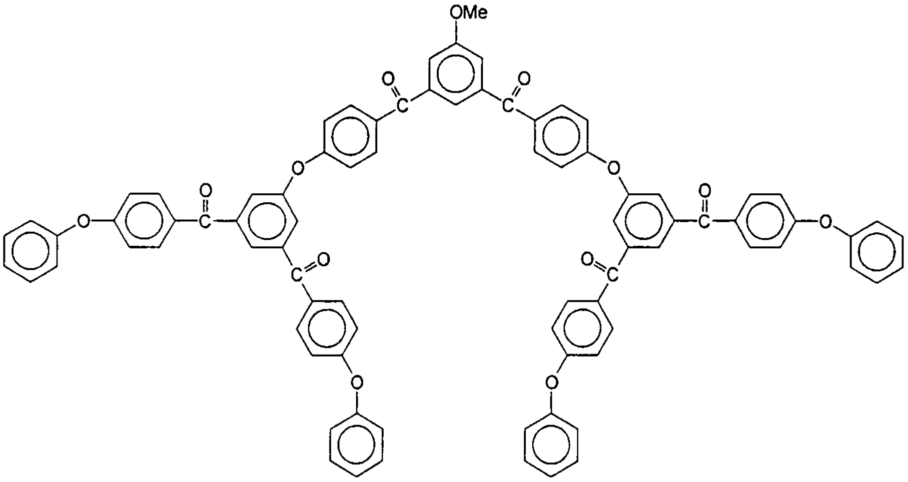


Figure 1.20 A poly(ether ketone) dendrimer.

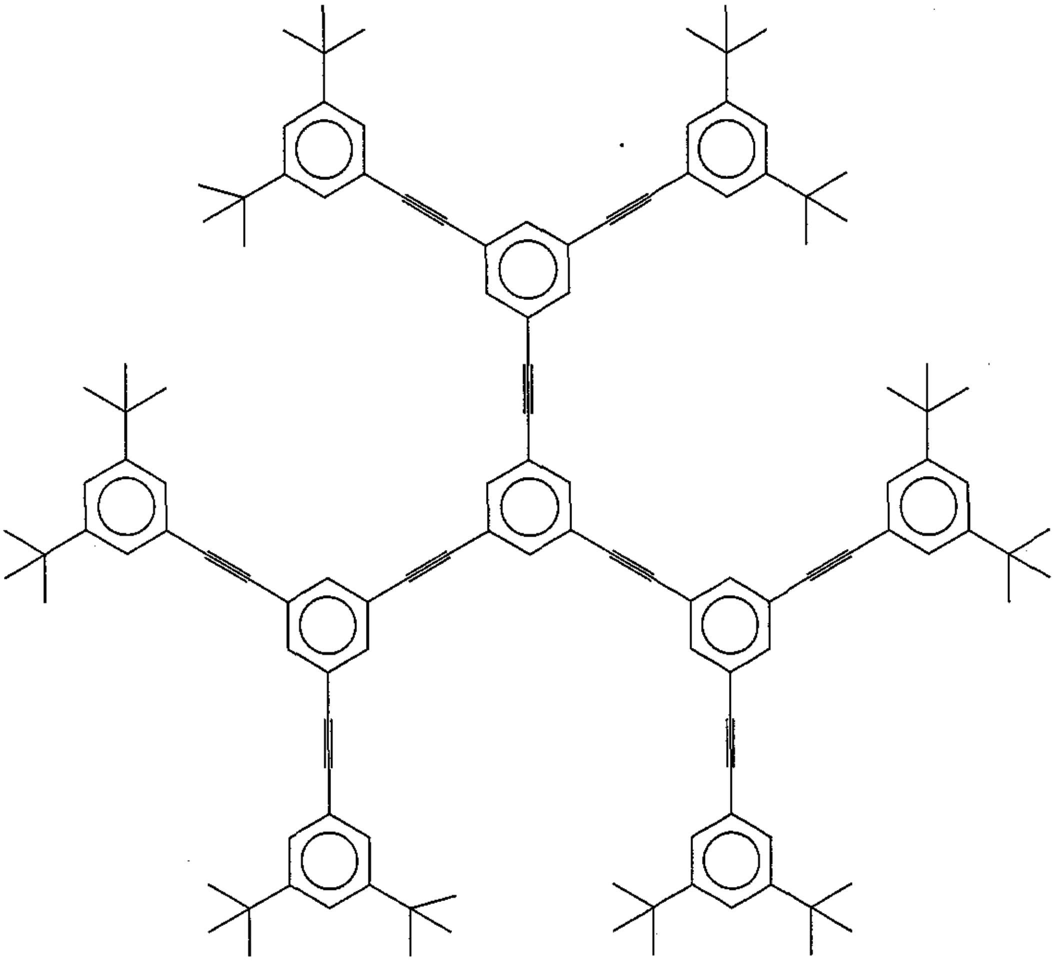


Figure 1.21 A phenylacetylene dendrimer.

1.3.3 A comparison of the divergent and convergent approaches to dendrimer synthesis

If the synthesis of very large dendrimers is required, then the divergent approach is preferred to the convergent route. This is because it is difficult to attach several large dendritic wedges to a central core using the convergent approach, due to steric hindrance. However, dendrimers have very congested surfaces and this leads to incomplete reactions when using the divergent route, as a consequence defects in the structure appear. Therefore, if dendrimers are required without any defects, then the convergent route is the superior approach since dendrons are more easily synthesised without defects. The convergent approach is also preferred if dendritic block copolymers are desired.

When considering manufacturing dendrimers in large quantities, the divergent route is more useful. This is because, when synthesis begins, only a small amount of material exists, and this rapidly increases in weight through the generations. Also, with careful choice of reagents and conditions, purification at each stage is not necessary. The convergent route is less suitable for large-scale synthesis of dendrimers since large amounts of material require purification during the synthesis.

Meijer, working with colleagues in DSM, described an excellent example of a large batch process, using carefully chosen conditions.[33] Using the divergent route of iterative Michael addition of amine to acrylonitrile followed by nitrile reduction designed by Vögtle,[4] synthesis of poly(propylene imine) dendrimers was achieved on a multi-kilogram scale (Figure 1.22). Water was used as the solvent for both the Michael reaction, and the reduction step. Careful control of the reduction conditions, using Raney cobalt as the catalyst, limits side reactions leading to cyclisation and this removes the need for purification between each step.

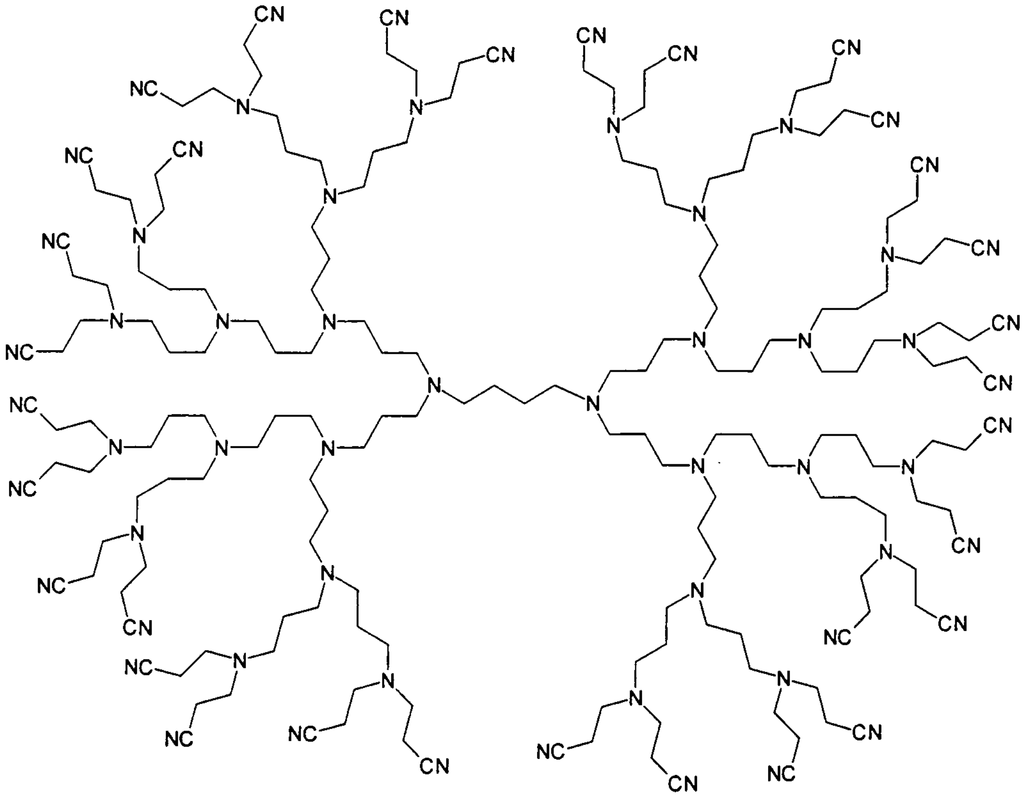
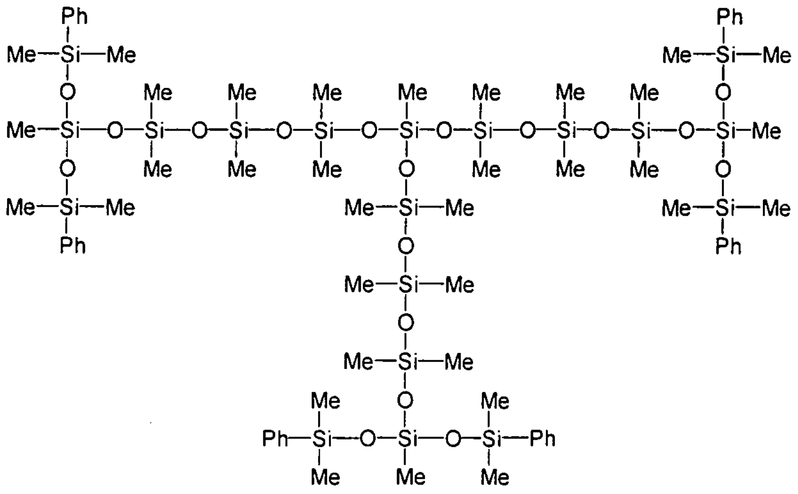


Figure 1.22 A dendrimer produced by Meijer on a pilot plant scale.

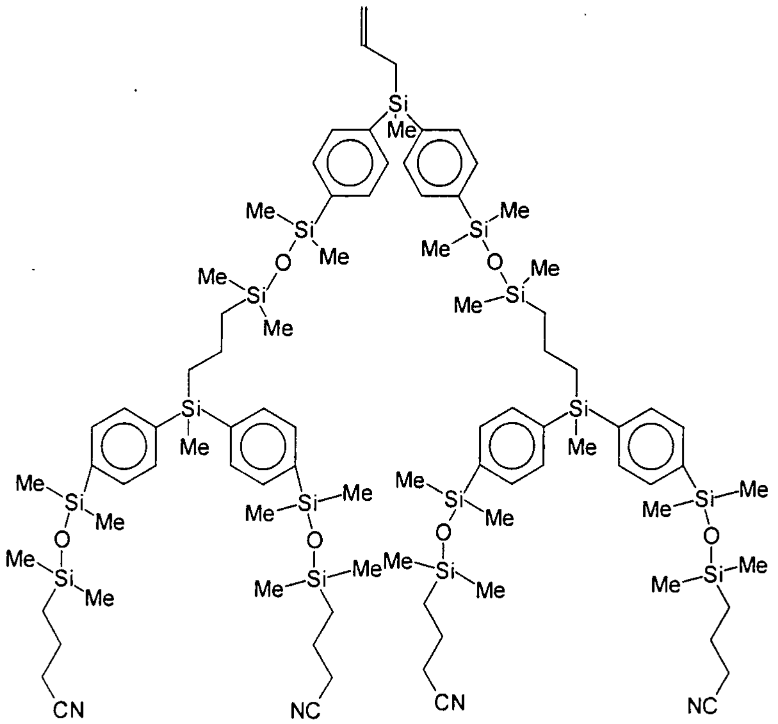
1.4 Novel dendrimer architectures

1.4.1 Dendrimers containing Silicon and Phosphorous

A variety of polysiloxane and silicone dendrimers have been synthesised. A general strategy for the synthesis of oligosiloxane and silicone structures was reported in 1990.[34] Since then, many dendrimers of this type have been made using both a divergent[35] and a convergent[36] strategy (Figure 1.23).



Constructed via a divergent strategy



Constructed via a convergent strategy

Figure 1.23 Polysiloxane dendrimers.

Silane dendrimers have also been prepared using a divergent strategy. Figure 1.24 illustrates the type of product obtained.[37,38]

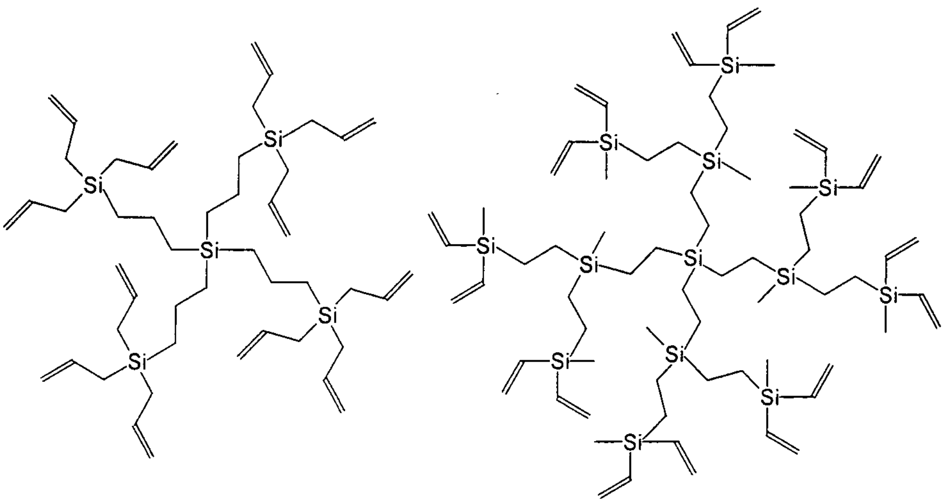


Figure 1.24 Silane dendrimers.

There are fewer reports of phosphorous containing dendrimers, however, cascade molecules have been synthesised in which the core and branch points of the cascade structure are quaternary phosphonium ions; an example is shown in Figure 1.25.[39,40]

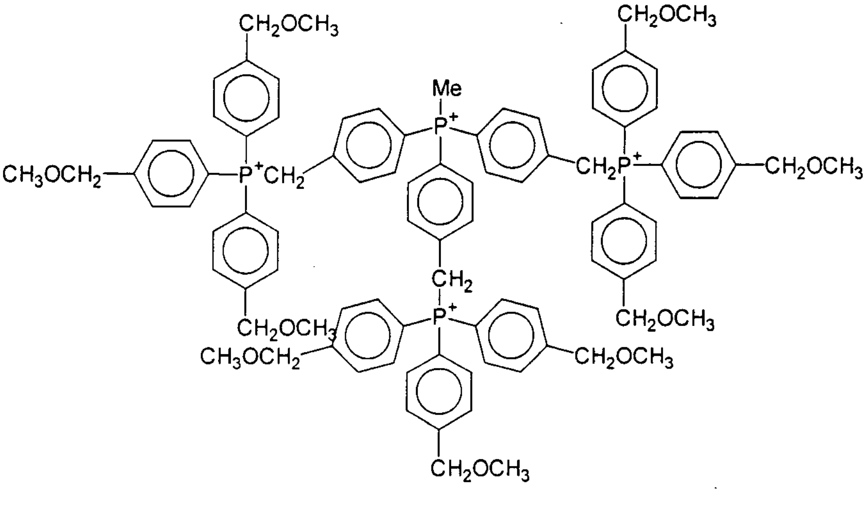


Figure 1.25 A phosphonium cascade molecule.

There are even fewer reports of neutral phosphorus-containing dendrimers. However, neutral phosphorous dendrimers have been synthesised in high yields, up to the fourth generation; Figure 1.26 shows an example.[41] These dendrimers can be used as multidentate ligands for palladium, platinum and rhodium.[42]

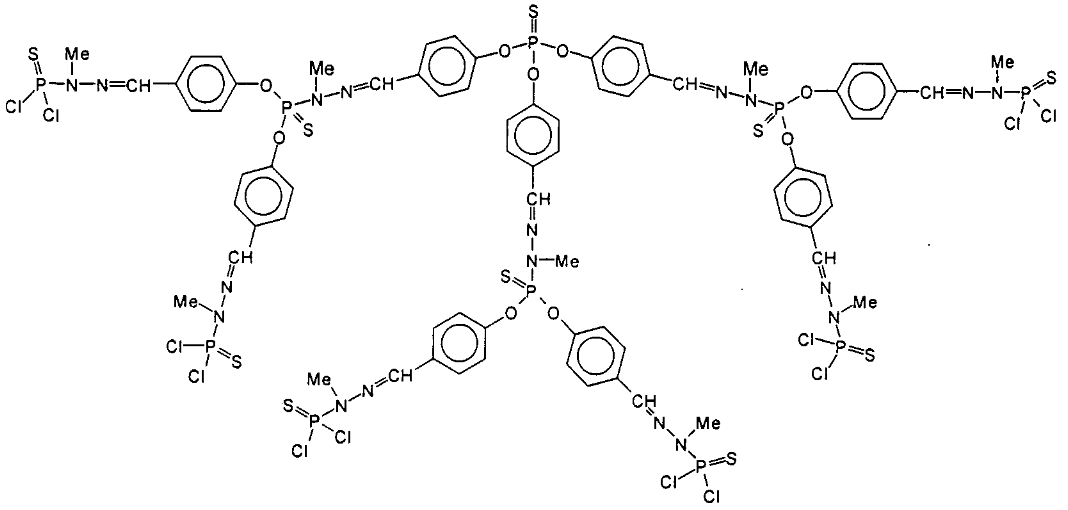
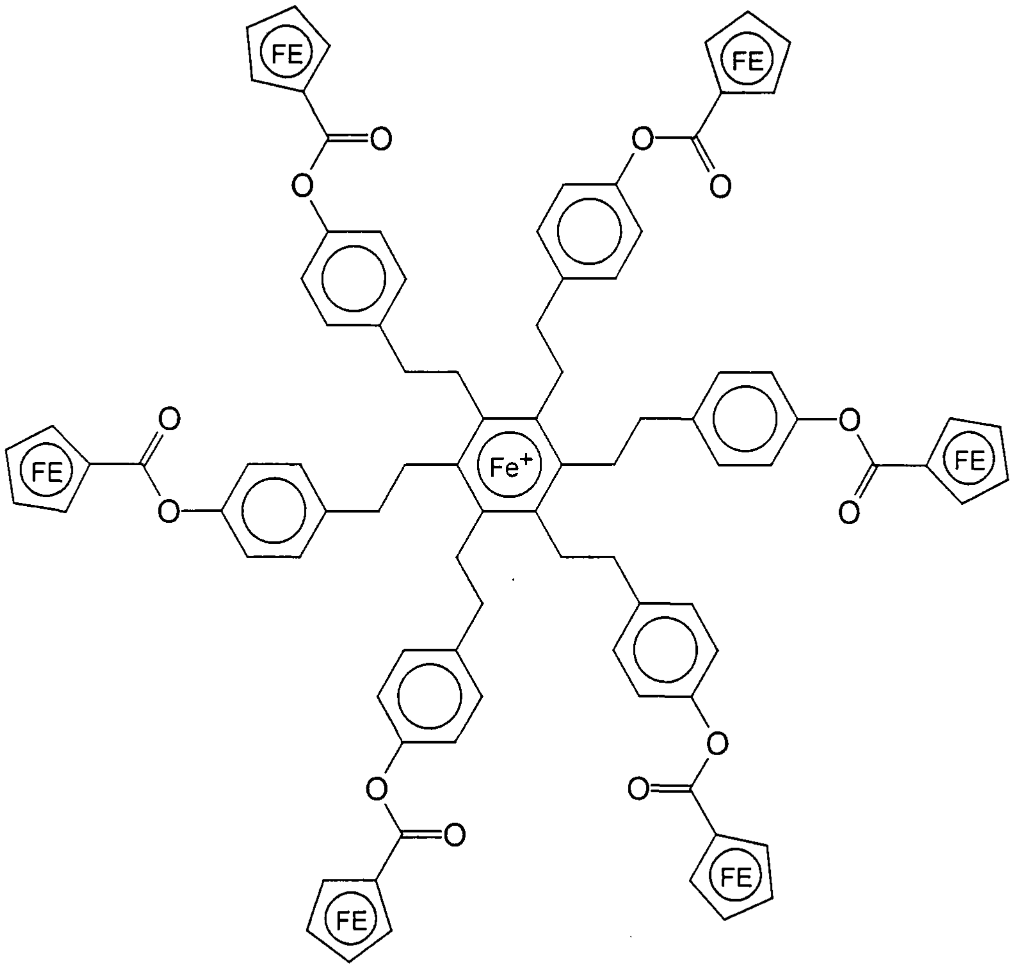


Figure 1.26 A neutral phosphorous-containing dendrimer.

1.4.2 Organometallic Dendrimers

The synthesis of dendrimers is not limited to those based on organic and inorganic elements, or even covalent bonds. Many dendritic structures have been reported containing a variety of transition metals as terminal groups and dendritic cores. The type of bonding contained in these dendrimers ranges from that seen in sandwich complexes (Figure 1.27),[43,44,45] metal-carbon σ-bonds[46] and co-ordination complexes.[47,48]



$Fe^{+} = \eta^{5}\text{-}C_5H_5Fe^{+}PF_6^{-}$

$FE = \eta^{5}\text{-}C_5H_5Fe$

Figure 1.27 A dendritic Iron sandwich complex.

It is even possible to build a dendrimer containing two different metals (Figure 1.28) and it has been postulated that such devices should be capable of harvesting solar energy and mimicking photosynthesis.[49]

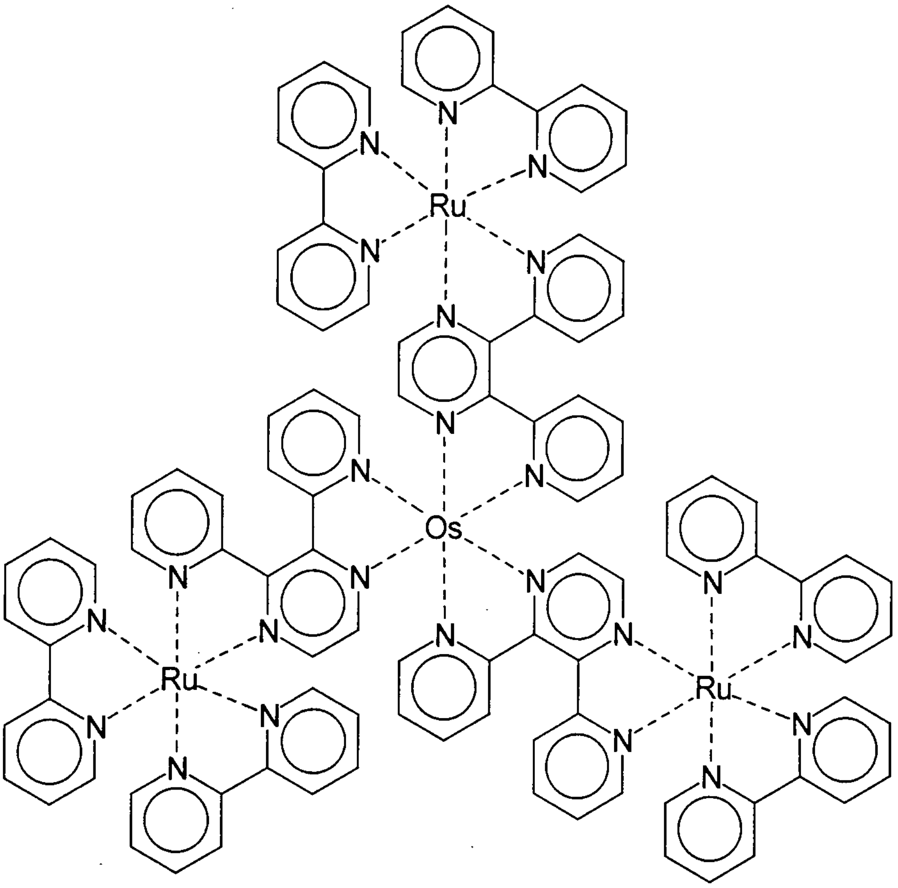
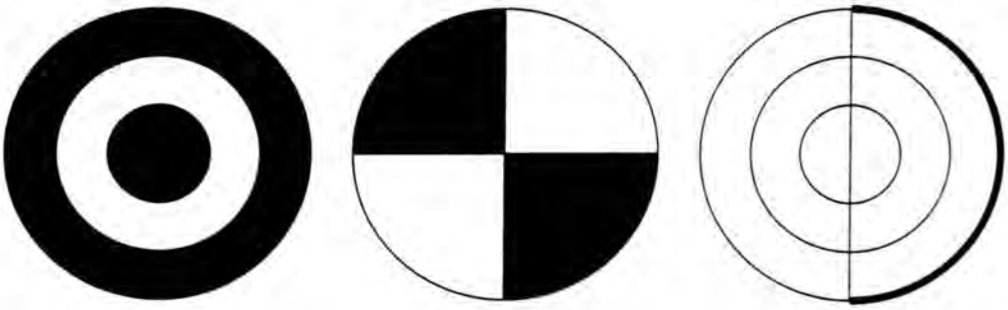


Figure 1.28 An organometallic dendrimer containing Ruthenium and Osmium.

1.4.3 Dendritic block copolymers, combs and amphiphiles

A large number of interesting architectures can be constructed because of the three-dimensional nature of dendrimers. A variety of copolymers have been reported by Fréchet and have been termed *layer-block*, *segment-block* and *surface-block* copolymers (Figure 1.29).[22,50]



Layer-block Segment-block Surface-block

Figure 1.29 Dendritic block copolymers.

Layer-block copolymers are synthesised by alternating the type of building block when constructing the dendrons. Attaching dendrons, composed of two different building blocks, to a central core creates segment-block copolymers. The two different types of building blocks that have been used to construct such block copolymers are polyether and polyester fragments.[51] Surface block copolymers possess the same building block throughout the dendrimer but have different terminal groups, e.g. Br, CN and H, on different segments of the surface.

The construction of dendrimers is not limited to using small molecules as the building blocks; monodisperse, linear polymers can also be used to create *Combburst*® macromolecules. Tomalia[52] reported the original approach that involved grafting a reactive polyoxazoline onto a polyethylene imine core. After removal of the amide groups from the side chains, the grafting process is repeated with more reactive polyoxazoline. This graft-on-graft approach leads to a very large increase in the molecular weight between dendrimer generations.

Gauthier reported another comb-graft structure;[53] he used a low molecular weight polystyrene chain with narrow weight distribution as the core moiety (Figure 1.30). The core is activated by chloromethylation in a statistical process that involves approximately 30% of the pendant phenyl rings (Step A). Generation growth is achieved by reacting this chloromethylated polymer with living polystyrene (Step B). Polymers with a molecular weight of 4,000,000 and a polydispersity of 1.3 have been isolated following this approach.

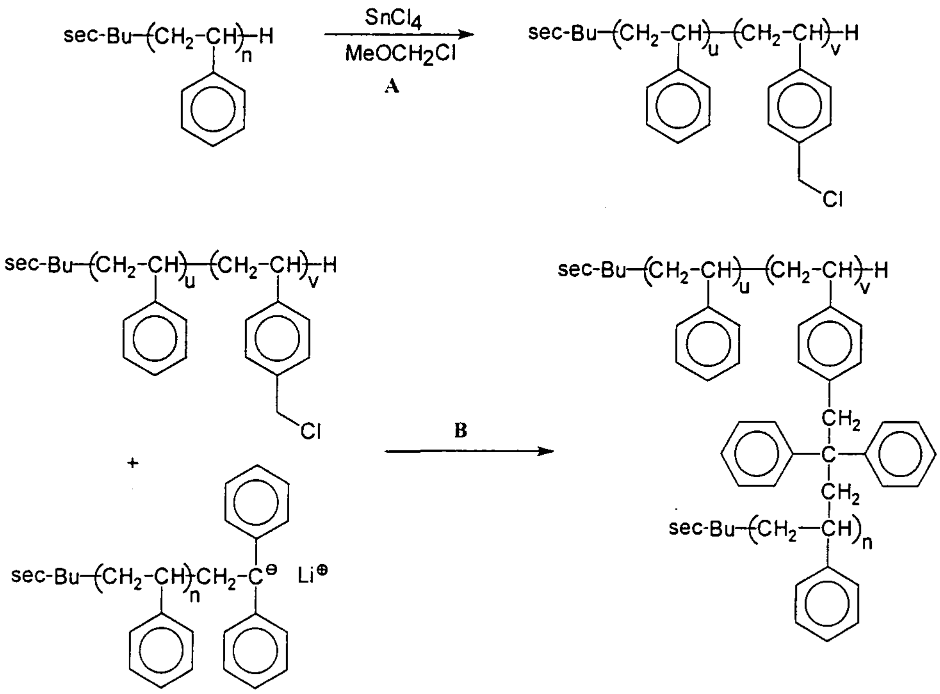


Figure 1.30 Gauthier's comb-graft macromolecule.

Polymers produced in this way do not have the precisely defined structures normally associated with dendrimers derived from controlled synthesis with small molecules. However, they do have branching densities similar to pure dendrimers. For example, the hydrodynamic volume of a highly branched polystyrene prepared by

Gauthier occupies 27 times less volume than a linear polystyrene of the same molecular weight.

Dendrimers have also been built onto the end of short, polystyrene chains to create a new class of amphiphiles (Figure 1.31).[13,14,54] Meijer constructed such structures from amine-terminated polystyrenes using the efficient poly(propylene imine) synthesis described previously in Section 1.3.3. Fréchet has also constructed a dendrimer of similar design comprising a polyether dendrimer wedge at either end of a poly(ethylene glycol) chain.[55]

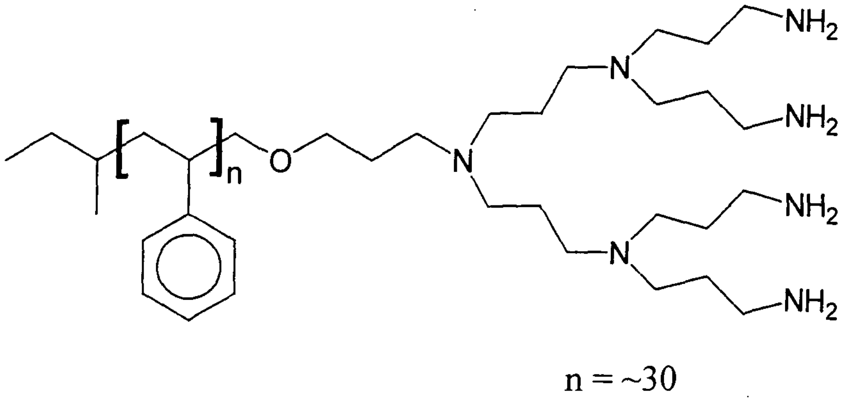


Figure 1.31 An example of an amphiphilic macromolecule.

1.5 Characterisation of dendrimers

Dendrimers are truly monodisperse species, as compared to conventional polymers, which display a molecular weight distribution. Dendrimers can be characterised very accurately as a consequence of this monodispersity and their high symmetry.

The molecular weight of dendrimers can be determined by using techniques such as electrospray[56] and matrix-assisted laser desorption/ionisation time of flight mass spectrometry (MALDI-TOF MS).[57,58,59,60] Direct laser desorption has also been used for Fourier transform mass spectrometry (LD-FTMS).[57]

Size exclusion chromatography (SEC) can be employed to monitor dendrimer growth and observe any species present in the sample that is due to incomplete reaction during the dendrimer synthesis.[12,57] Pure dendrimers will show a single, narrow peak, compared to a multimodal distribution indicative of incomplete reaction.

The structure of dendrimers can be studied by conventional ^{13}C and ^{1}H nuclear magnetic resonance (NMR) spectroscopy. NMR and Infrared (IR) spectroscopy can monitor the composition of the end-groups.

1.6 Properties and uses of dendrimers

1.6.1 A comparison of dendrimers with analogous linear polymers

The properties of dendrimers have not yet been extensively examined, however, the number of studies is steadily increasing. Research is predominantly focused on the comparison of linear polymers with structurally analogous dendrimers; in particular, the novel solution properties of dendrimers have been discussed. One of the most striking differences between dendrimers and linear polymers is in their respective intrinsic viscosity/molecular weight relationships. Linear polymers obey the Mark-Houwink-Sakurada equation: $[\eta] = KM^a$. In other words, as the molecular weight of the polymer increases, the intrinsic viscosity increases. However, dendrimers do not obey this relationship across the full range of molecular weights. In fact, the intrinsic viscosity of a family of dendritic molecules reaches a maximum and decreases thereafter with increasing molecular weight (Figure 1.32).[61] This can be explained qualitatively on the basis of the conformational changes dendrimers undergo through increasing generations. At low generations the dendrimer adopts a relatively mobile conformation and, in terms of hydrodynamic volume, will be similar to a conventional linear polymer; however, as the dendrimer increases in size the structure becomes more rigid and approximates to a hard sphere. During this change the density of the dendrimer increases since the molecular mass of the dendrimer increases faster than its hydrodynamic volume. Thus, dendrimers of low generation will have a molecular weight/viscosity relationship similar to that defined by the Mark-Houwink-Sakurada equation; however, the relationship between the molecular mass and intrinsic viscosity of hard spheres obeys a different relationship:

$$[\eta] \propto \frac{V_h}{M}$$

where Vh is the hydrodynamic volume, M is the mass and $[\eta]$ is the intrinsic viscosity. Since dendrimers of higher generation approximate to hard spheres, this expression is more appropriate for accounting for trends in their intrinsic viscosity, and since their hydrodynamic volumes increase more slowly than their masses, the value for $[\eta]$ will decrease with increasing mass.

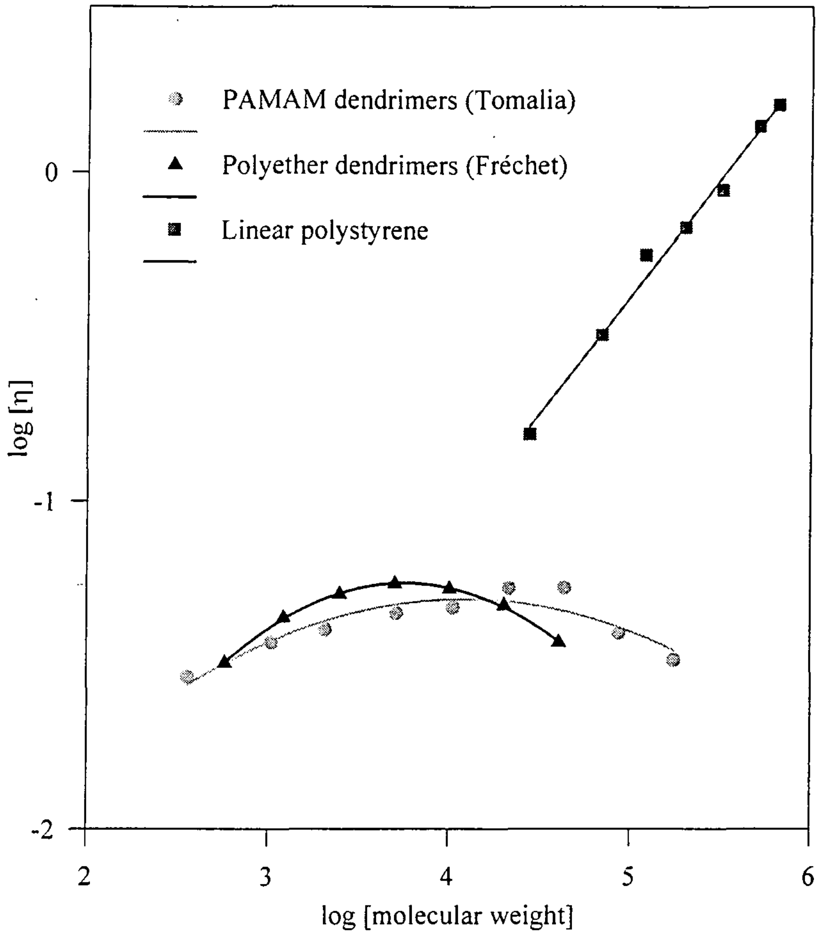


Figure 1.32 The relationship of molecular weight to intrinsic viscosity for linear polymers and dendrimers.

Another interesting solution property of dendrimers is that they have enhanced solubility compared to analogous linear polymers. Solubility enhancements of 10^5

have been reported for poly(phenylenes) compared to linear poly(*p*-phenylene).[18] The increased solubility of dendrimers is attributed to both their branched architecture and the large number of end groups.[62]

In contrast to the solution properties of dendrimers, thermal properties, e.g. thermogravimetric behaviour[62] and glass transition temperatures,[63] are similar to analogous linear polymers.

1.6.2 Uses of dendrimers

Since the area of dendrimer technology is in its infancy, dendrimers have not yet reached the commercial market in any significant way. However, there are many possible uses for these new and exciting materials. It is possible that dendrimers could be used as a basic constituent of solvent-free, or at least very low solvent content, paints due to their unusual low viscosity at high concentration. It has been dramatically demonstrated by Meijer using Bengal Rose that dendrimers can also be used to encapsulate small molecules[64,65,66] and this may lead to efficient drug-delivery systems. Dendrimers could also be used for chemical sensing,[67,68] or abstracting small organic molecules from solution using this *dendritic-box* phenomena. Optically active dendrimers have been designed which have potential applications in chiral recognition and asymmetric synthesis,[69] and redox active dendrimers may open the way for molecular electronics devices and multielectron redox catalysis.[45,70] Phosphorous-containing dendrimers may also be useful in catalysis, and co-ordination chemistry.[41,42] Electroluminescent diodes with single-organic-layer configuration have been built using dendritic materials[71] and dendrimers have been synthesised which have liquid crystal properties.[72,73] Aromatic ester dendrimers have displayed properties that may be desirable in the production of orientated PET fibres and films[74] and macromolecular amphiphiles prepared by Meijer may be useful as high molecular weight surfactants.[13,14,54]

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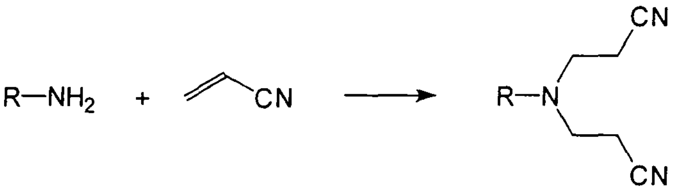
CHAPTER 2

Synthesis and Characterisation of Poly(propylene imine) Dendrimer Wedges

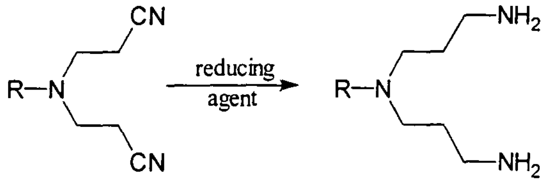
2. Synthesis and Characterisation of Poly(propylene imine) Dendrimer Wedges

The synthesis of poly(propylene imine) dendrimer wedges with various foci, most importantly a species that absorbs in the UV region, is described in this chapter. The dendritic wedges were synthesised in a step-wise way via a repetitive reaction sequence using Vögtle[1] and DSM[2] methodology; the process is summarised in Figure 2.1.

Step 1 Michael reaction:



Step 2 Nitrile-group reduction:



Repeating steps 1 and 2:

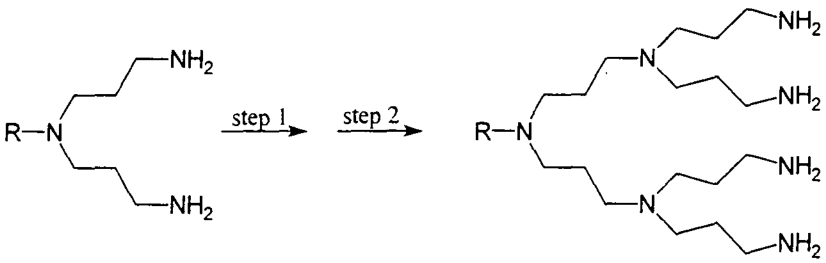


Figure 2.1 Iterative steps in the divergent synthesis of a poly(propylene imine) dendrimer wedge.

Complete hydrogenation is difficult to achieve and side reactions occur using most catalyst systems (Figure 2.2); however, the most common cause of defective growth when synthesising poly(propylene imine) dendrimers via this route is incomplete Michael addition (A).[3] Retro-Michael addition (B) and cyclisation (C) can occur during the hydrogenation step and these side reactions also limit the growth of uniform dendrimers. These side reactions, i.e. B and C, can occur when using Raney cobalt, which is generally accepted to be the best hydrogenation catalyst.

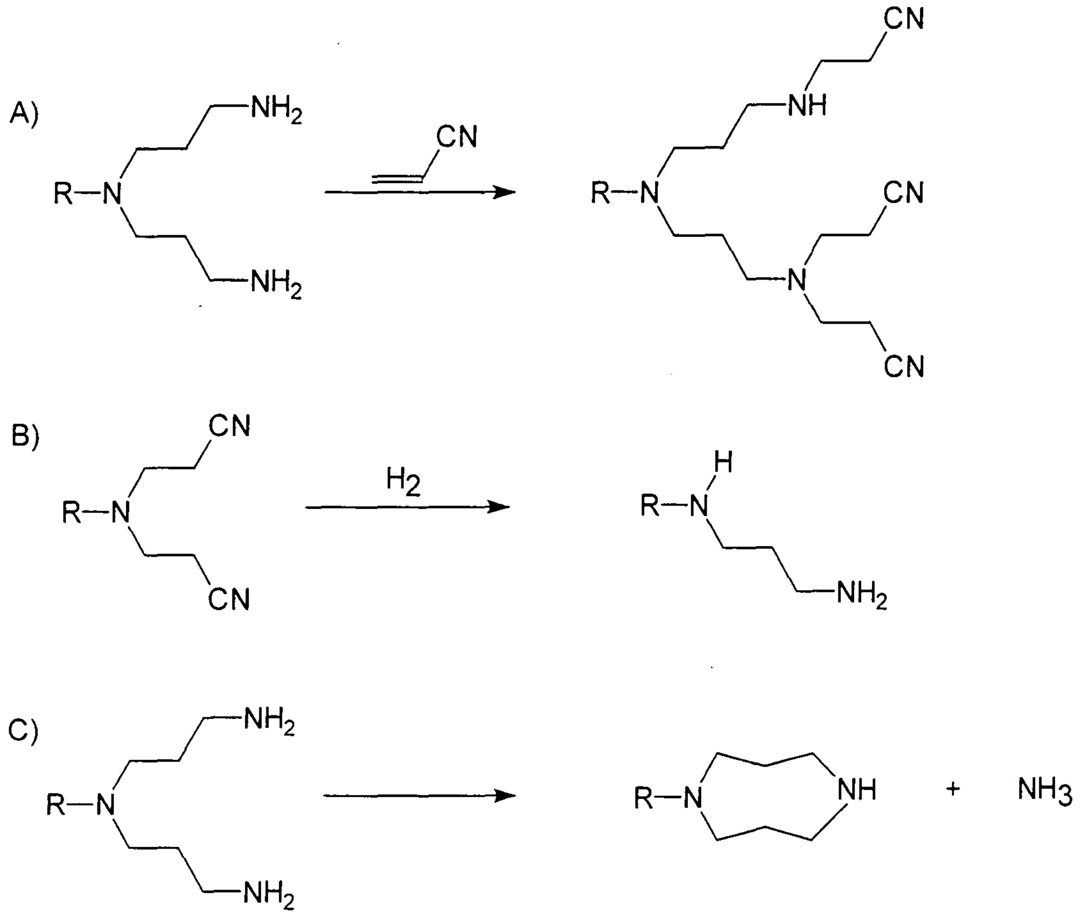


Figure 2.2 Side reactions during poly(propylene imine) dendrimer synthesis.

2.1 The Michael reaction

An alkene which is activated by an electron-withdrawing group is susceptible to attack by a nucleophile. This reaction is known as the Michael Reaction and the final outcome depends on the nature of the reagents. In the case of interest in this work, an N-H bond is added to a carbon-carbon double bond in an anti-Markovnikov sense. Attack by the amine loan pair takes place at the methylene carbon since there is a slight positive charge at this site. In contrast, attack at the methine carbon would result in a primary carbanion that would derive no resonance stabilisation from the cyano group. However, reaction at the nitrile carbon sometimes competes. Michael Addition with acrylonitrile is also known as *cyanoethylation* and can be acid or base catalysed. The mechanistic rationalisation is shown below (Figure 2.3).

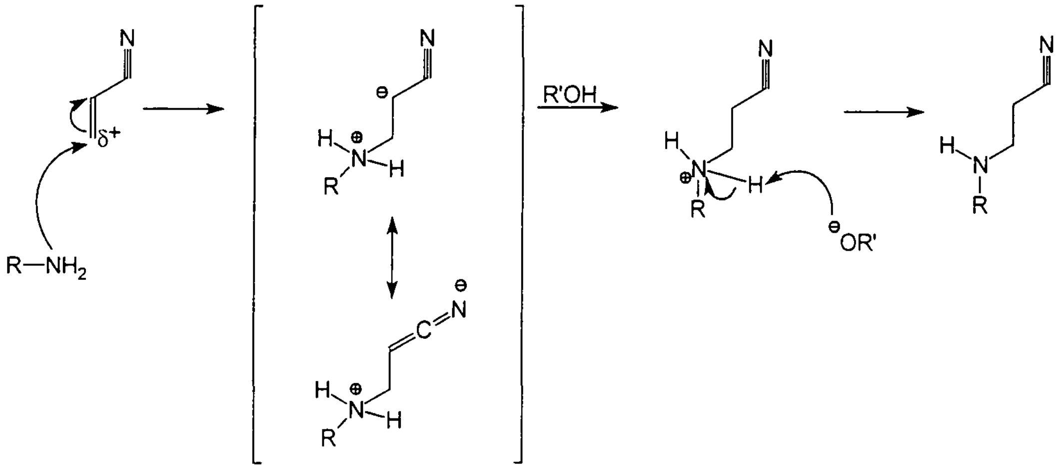


Figure 2.3 Mechanism of Michael Addition to acrylonitrile.

Since a secondary amine is marginally more nucleophilic than a primary amine, a second Michael reaction takes place in most cases in the presence of excess acrylonitrile. The Michael addition reaction can be performed in a variety of solvents such as water, methanol and acrylonitrile, the latter requiring ethanoic acid as catalyst.

A simple aliphatic primary amine was chosen to begin studies into the variety of procedures available for the synthesis of poly(propylene imine) dendrimers and to assess which route might be the most practicable.

2.1.1 Water as solvent for the Michael reaction

Hexylamine was chosen as the initial starting material (Figure 2.4) because it is the largest aliphatic amine readily available for purchase that is soluble in water, however, it is only sparingly soluble. Water is potentially a useful solvent for the reaction because it is also used in high-pressure hydrogenation of nitrile-groups with various catalysts.[2,3,4] This means that large-scale production of dendrimer wedges could be possible without the need for isolation and purification at each stage, should scale up be desirable in the future.

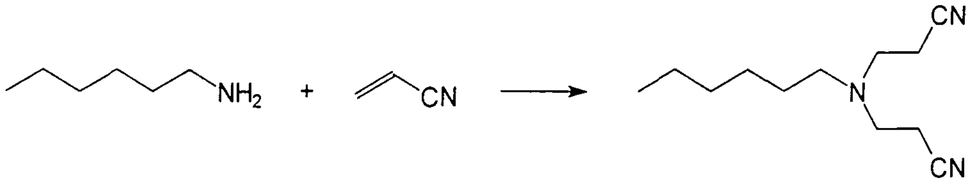


Figure 2.4 Cyanoethylation of hexylamine.

The reaction proceeded well with no mono-cyanoethylated product isolated from the reaction mixture. The desired product, *Hex-dendr-*$(CN)_2$, was easily extracted from the reaction mixture and was distilled to give a colourless oil in 68% yield. The product was characterised and examination of the n.m.r. data indicated a pure product (see Experimental Section 2.6.1).

The cyanoethylation of *Hex-dendr-*$(NH_2)_2$ was also satisfactorily performed in water using a similar procedure to give *Hex-dendr-*$(CN)_4$ (see Experimental Section 2.6.3).

2.1.2 Methanol as solvent for the Michael reaction

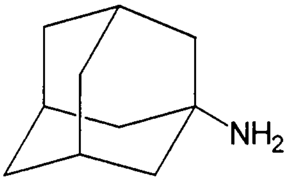


Figure 2.5 1-Adamantanamine.

The synthesis of wedges with an adamantyl group was attempted, principally to ascertain whether wedge formation was possible with a bulky group attached to the amine functionality. 1-Adamantanamine (Figure 2.5), which is not soluble in water, was used as the hindered amine. The same Vögtle methodology was used for the preparation of each generation of adamantyl wedges as was used for the wedges grown from n-alkylamines, using methanol rather than water as reaction medium (Section 2.6.4).

Presumably as a consequence of steric hindrance, mainly the mono-cyanoethylated product, *Ad-dendr-(CN)$_1$*, was obtained (Figure 2.6).

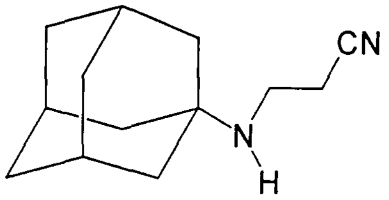


Figure 2.6 *Ad-dendr-(CN)$_1$*.

A side product was obtained when performing the Michael reaction in methanol (Figure 2.7). This was produced in significant amounts under the more lengthy and severe conditions required to force the cyanoethylation of the sterically hindered amine to completion. It was removed readily by evaporation under reduced pressure at room temperature. In the case of the higher generation wedges, the Michael reaction proceeded to completion with neither a mono-cyanoethylated product nor a methanol-acrylonitrile adduct observed. This is due to less steric hindrance of primary amines at higher, intermediate sized, dendrimer generations. Of course, as has been discussed in Section 1.3.3, at very high generations the surface of the dendrimer becomes congested and incomplete Michael reactions again occur.

Figure 2.7 Methanol-acrylonitrile Michael addition product.

From this work it is clear that, depending on the solubility of the dendrimer focus, either water or methanol is a suitable vehicle for performing the Michael reaction, under appropriate conditions.

2.2 Nitrile-group reduction

2.2.1 Sodium borohydride with cobalt (II) chloride hexahydrate[1]

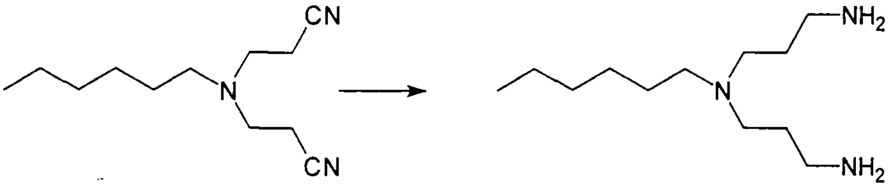


Figure 2.8 Reduction of nitrile-groups.

Reduction of nitrile groups was attempted on *Hex-dendr-(CN)*$_2$ (Figure 2.8) (see Experimental Section 2.6.2). The addition of the solid sodium borohydride to the stirred mixture of *Hex-dendr-(CN)*$_2$ and cobalt (II) chloride in methanol was slow and tiresome because hydrogen gas was given off violently after each small portion was added. The yield (69%) was better than might have been expected from the literature (40-60%),[1] but even so, characterisation of the product indicated that incomplete reduction had occurred. This approach was discarded although it was the first method used to make these dendritic wedges.

2.2.2 Diisobutylaluminum hydride[5]

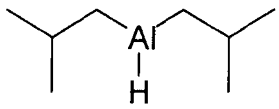


Figure 2.9 Diisobutylaluminum hydride

Diisobutylaluminum hydride (Figure 2.9) was used as a reducing agent for *Hex-dendr-(CN)*$_2$ (Section 2.6.2) and this reduction proceeded much more satisfactorily than the experiment using sodium borohydride; good yields (87%) were recovered in agreement with literature reports (89%).[5] Although there is an inherent problem relating to the instability of diisobutylaluminum hydride in air and water, which would be likely to cause problems should scale-up be required, it gave the cleaner and more complete reduction, and is therefore a superior reagent to sodium borohydride for this reaction and suitable for the small scale (ca. 0.50 to 2.00g of starting material) work reported here.

2.2.3 Raney nickel[4]

Raney nickel was chosen as the hydrogenation catalyst for large-scale reductions since it is cheap, easy to handle and readily available. The reduction was performed on *Hex-dendr-(CN)*$_2$ in a 2L stirred stainless steel autoclave using mainly water (600ml) as reaction medium, but a little methanol (200ml) was also added to aid solution and speed up reduction since autoclave time was limited (see Experimental Section 2.6.2). The product was relatively soluble in water and consequently quite difficult to extract from the water layer at the end of the reaction. Therefore, the recovered yields of *Hex-dendr-*$(NH_2)_2$ were relatively poor (65%) but in line with literature values (ca. 65%).[4] Further work showed that a much better yield was gained when even smaller amounts of water (ca. 100ml) and more methanol (ca. 700ml) were used in the reaction. Yields were closer to those that might be expected when using Raney cobalt (ca. 85%) in pure water.[2] For the scale of operation used in this work, an aqueous methanol/Raney nickel system proved satisfactory. For industrial scale reductions Raney cobalt in pure water has been advocated, however acquisition of Raney cobalt proved prohibitively expensive.

2.3 Monitoring iterative steps using FTIR and n.m.r. spectroscopy

The iterative steps in the dendrimer wedge, *UV-dendr-*$(NH_2)_4$, synthesis can be conveniently followed using ^{13}C nuclear magnetic resonance (n.m.r.) and Fourier Transform Infrared (FTIR) spectroscopy and the key data is summarised in Figure 2.10. In the 15–55ppm range in the ^{13}C n.m.r. spectra, the methylene carbons associated with the sequence of structures are easily identified. Thus, although quantitative ^{13}C n.m.r. spectroscopy was not performed, the heights of the peaks are approximately in the expected ratios for the numbers of methylene units in the various structures. All the methylenes adjacent to amines occur in the chemical shift range 40-55ppm, than those adjacent to the cyano groups occur in the range 20-30ppm and the methylene groups located between them are found at ca. 25-30ppm. The combination of shift and intensity data provides unambiguous support for the assigned structures.

FTIR spectroscopy can be used to monitor the appearance and disappearance of the N-H stretching band at ca. 3300cm^{-1} and CN stretching band at ca. 2247cm^{-1} during the iterative steps of the synthesis of poly(propylene imine) dendrimers and the FTIR spectra for these species are shown in Figure 2.10. The N-H and CN stretching bands provided a simple and quick method for monitoring the extent of reaction in each step.

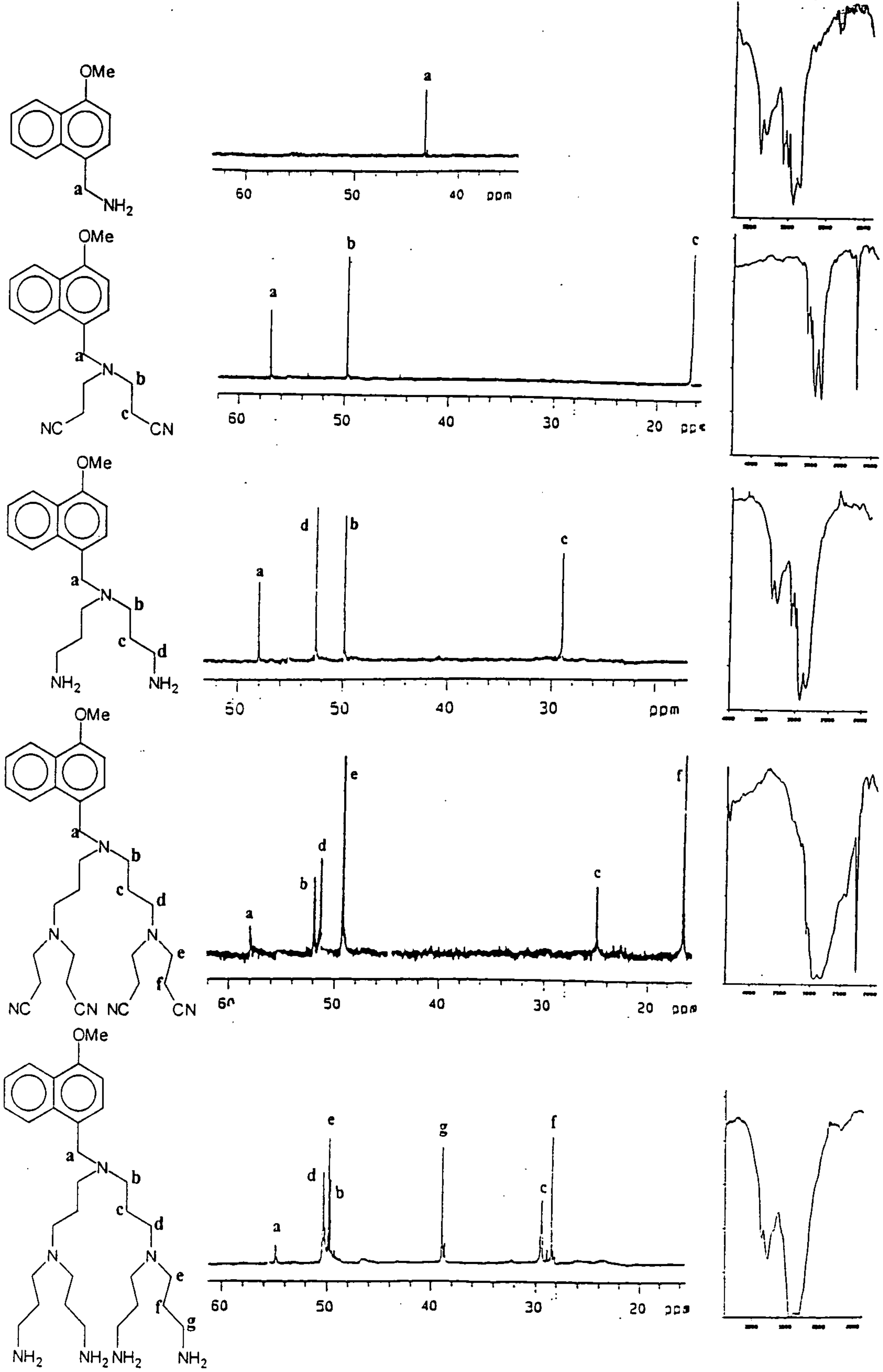


Figure 2.10 Monitoring dendrimer growth spectroscopically.

2.4 Dendrimer wedges with chromophores at the focus

As has already been mentioned in the Preface, it is thought that a relatively straightforward analytical probe for surface recognition may be to observe a change in the optical density of an aqueous solution of surface recognising wedges carrying chromophores. A change in optical density would be detected when some of the material became bound to a cotton surface introduced into the solution and for this reason the construction of a dendrimer wedge with a commercially available dye at its focus was attempted.

2.4.1 Fast Blue as a dendritic focus

Fast Blue BB (Figure 2.11) is a dye precursor which can be converted to a diazonium salt by reaction with sodium nitrite in acidic solution. This solution of the diazonium salt is frequently used as a stain in biological systems,[6] it is therefore unlike conventional dyes (e.g. Basic, Direct, Vat and Reactive dyes) which are designed specifically to bind to cellulose and synthetic fibre surfaces. Consequently, an hypothesis was made to the effect that there would be a substantial difference between the binding of the pure dye precursor Fast Blue BB to cellulose compared to the situation where it was bound to the focus of a dendritic wedge displaying specific surface recognition.

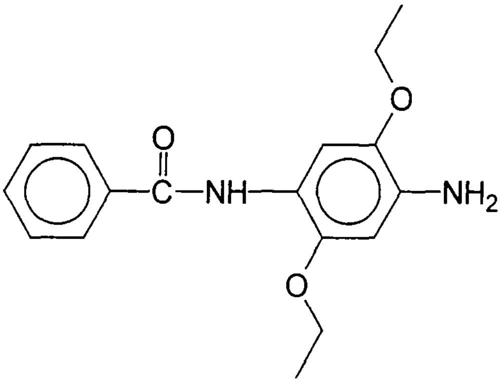
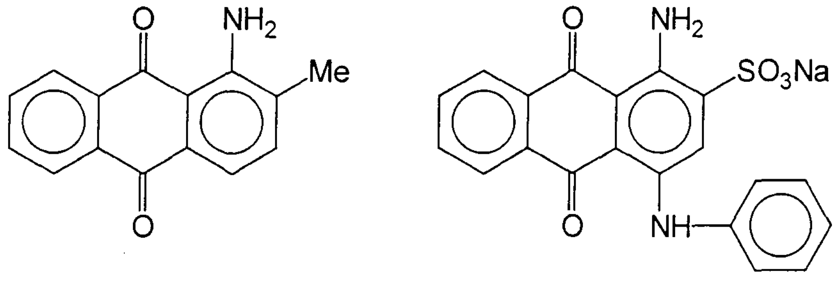


Figure 2.11 Fast Blue BB.

The dye precursor was purified to produce a yellow solid by sublimation, leaving behind a brown residue. The pure dye precursor was found to oxidise when stored in the air for two days or more and consequently was used immediately after purification. Cyanoethylation of the dye precursor was slow (see Experimental Section 2.6.6). This is expected since the nucleophilicity of primary aromatic amines is generally less than aliphatic amines. However, it was possible to mono-cyanoethylate after about a week with a substantial excess of acrylonitrile to produce *FB-dendr-(CN)*$_1$. It was impossible to perform a second Michael-type reaction as a consequence of the increased steric hindrance and low nucleophilicity of the secondary aromatic amine. Since secondary amines are marginally more nucleophilic than primary amines, the steric hindrance must be the dominant effect. However, the mono-cyanoethylated product was reduced using diisobutylaluminum hydride to give a spacer-arm onto which a dendrimer wedge was easily built (see Experimental Section 2.6.7). Unfortunately, it was found that the dendrimers with Fast Blue BB at the focus did not possess a suitably large extinction coefficient or sufficient chemical stability for surface adsorption studies and this system was abandoned at this stage.

2.4.2 Anthraquinone dyes as dendron foci

The anthraquinone dyes chosen were Disperse Orange 11, which is water insoluble, and Acid Blue 25, which is water soluble (Figure 2.12). They were chosen because they are not effective dyes for cotton and have high extinction coefficients. It was also thought that once these dyes were attached to a dendritic wedge it might be possible to compare any difference in surface activity towards cellulose that might occur in water. In other words, theses two molecules could be used as probes to find out if an inherently insoluble dye like Disperse Orange 11, when attached to a dendritic wedge, would bias the deposition on the cellulose surface as compared to the inherently soluble Acid Blue 25.



Disperse Orange 11 Acid Blue 25

Figure 2.12 The second dye foci considered.

Unfortunately cyanoethylation of Disperse Orange 11 did not occur in either methanol or in neat acrylonitrile with ethanoic acid as catalyst. Large excesses of acrylonitrile were used along with high temperatures and long reaction times. The low nucleophilicity of the primary aromatic amine is one reason why the desired product was not obtained, another contributory factor could be the relatively low solubility of Disperse Orange 11 in both methanol and neat acrylonitrile. When attempting to perform the cyanoethylation only millimolar amounts of dye (as supplied) were dissolved completely in 100ml of methanol. Acid Blue 25 did not cyanoethylate either, despite the fact that it was appreciably soluble in water.

It was thought that a possible solution to the cyanoethylation problem would be to react the dyes with ethylene oxide to create a spacer-arm and subsequently cyanoethylate the alcohol since this species is likely to be less hindered and more reactive (Figure 2.13). This approach was also unsuccessful in that the reaction with ethylene oxide failed.

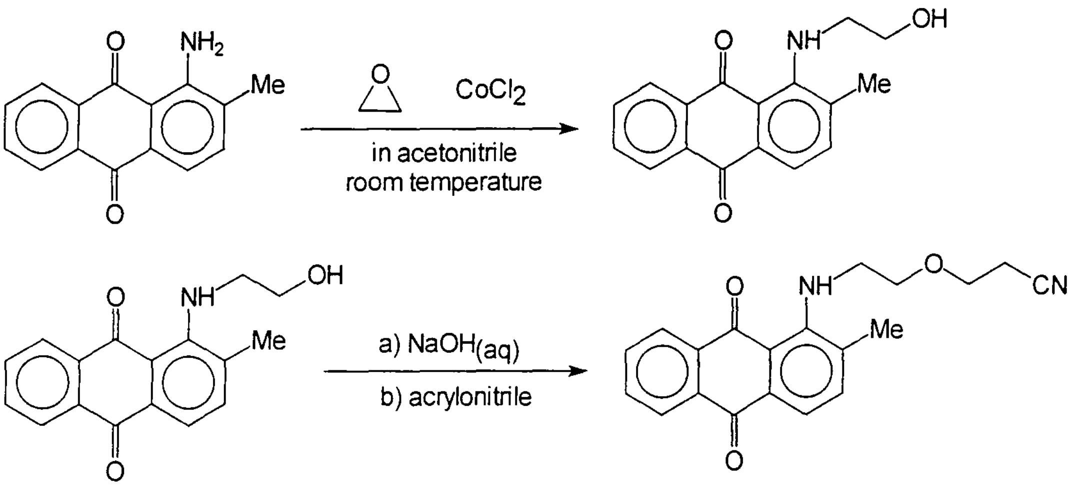


Figure 2.13 Proposed attachment and cyanoethylation of a spacer arm.

2.5 Dendrimers that absorb in the UV-region

As indicated in the previous two sections a significant amount of work was carried out attempting to adapt commercially available dyes but none of the routes examined proved to be suitable for making usable, labelled dendritic wedges. It was decided to attempt to design and synthesise a dye with all the desired properties; namely, good solubility in methanol, ease of cyanoethylation, stability to reduction and an extinction coefficient of a suitable value (of the order of 10^3 $M^{-1}cm^{-1}$). Consequently, a new synthetic strategy was devised (Figure 2.14). A poly(propylene imine) dendrimer wedge was built up from a methoxy-naphthonitrile. Reduction of the cyano-group to an aliphatic primary amine allowed easy construction of the wedge (see Experimental Sections 2.6.8-2.6.12). On subsequent diazonium coupling of the naphthalene with *p*-nitrobenzene diazonium sulphate a bright red product was obtained which was shown by Thin Layer Chromatography (TLC) to be an extremely complex mixture. However, it should be noted that the uncoupled dendrimer wedges with a methoxy-naphthalene focus are UV-active and hence, also suitable vehicles for attaching surface-functional moieties and monitoring surface activity via spectrometric measurement of their concentrations in aqueous solutions.

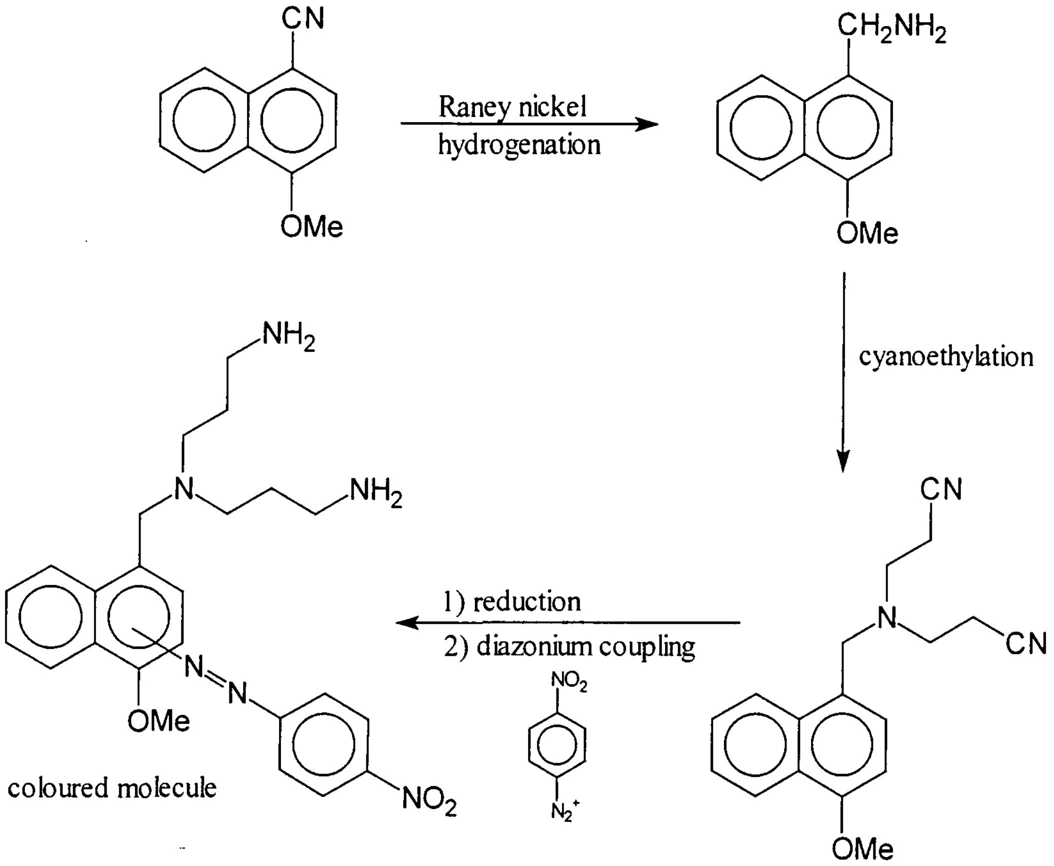
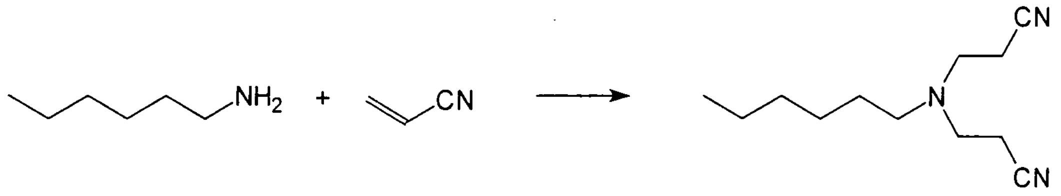


Figure 2.14 The synthetic pathway using diazonium coupling to a core functionalised wedge.

2.6 Experimental

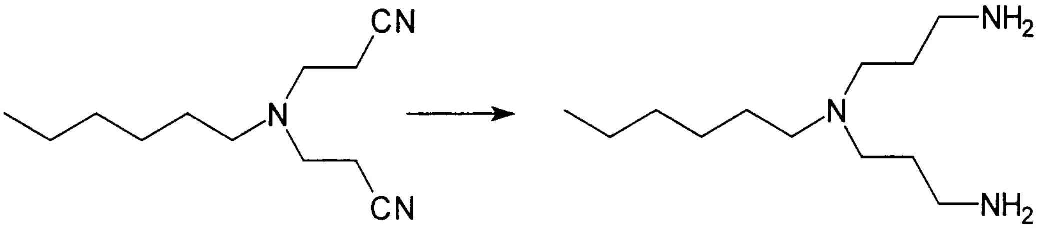
Sections 2.6.1-2.6.7 describe a set of trial experiments and are included here for the sake of completion. Since none of the materials produced were used further in the project, the analysis and characterisation carried out is generally incomplete but sufficient data is reported to establish the outline results in these sections.

2.6.1 Cyanoethylation of hexylamine via the Michael reaction



Acrylonitrile (78.68g, 1.45mol.) was added with stirring over 30 minutes to a solution of hexylamine (50.00g, 0.50mol.) in water (200ml) in a two-necked flask, equipped with a dropping-funnel and condenser. Since the amine was only sparingly soluble, the stirring was continued for 60 hours at room temperature. The excess acrylonitrile was removed by vacuum distillation as an azeotrope with water (40°C, 12mmHg). The residue in the reaction vessel separated into two layers. The organic layer was separated from the aqueous layer, washed with water, dissolved in chloroform (100ml) and dried over magnesium sulphate. The magnesium sulphate was removed by filtration, and the solvent using a rotary evaporator at water pump pressure. The product was fractionally distilled giving only one fraction (68.72g, 68%, 102°C, 0.27mmHg) as a clear and colourless liquid which yellowed after a few days, a characteristic of amines. The product, *Hex-dendr-(CN)$_2$*, was characterised by spectroscopy: ^{13}C n.m.r. ($CDCl_3$, 100MHz) δ13.89 ($\underline{C}H_3$), δ16.70 ($CH_2\underline{C}H_2CN$), δ22.42, δ26.56, δ27.10, δ31.47 (chain $\underline{C}H_2$), δ49.36 ($\underline{C}H_2CH_2CN$), δ53.25 ($\underline{C}H_2N$), δ118.69 ($\underline{C}N$) (Appendix 1.1). ^{1}H n.m.r. ($CDCl_3$, 400MHz) δ0.82 (3H, $C\underline{H}_3CH_2$), δ1.22 (6H $C_2H_5C_3\underline{H}_6CH_2N$), δ1.37 (2H $CH_3C\underline{H}_2$), δ2.42 (4H, $CH_2N(C\underline{H}_2CH_2CN)_2$), δ2.44 (2H, $C\underline{H}_2N(CH_2CH_2CN)_2$), δ2.77 (4H, $CH_2N(CH_2C\underline{H}_2CN)_2$), (Appendix 1.2). FTIR, ν_{max}/cm^{-1}: 2929.0, 2856.1 (C-H stretch), 2247.4 (CN stretch) (Appendix 1.4). GC Mass Spectrometry: m/z 207, (Theory: m/z 207).

2.6.2 Reduction of *Hex-dendr-(CN)₂*



Cobalt (II) chloride hexahydrate and sodium borohydride as reducing reagent

Hex-dendr-$(CN)_2$ (11.76g, 56.81mmol.) was dissolved in methanol (400ml) in a one-necked flask and cobalt (II) chloride hexahydrate (47.63g, 0.20mol.) was added. Sodium borohydride (75.6g, 1.99mol.) was added as a solid in small portions over 90 minutes with stirring, there was violent gas evolution after each addition. The resultant mixture was stirred for 2 hours at room temperature and cautiously acidified with concentrated HCl (400ml). The solvents were removed using a rotary evaporator at water pump pressure and the deep blue residue was treated with a mixture of concentrated ammonia (500ml) and chloroform (370ml). A flesh-coloured solid was produced which was extracted with chloroform (6x150ml) and the combined extracts were dried over magnesium sulphate. After filtration, the solvent was removed using a rotary evaporator at water pump pressure and the crude, oily product was taken up in anhydrous benzene (100ml) and dried for 20 hours over a 3Å molecular sieve. The solvent was removed using a rotary evaporator at water pump pressure to give the product, impure *Hex-dendr-$(NH_2)_2$* (8.45g, 69%). The impure product was identified by ^1H n.m.r. ($CDCl_3$, 200MHz) and ^{13}C n.m.r. ($CDCl_3$, 50MHz) spectroscopy, by later comparison with the spectra of an authentic, pure sample. FTIR, ν_{max}/cm^{-1}: 3277.6 (N-H stretch), 2358.5 (CN stretch), gave further confirmation that this method resulted in incomplete reduction of the cyano group. Despite earlier literature reports,[1] his technique was abandoned as inconvenient and ineffective.

Diisobutylaluminum hydride (DIBAH) as reducing reagent

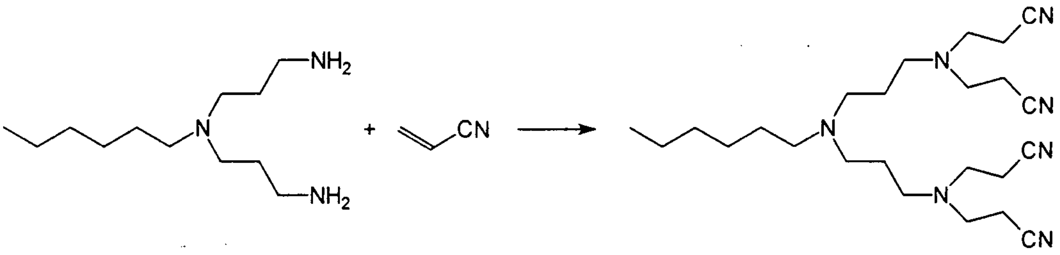
Hex-dendr-(CN)$_2$ (2.08g, 10.05mmol.) was added to THF (200ml, dried over calcium hydride) in a two-necked flask, fitted with a dropping-funnel and condenser, and DIBAH (100ml of a 1M solution in hexane) was added cautiously with stirring over 80 minutes. Because of DIBAH's reported explosive behaviour on contact with air and water, all apparatus used was dried completely beforehand and constantly flushed with nitrogen gas. The solution went yellow and was refluxed for 24 hours. To destroy excess DIBAH, methanol (20ml) was cautiously added to the reaction mixture with stirring over 40 minutes at room temperature. A white precipitate was formed which was removed by filtration and washed with methanol (300ml). The methanol was removed using a rotary evaporator at water pump pressure to give a waxy, yellow product, *Hex-dendr-(NH$_2$)$_2$* (1.88g, 87%). The crude product was identified by ^{1}H n.m.r. (D_2O, 200MHz) and ^{13}C n.m.r. (D_2O, 50MHz) spectroscopy by later comparison with an authentic, pure sample; this analysis indicated that a slightly impure product had been obtained. The FTIR spectrum showed a strong N-H stretch, ν_{max}/cm^{-1}: 3280.3cm^{-1}, but with neither unreacted nitrile, nor any other unexpected peaks. CI Mass Spectrometry: m/z 217, and EI Mass Spectrometry: m/z 216, (Theory: m/z 216).

Raney nickel as reducing agent

Hex-dendr-(CN)$_2$ (16.01g, 0.077mol.) was dissolved in methanol (800ml) in a beaker with stirring. A solution of sodium hydroxide (5.68g) in water (100ml) and Raney nickel (10.34g slurried in water, 80ml) were added. The mixture was stirred in a 2L, glass-lined, stainless steel autoclave at 70°C for 16 hours under a hydrogen atmosphere (700psi). After cooling and venting, the reaction mixture was filtered and the Raney nickel was washed with methanol (200ml) and water (200ml). The methanol was removed using a rotary evaporator at water pump pressure and water (200ml) was added to the residue. The water layer was extracted with dichloromethane (3x200ml) and the combined organic extracts were dried over magnesium sulphate. The magnesium sulphate was removed by filtration and washed with dichloromethane (2x100ml). The solvent was removed using a rotary evaporator at water pump pressure to yield a pale yellow oil, *Hex-dendr-(NH*$_2$*)*$_2$ (14.53g, 87%), which solidified on standing. The product was characterised by spectroscopy: ^{13}C n.m.r. (CDCl$_3$, 100MHz) δ13.83 ($\underline{C}H_3$), δ26.76 ($CH_2N(CH_2\underline{C}H_2CH_2NH_2)_2$), δ22.23, δ29.47, δ31.73 δ32.48 (chain $\underline{C}H_2$), δ39.97 ($CH_2N(CH_2CH_2\underline{C}H_2NH_2)_2$), δ49.91 ($CH_2N(\underline{C}H_2CH_2CH_2NH_2)_2$), δ51.81 ($\underline{C}H_2N(CH_2CH_2CH_2NH_2)_2$), (Appendix 1.4). ^{1}H n.m.r. (CDCl$_3$, 400MHz) δ0.73

(3H, $C\underline{H}_3CH_2$), δ1.15 (6H $C_2H_5C_3\underline{H}_6CH_2N$), δ1.35 (2H $CH_3C\underline{H}_2$), δ1.51 (4H, $CH_2N(CH_2C\underline{H}_2CH_2NH_2)_2$), δ2.50 (10H, $C\underline{H}_2N(C\underline{H}_2CH_2C\underline{H}_2NH_2)_2$), (Appendix 1.5). FTIR, ν_{max}/cm^{-1}: 3280.3 (N-H stretch), 2927.4, 2856.3 (C-H stretch) (Appendix 1.6). CI Mass Spectrometry: m/z 217, and EI Mass Spectrometry: m/z 216, (Theory: m/z 216).

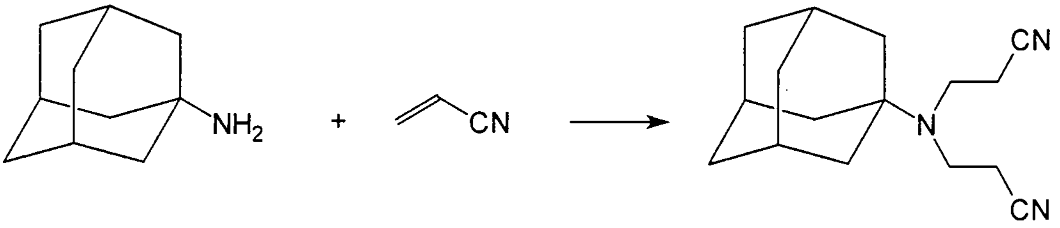
2.6.3 Synthesis of *Hex-dendr-(CN)₄*



Hex-dendr-$(NH_2)_2$ (3.20g, 14.86mmol.) was dissolved in water (50ml) in a two-necked flask, fitted with a dropping-funnel and condenser. Acrylonitrile (12.67g, 0.239mol.) was added over 30 minutes with stirring, and the reaction mixture was stirred at 65°C for 1 hour and at room temperature for 16 hours. The excess acrylonitrile was removed by vacuum distillation as an azeotrope with water (40°C, 12mmHg). The water was extracted with dichloromethane (3x50ml) and the combined organic extracts were dried over magnesium sulphate. The magnesium sulphate was removed by filtration and the solvent using a rotary evaporator at water pump pressure. A yellow, viscous oil, *Hex-dendr-$(CN)_4$* (4.40g, 69%), was isolated and characterised by spectroscopy: ^{13}C n.m.r. ($CDCl_3$, 100MHz) δ13.95 ($\underline{C}H_3$),

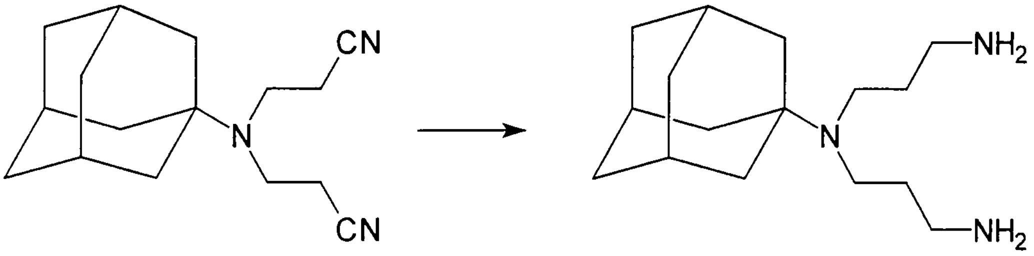
δ16.76 ($CH_2\underline{C}H_2CN$), δ24.91 ($CH_2N(CH_2\underline{C}H_2CH_2N(CH_2CH_2CN)_2)_2$), δ22.53, δ26.77, δ27.13, δ31.67 (chain $\underline{C}H_2$), δ49.13 ($CH_2N(CH_2CH_2CH_2N(\underline{C}H_2CH_2CN)_2)_2$), δ51.27, δ51.46, ($CH_2N(\underline{C}H_2CH_2\underline{C}H_2N(CH_2CH_2CN)_2)_2$), δ53.82 ($\underline{C}H_2N(CH_2CH_2CH_2N(CH_2CH_2CN)_2)_2$), δ118.61 ($CH_2CH_2\underline{C}N$) (Appendix 1.7). ^{1}H n.m.r. ($CDCl_3$, 400MHz) δ0.54 (3H, $C\underline{H}_3CH_2$), δ0.93 (6H $C_2H_5C_3\underline{H}_6CH_2N$), δ1.05 (2H $CH_3C\underline{H}_2$), δ1.23 (4H, $CH_2N(CH_2C\underline{H}_2CH_2N(CH_2CH_2CN)_2)_2$), δ2.12 (18H, $C\underline{H}_2N(C\underline{H}_2CH_2C\underline{H}_2N(C\underline{H}_2CH_2CN)_2)_2$), δ2.50 (8H, $CH_2C\underline{H}_2CN$) (Appendix 1.8). FTIR, ν_{max}/cm^{-1}: 2928.9, 2854.5 (C-H stretch), 2248.9 (CN stretch) (Appendix 1.9). GC Mass Spectrometry: m/z 428, (Theory 428).

2.6.4 Cyanoethylation of 1-adamantanamine



1-Adamantanamine (1.98g, 13.09mmol.) was dissolved in methanol (20ml) with stirring in a two-necked flask, equipped with a dropping-funnel and condenser. Acrylonitrile (12.53g, 0.236mol.) was added over 15 minutes with stirring and the mixture was heated at reflux (85°C) for a week. Methanol and unreacted acrylonitrile were removed using a rotary evaporator at water pump pressure. The resulting residue was separated using Kugelröhr distillation apparatus, removing some methanol-acrylonitrile addition product, to yield predominantly the mono-cyanoethylated species, *Ad-dendr-(CN)₁* (2.32g), and only a little of the required product, *Ad-dendr-(CN)₂* (0.34g). Consequently, the reaction was repeated with more acrylonitrile (12.02g). Methanol and acrylonitrile were again removed using a rotary evaporator at water pump pressure and the mixture was separated using Kugelröhr distillation apparatus to give a waxy yellow solid, *Ad-dendr-(CN)₂* (0.82g, 24%), which was characterised by spectroscopy: ^{13}C n.m.r. ($CDCl_3$, 100MHz) δ20.71 ($N(CH_2\underline{C}H_2CN)_2$), δ29.30 (ring $\underline{C}H$), δ36.27 (ring ($\underline{C}H_2CHCH_2)_3CN$), δ36.51 ($N(\underline{C}H_2CH_2CN)_2$), δ36.62 (quartenary ring C), δ45.27 (ring ($\underline{C}H_2)_3CN$), δ118.83 ($\underline{C}N$). There are peaks that can be attributed to some residual mono-cyanoethylated product at δ20.11, δ36.62, δ45.16, and δ118.95, (Appendices 1.10 and 1.11). ^{1}H n.m.r. ($CDCl_3$, 400MHz) δ1.60 (12H, ring $C\underline{H}_2$), δ2.04 (3H, ring $C\underline{H}$), δ2.39 (4H, $N(C\underline{H}_2CH_2CN)_2$), δ2.87 (4H, $N(CH_2C\underline{H}_2CN)_2$). There are peaks that can be attributed to some residual mono-cyanoethylated product at δ2.42 and δ2.83, (Appendix 1.12). FTIR, ν_{max}/cm^{-1}: 3372.3 (OH / N-H stretch), 2905.4, 2850.0 (C-H stretch), 2245.7 (CN stretch) (Appendix 1.13). GC Mass Spectrometry: m/z 257, (Theory: m/z 257).

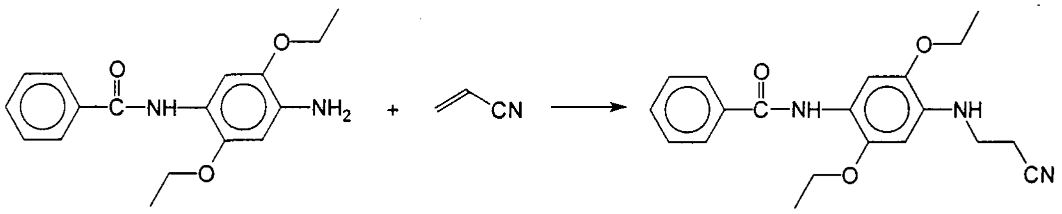
2.6.5 Reduction of *Ad-dendr-(CN)₂*



Ad-dendr-$(CN)_2$ (0.82g, 3.19mmol.) was dissolved in THF (200ml, dried over sodium wire) in a two-necked flask, fitted with a dropping-funnel and condenser, and DIBAH (30ml of a 1M solution in hexane) was added with stirring over 30 minutes. The mixture was refluxed (95°C) for 5 days and methanol (20ml) was added over 20 minutes at room temperature to destroy the excess DIBAH. A white solid appeared which was removed by filtration and washed with methanol (4x100ml). The solvents were removed using a rotary evaporator at water pump pressure to give a pale yellow solid, *Ad-dendr-$(NH_2)_2$* (0.78g, 93%), which was characterised by spectroscopy: ($CDCl_3$, 100MHz) δ26.53 ($N(CH_2\underline{C}H_2CH_2NH_2)_2$), δ28.66 (ring $\underline{C}H$), δ34.84 (ring $(\underline{C}H_2CHCH_2)_3CN$), δ36.68 ($N(\underline{C}H_2CH_2CH_2NH_2)_2$), δ37.10 ($N(CH_2CH_2\underline{C}H_2NH_2)_2$), δ38.07 (ring $(\underline{C}H_2)_3CN$). There are peaks that can be attributed to the reduced mono-cyanoethylated adduct at δ36.88 and δ37.19, (Appendix 1.14). ^1H n.m.r. ($CDCl_3$, 400MHz) δ1.53 (4H, $N(CH_2C\underline{H}_2CH_2NH_2)_2$), δ1.60 (12H, ring $C\underline{H}_2$), δ2.04 (3H, ring $C\underline{H}$), δ2.77, δ2.84 (8H, $N(C\underline{H}_2CH_2C\underline{H}_2NH_2)_2$). There are peaks that can be attributed to the reduced mono-cyanoethylated adduct at δ3.03 and δ3.07 (Appendix 1.15). FTIR, ν_{max}/cm^{-1}:

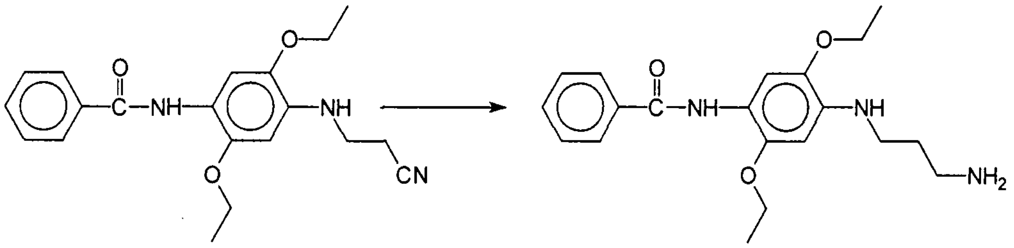
3278.9.3 (N-H stretch), 2903.6, 2847.9 (C-H stretch) (Appendix 1.16). CI Mass Spectrometry: m/z 266, and EI Mass Spectrometry: m/z 265, (Theory: m/z 265).

2.6.6 Cyanoethylation of Fast Blue BB



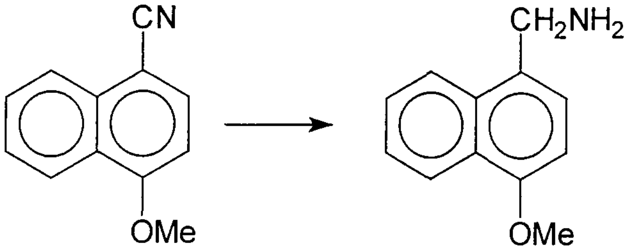
Purified Fast Blue BB (3.43g, 11.42mmol.) was dissolved in methanol (200ml) in a two-necked flask fitted with a dropping-funnel and condenser. Acrylonitrile (6.57g, 0.124mol.) was added drop-wise and the mixture was stirred at 80°C for 5 days. The solvents were removed using a rotary evaporator at water pump pressure and the remaining material was dissolved in a minimum volume of methanol (ca. 100ml). The solution was left at room temperature and yellow crystals formed overnight, *FB-dendr-(CN)*$_1$ (1.338g, 39%), which were characterised by spectroscopy: ^{13}C n.m.r. ($CDCl_3$, 100mhz) δ14.85 and δ15.01 ($CH_2\underline{C}H_3$), δ18.18 ($NHCH_2\underline{C}H_2CN$), δ40.11 ($NH\underline{C}H_2CH_2CN$), δ64.58 and δ65.33 ($O\underline{C}H_2CH_3$), δ96.54, δ105.13, δ126.67, δ128.64, δ131.39 (aromatic $\underline{C}H$), δ118.02 ($NHCH_2CH_2\underline{C}N$), δ118.78, δ132.498, δ135.229, δ140.110, δ142.135 (aromatic quaternaries), δ164.83 ($\underline{C}$=O), (Appendices 1.17 and 1.18). ^{1}H n.m.r. (400MHz, $CDCl_3$) δ1.36 (3H, $CH_2C\underline{H}_3$), δ1.39 (3H, $CH_2C\underline{H}_3$), δ2.58 (2H, $NHC\underline{H}_2CH_2CN$), δ3.48 (2H, $NHCH_2C\underline{H}_2CN$), ~δ4.0 (4H, OC$\underline{H}_2$CH$_3$), δ6.21 (1H, N$\underline{H}$C=O), δ7.43 - δ8.37 (aromatic H's) (Appendix 1.19). FTIR, ν_{max}/cm^{-1}: 3379.9 (amide N-H stretch), 3328.8 (aryl N-H stretch), 2977.9, 2925.8 (C-H stretch), 2246.1 (CN stretch), 1646.3 (C=O stretch) (Appendix 1.20). CI Mass Spectrometry: m/z 354, and EI Mass Spectrometry: m/z 353, (Theory: m/z 353).

2.6.7 Reduction of *FB-dendr-(CN)$_1$*



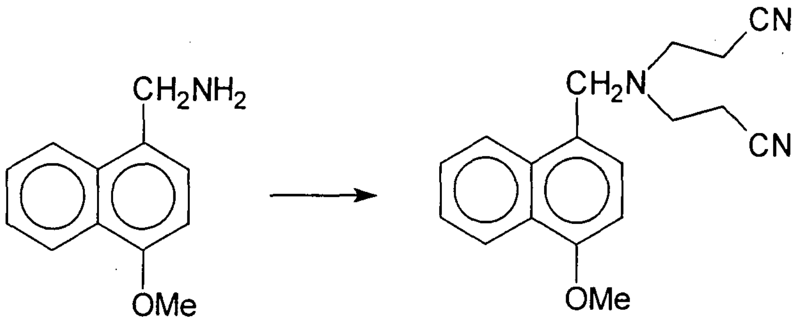
FB-dendr-(CN)$_1$ (0.62g, 1.53mmol.) was dissolved in THF (50ml, dried over sodium wire) in a two-necked flask fitted with a dropping-funnel and a condenser. DIBAH (15ml of a 1M solution in hexane) was added over 15 minutes with stirring and the mixture was refluxed at 90°C for 24 hours. Methanol (20ml) was added cautiously over 20 minutes to destroy the excess DIBAH and a yellow-white precipitate was produced. The solid was removed by filtration and washed with methanol (3x50ml). The solvent was removed using a rotary evaporator at water pump pressure and a dark brown solid product was isolated. This solid was separated using a Kugelröhr distillation apparatus to give *FB-dendr-(NH$_2$)$_1$* as an orange solid was isolated, (0.349g, 55.7%), which was characterised by spectroscopy: ^{13}C n.m.r. (CDCl$_3$, 100MHz) δ14.93 and δ15.11 ($CH_2\underline{C}H_3$), δ33.35 ($NHCH_2\underline{C}H_2CH_2NH_2$), δ40.15 ($NHCH_2CH_2\underline{C}H_2NH_2$), δ41.84 ($NH\underline{C}H_2CH_2CH_2NH_2$), δ64.76 and δ65.61 ($O\underline{C}H_2CH_3$), δ96.33, δ104.97, δ126.73, δ128.67, δ131.68 (aromatic $\underline{C}H$), δ116.36, δ132.498, δ135.229, δ140.110, δ142.135 (aromatic quaternaries), δ159.35 ($\underline{C}$=O), (Appendix 1.21). ^{1}H n.m.r. (400MHz, $CDCl_3$) δ1.38 (3H, $CH_2C\underline{H}_3$), δ1.43 (3H, $CH_2C\underline{H}_3$), δ1.79 (2H, $NHCH_2C\underline{H}_2CH_2NH_2$), δ2.83 (2H, $NHC\underline{H}_2CH_2CH_2NH_2$), δ3.19 (2H, $NHCH_2CH_2C\underline{H}_2NH_2$), ~δ4.0 (4H, $OC\underline{H}_2CH_3$), δ6.30 (1H, $N\underline{H}C$=O), δ7.49 - δ8.42 (aromatic H's) (Appendix 1.22). FTIR, ν_{max}/cm^{-1}: 3352.0, 3425.1 (N-H stretch), 2974.9, 2930.0 (C-H stretch) (Appendix 1.23). CI Mass Spectrometry: m/z 358, and EI Mass Spectrometry: m/z 358, (Theory: m/z 357.5).

2.6.8 Reduction of 4-methoxy-1-naphthonitrile



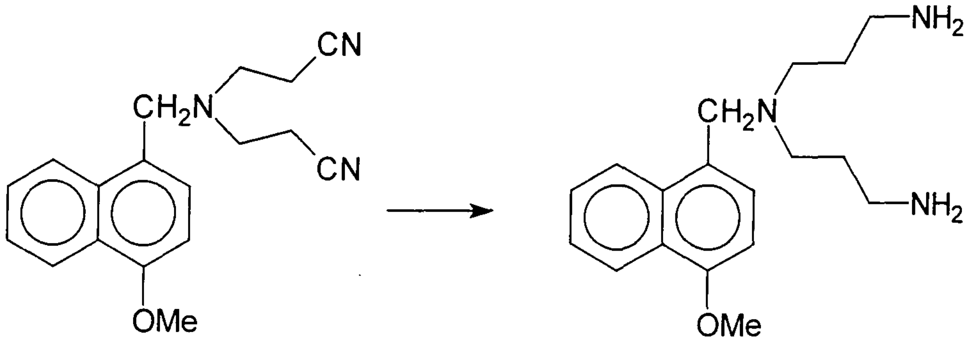
4-Methoxy-1-naphthonitrile (9.99g, 0.055mol.) was dissolved in methanol (800ml) in a beaker with stirring. A solution of sodium hydroxide (5.68) in water (100ml) and Raney nickel (10.34g slurried in water, 80ml) were added. The mixture was stirred at 70°C for 16 hours in a 2L, glass-lined, stainless steel autoclave under a hydrogen atmosphere (700psi). After cooling and venting, the reaction mixture was filtered and the Raney nickel was washed with methanol (200ml) and water (200ml). The methanol was removed using a rotary evaporator at water pump pressure and water (200ml) was added to the residue. The water layer was extracted with dichloromethane (3x200ml) and the combined organic extracts were dried over magnesium sulphate. The magnesium sulphate was removed by filtration and washed with dichloromethane (2x50ml). The solvent was removed using a rotary evaporator at water pump pressure to give *1-aminomethyl-4-methoxy-naphthalene* as a viscous, yellow oil which solidified on cooling, (9.07g, 89%); found: C 76.94; H 6.77; N 7.09%, m/z M+1 = 188 determined by GC Mass Spectrometry; $C_{12}H_{13}ON$ requires: C 76.98; H 7.00; N 7.48%, m/z = 187. ^{13}C n.m.r. (100MHz, d_6-methyl sulfoxide) δ43 ($\underline{C}H2$), δ56 ($\underline{C}H_3$), δ103, δ122, δ123.5, δ124.5, δ125, δ126 ($\underline{C}H$), δ125 ($\underline{C}CH_2$), δ131, δ132 (C-9 and C-10), δ153.5 ($\underline{C}OMe$) (Appendices 1.24 and 1.25). ^1H n.m.r. (400MHz, d_6-methyl sulfoxide) δ4.0 (3s, $C\underline{H}_3$), δ4.1 (2s, $C\underline{H}_2$), δ6.9 (1d, C-3 $\underline{H}$), δ7.4 (1d C-2 $\underline{H}$), δ7.5 (2m, C-6 and C-7 $\underline{H}$), δ8.0 and δ8.1 (1d, C-5 and C-8 $\underline{H}$) (Appendix 1.26). FTIR, ν_{max}/cm^{-1}: 3372, 3290 (N-H stretch), 3070.0, 3000.5, 2933.7 (C-H stretch) (Appendix 1.27).

2.6.9 Cyanoethylation of 1-aminomethyl-4-methoxy-naphthalene



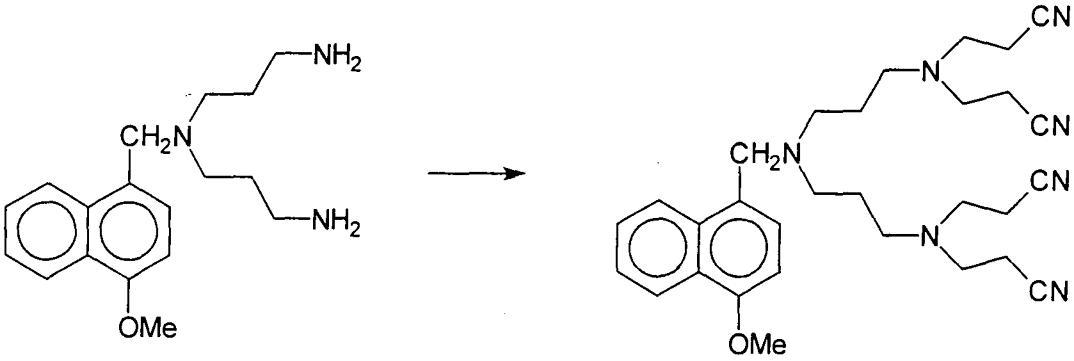
1-Aminomethyl-4-methoxy-naphthalene (8.77g, 0.047mol) was dissolved in methanol (100ml) in a two-necked flask equipped with a dropping-funnel and condenser. Acrylonitrile (19.96g, 0.377mol) was added drop-wise over 20 minutes, with stirring. The reaction mixture was stirred at 70°C for 48 hours. The solvents were removed using a rotary evaporator at water pump pressure and a little methanol-acrylonitrile addition product was removed using Kugelröhr distillation apparatus to give *UV-dendr-(CN)$_2$* as a yellow, viscous oil, (12.84g, 93%), which was characterised by spectroscopy: ^{13}C n.m.r. (100MHz, $CDCl_3$) δ16.4 ($\underline{C}H_2CN$), δ49.6 ($\underline{C}H_2CH_2CN$), δ55.4 ($O\underline{C}H_3$), δ56.9 ($\underline{C}H_2N$), δ102.8, δ122.3, δ123.9, δ125.3, δ126.7, δ127.6 ($\underline{C}H$), δ118.5 ($\underline{C}N$), δ124.5, δ125.8, δ132.6, δ155.6 (quaternary carbons) (Appendices 1.28 and 1.29). ^{1}H n.m.r. (400MHz, $CDCl_3$) δ2.3 (4t, $C\underline{H}_2CH_2CN$), δ2.9 (4t, $C\underline{H}_2CN$), δ4.0 (3s, $C\underline{H}_3$), δ4.1 (2s, $C\underline{H}_2N$), δ6.7 (1d, C-3 $\underline{H}$), δ7.3 (1d C-2 $\underline{H}$), δ7.5 (2m, C-6 and C-7 $\underline{H}$), δ8.2 and δ8.3 (1d, C-5 and C-8 $\underline{H}$) (Appendix 1.30). FTIR, ν_{max}/cm^{-1}: 3073.1, 3004.8, 2937.2, 2838.9 (C-H stretch), 2247 (CN stretch) (Appendix 1.31). This product was pure enough to be used in the next step.

2.6.10 Reduction of *UV-dendr-(CN)₂*



UV-dendr-(CN)₂ (14.94g, 0.051mol.) was dissolved in methanol (800ml) in a beaker. A solution of sodium hydroxide (5.65g) in water (100ml) and Raney nickel (9.81g slurried in water, 50ml) were added. The mixture was stirred at 70°C for 16 hours in a 2L, glass-lined, stainless steel autoclave under a hydrogen atmosphere (800psi). After cooling and venting, the reaction mixture was filtered and the Raney nickel was washed with methanol (200ml) and water (200ml). The methanol was removed using a rotary evaporator at water pump pressure. Water (100ml) was added to the residue which was extracted with dichloromethane (3x100ml). The combined organic extracts were dried over magnesium sulphate. The magnesium sulphate was removed by filtration and the solvent by using a rotary evaporator at water pump pressure to yield *UV-dendr-(NH₂)₂* as a yellow oil which solidified on cooling, (10.15g, 66%); found: C 71.35; H 9.45; N 13.64%, m/z M+1 = 302 determined by GC Mass Spectrometry; $C_{18}H_{27}ON_3$ requires: C 71.72; H 9.03; N 13.94%, m/z = 301. ^{13}C n.m.r. (100MHz, $CDCl_3$) δ28.99 ($CH_2\underline{C}H_2CH_2NH_2$), δ49.88 ($CH_2CH_2\underline{C}H_2NH_2$), δ52.63 ($\underline{C}H_2CH_2CH_2NH_2$), δ55.31 ($O\underline{C}H_3$), δ58.09 ($\underline{C}H_2N$), δ103.89, δ123.02, δ124.82, δ125.41, δ126.12 and δ127.08 ($\underline{C}H$), δ125.94, δ130.19, δ138.01 and δ157.10 (quaternary carbons) (Appendix 1.32). ^{1}H n.m.r. (400MHz, $CDCl_3$) δ1.57 (4m, $CH_2C\underline{H}_2CH_2NH_2$), δ2.36 (4t, $CH_2CH_2C\underline{H}_2NH_2$), δ2.43 (4t, $C\underline{H}_2CH_2CH_2NH_2$), δ3.71 (2s, $C\underline{H}_2N$), δ3.93 (3s, $C\underline{H}_3$), δ6.82 (1d, C-3 $\underline{H}$), δ7.22 (1d C-2 $\underline{H}$), δ7.50 (2m, C-6 and C-7 $\underline{H}$), δ7.92 and δ8.18 (1d, C-5 and C-8 $\underline{H}$) (Appendix 1.33). FTIR, ν_{max}/cm^{-1}: 3369.4, 3286.7 (N-H stretch), 3071.8, 3001.5, 2934.0 (C-H stretch) (Appendix 1.34).

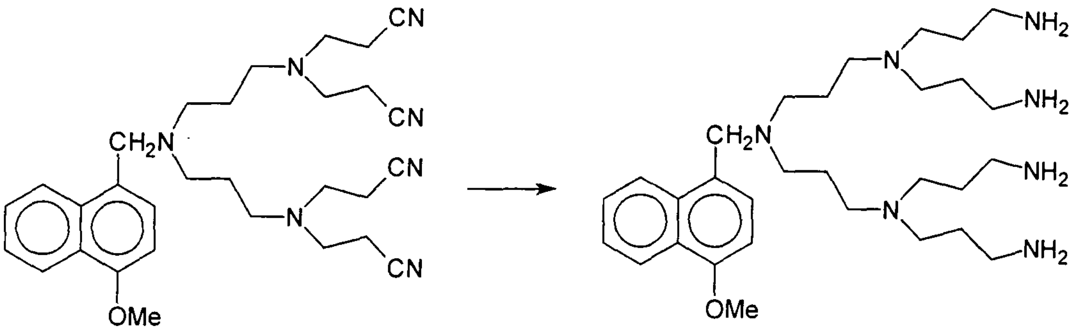
2.6.11 Cyanoethylation of *UV-dendr-(NH$_2$)$_2$*



UV-dendr-(NH$_2$)$_2$ (10.15g, 0.034mol) was dissolved in methanol (100ml) in a two-necked flask equipped with a dropping-funnel and a condenser. Acrylonitrile (25.21g, 0.476mol) was added drop-wise with stirring over 20 minutes and the mixture was stirred at 70°C for 50 hours. The solvents were removed using a rotary evaporator at water pump pressure and the product was separated using Kugelröhr distillation apparatus to give *UV-dendr-(CN)$_4$* as a waxy, yellow product, (7.09g, 41%), which was characterised by spectroscopy: ^{13}C n.m.r. (100MHz, $CDCl_3$)

δ16.54 (NCH$_2$C̲H$_2$CN), δ25.01 (NCH$_2$C̲H$_2$CH$_2$N), δ49.27 (NC̲H$_2$CH$_2$CN), δ51.31 (NCH$_2$CH$_2$C̲H$_2$N), δ51.92 (NC̲H$_2$CH$_2$CH$_2$N), δ55.34 (OC̲H$_3$), δ57.97 (Ar-C̲H$_2$N), δ100-130 (protonated aromatics) (Appendices 1.35 and 1.36). ^{1}H (400MHz, CDCl$_3$) ~δ1-3 (CH̲$_2$), ~δ4 (OCH̲$_3$), ~δ6.6-8.3 (aromatic CH̲) (Appendix 1.37). FTIR, ν_{max}/cm^{-1}: 3071.6, 2941.8 (C-H stretch), 2245.4 (CN stretch) (Appendix 1.38). This product was pure enough to be used in the next step.

2.6.12 Reduction of *UV-dendr-(CN)$_4$*



UV-dendr-(CN)$_4$ (7.09g, 0.014mol.) was dissolved in methanol (700ml) in a beaker with stirring. A solution of sodium hydroxide (5.66g) in water (100ml) and Raney nickel (14.50g slurried in water, 50ml) was added. The mixture was stirred at 70°C for 16 hours in a 2L, glass-lined, stainless steel autoclave under a hydrogen atmosphere (1000psi). After cooling and venting, the reaction mixture was filtered and the Raney nickel was washed with methanol (200ml) and water (200ml). The methanol was removed using a rotary evaporator at water pump pressure. Water

(100ml) was added to the residue which was extracted with dichloromethane (3x100ml). The combined organic extracts were dried over magnesium sulphate. The magnesium sulphate was removed by filtration and the solvent using a rotary evaporator at water pump pressure to yield *UV-dendr-(NH_2)$_2$* as a waxy, yellow product, (4.34g, 59%); found: C 67.84; H 10.34; N 18.21%, m/z $M+H^+$ = 530 determined by MALDI Mass Spectrometry (Appendix 1.43); $C_{30}H_{54}ON_7$ requires: C 68.14; H 10.29; N 18.54%, m/z = 529. ^{13}C n.m.r. (100MHz, $CDCl_3$) δ29.50 ($CH_2\underline{C}H_2CH_2NH_2$), δ30.55 ($NCH_2\underline{C}H_2CH_2N$), δ44.41 ($CH_2CH_2\underline{C}H_2NH_2$), δ51.63 ($NCH_2CH_2\underline{C}H_2N$), δ51.70 ($N\underline{C}H_2CH_2CH_2NH_2$), δ52.23 ($N\underline{C}H_2CH_2CH_2N$), δ55.24 ($O\underline{C}H_3$), δ56.92 ($\underline{C}H_2N$), δ102.66, δ122.00, δ124.71, δ125.65, δ125.74, δ126.00 and δ127.23 ($\underline{C}H$), δ125.78, δ133.13, δ137.30 and δ156.08 (quaternary carbons) (Appendices 1.39 and 1.40). ^1H n.m.r. (400MHz, $CDCl_3$) δ1.58 (12m, $NCH_2C\underline{H}_2CH_2N$), δ2.33 - δ2.60 (24m, $NC\underline{H}_2CH_2C\underline{H}_2N$), δ3.86 (2s, $C\underline{H}_2N$), δ3.99 (3s, $C\underline{H}_3$), δ6.71 (1d, C-3 $\underline{H}$), δ7.47 (3m, C-2 $\underline{H}$, C-6 and C-7 $\underline{H}$), δ8.25 (2m, C-5 and C-8 $\underline{H}$) (Appendix 1.41). FTIR, ν_{max}/cm^{-1}: 3361.1, 3274.9 (N-H stretch), 2929.8 (C-H stretch) (Appendix 1.42).

2.7 References

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CHAPTER 3

Terminal-Group Modification of Poly(propylene imine) Dendrimer Wedges

3 Terminal-Group Modification of Poly(propylene imine) Dendrimer Wedges

3.1 Introduction

Cellulose is a linear homopolymer of glucose and is the most abundant organic polymer on Earth. The glucose repeat units are linked in the 1,4-β configuration, by contrast with the 1,4-α configuration in starch (Figure 3.1). The β configuration allows the chains to crystallise in a linear conformation via inter and intra-molecular hydrogen-bonding, so natural cellulose as found in wood and natural fibres such as flax and cotton is highly crystalline (90-95%). The crystallites are organised in fibrils that are aligned along the fibre axis, producing a tensile modulus of ca. 100 GPa when stressed. Cotton fibre is almost pure cellulose (ca. 98%) but wood is a natural biocomposite, with 50-60% cellulose content embedded in lignin, a phenyl propene polymer.

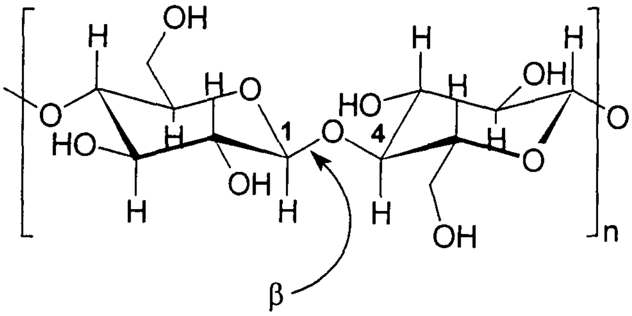


Figure 3.1 1,4-β-glycosidic bonds of unbranched cellulose.

3.1.1 The cellulose surface and its interaction with water

Understanding the structure of the surface of cellulose as found in cotton is important when considering the types of molecules that are likely to adsorb onto it. The microstructure of the fibres is important but the pore structure and surfaces of pores can be critical to the modification of fibres with finishes, such as optical brighteners and softeners.[1] However, the extent of our knowledge concerning penetration of water-soluble solutes into cotton fibres and interactions of solutes with pore surfaces is limited. Since this work attempts to attach a surface modifier onto a cotton surface in aqueous solution, the role of water must also be analysed.

Pores arise from discontinuities of molecular packing in polymeric substrates such as cellulose. Networks of channels do not exist in the dry fibres, but on the addition of a suitable swelling agent, such as water, the channels and pores appear. This is well illustrated by comparing the surface area for the dry fibres, ca. 0.6-0.7m^2/g, to that of the same fibre in a saturated water vapour environment, ca. 137m^2/g. There is evidence that water within a moist cellulosic substrate shows properties that are significantly different from those of bulk water, and that between 0.03 and 0.10g of water per gram of substrate can be considered to be "bound water,"[2,3,4] and has also been described as a "perturbed layer" (Figure 3.2).[5] It has been reported that the water bound to the surface of cellulose (perturbed layer) is held by a set of hydrogen-bonds that are effectively weaker than those in clusters of water molecules (unperturbed liquid),[6] thus, it may be possible to displace surface water by molecules which bind more strongly.

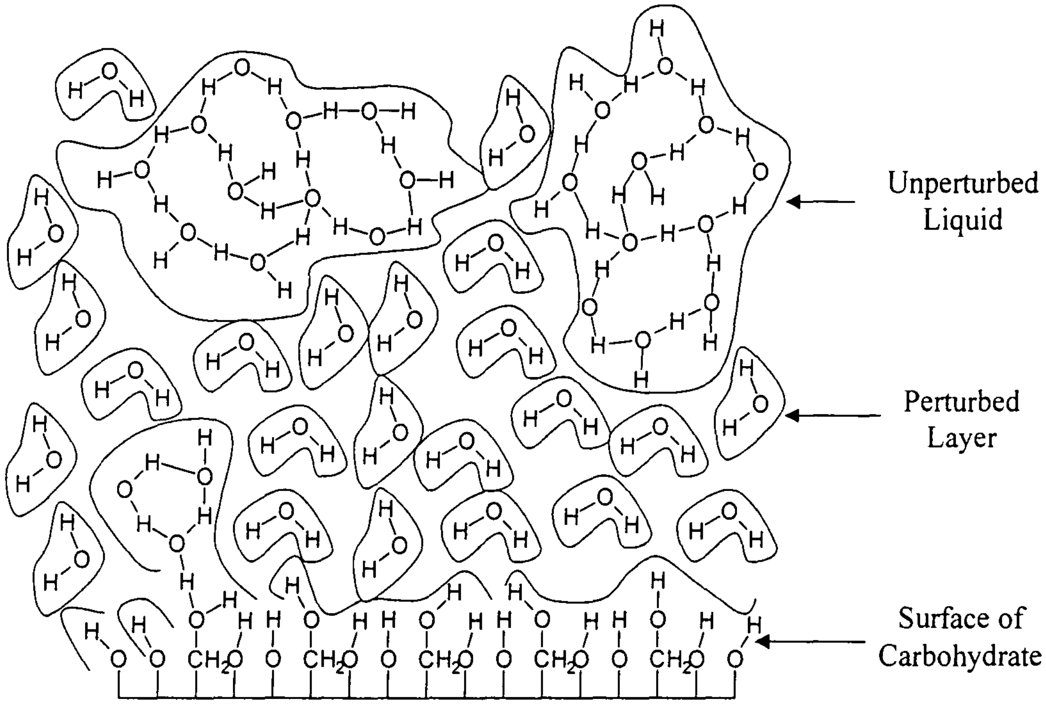


Figure 3.2 Model for the carbohydrate-water interface.

Research suggests that there are two quite different types of accessible surfaces.[7] One has a higher proportion of free, i.e. non-inter- or intra-molecular bonded hydroxyl groups and the other has quite highly ordered hydrogen-bonded hydroxyl groups. Both these types of surfaces can be considered polar and capable of interaction with water.

Adsorption of water-soluble solutes onto a cellulosic surface can occur in two ways. Firstly, a solute molecule can penetrate a pore by a sieving action and this is controlled by the size of the pore relative to the size of the solute. Another mechanism of adsorption depends on the ability of the solute to displace the "bound water" at the cellulose-water interface so that it becomes part of the bulk solvent.

All water at the surface is displaceable by solutes that have high proportions of groups capable of strong donor and acceptor hydrogen-bonding, such as saccharides.[8] Water-soluble solutes that are not capable of such hydrogen bonding find that only a fraction of the total water is displaceable and cannot, therefore, disrupt this water and adsorb onto the surface.

3.2 Synthesis of carbohydrate-terminated dendrimers

In Section 3.1.1 it was stated that species that are capable of comprehensive hydrogen-bonding should be capable of adsorbing onto cellulosic surfaces by disrupting the "bound water." To complement this work, it is reported that carbohydrates do indeed bind to cellulose via comprehensive inter-molecular hydrogen-bonding.[9,10,11] Consequently, it was hoped that a dendrimer with cellulosic fragments as end groups might adsorb onto a cellulose surface. The attachment of lactobiono-lactone onto UV-active dendritic wedges was attempted in order to supply this recognition and binding capability, and the multiplication of effects could be examined by using mono-, di- and tetra-functionalised derivatives.

Lactobiono-lactone, as supplied, contains ca. 16% lactobionic acid. Heating this mixture in methanol affords the methyl ester of lactobionic acid. On adding dendritic wedges with primary amine functionality, a lactobionamide is produced (Figure 3.3).[12,13,14]

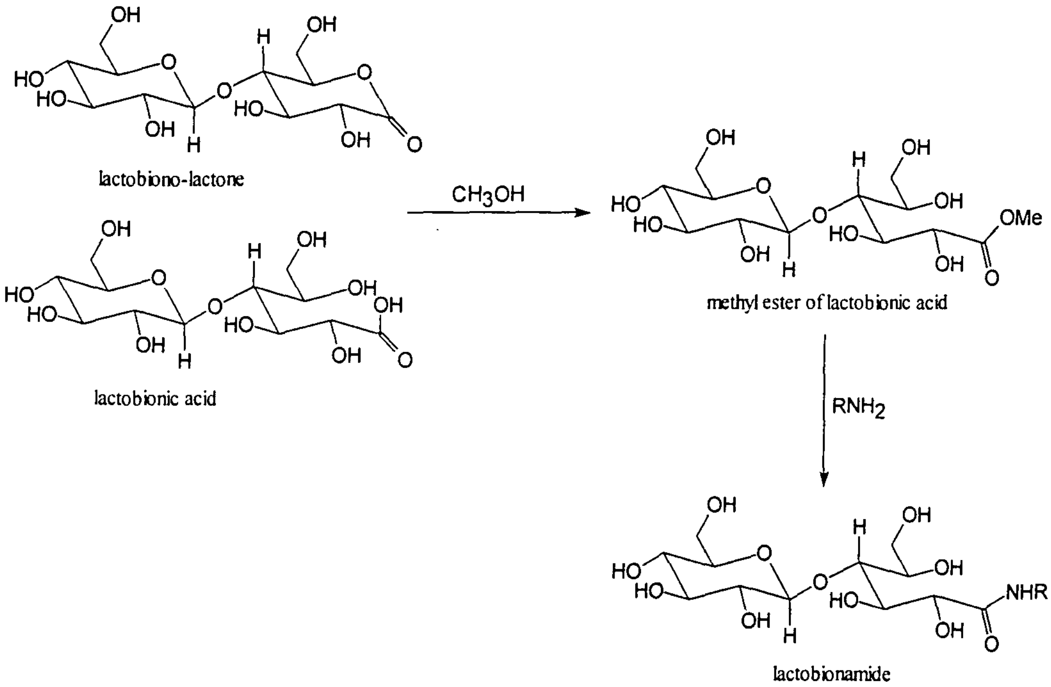


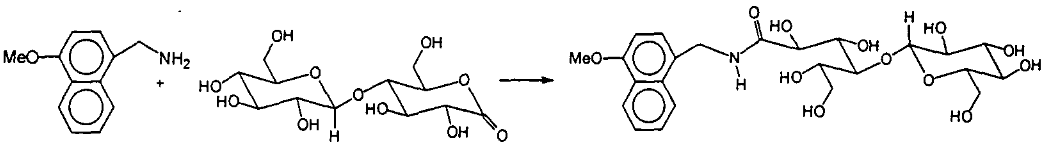
Figure 3.3 Attachment of lactobiono-lactone onto dendritic wedges.

This process was used to attach lactobiono-lactone to *UV-dendr-*$(NH_2)_1$, *UV-dendr-*$(NH_2)_2$ and *UV-dendr-*$(NH_2)_4$. This was a straightforward process but was quite time consuming in optimising the functionalisation and purification of the probe molecules.

The functionalisation of *UV-dendr-*$(NH_2)_1$ and *UV-dendr-*$(NH_2)_2$ proceeded to completion, however the MALDI-TOF mass spectra of *UV-dendr-(carb)*$_4$ showed peaks at m/z $M+H^+$ = 870, 1209 and 1549 which can be attributed to *UV-dendr-*$(NH_2)_4$ attached to only 1, 2 and 3 carbohydrate residues respectively. These peaks were still present in the spectrum of the product obtained when a much longer reaction time was used. It is postulated that these species due to incomplete functionalisation are present in small quantities since both the ^1H n.m.r. spectrum and the elemental analysis are consistent with the formation of the fully tetra-functionalised compound. Furthermore, the FTIR spectrum shows no presence of lactobiono-lactone starting material, which could give rise to misleading, yet seemingly correct analytical results. It is concluded that the small amounts of species due to incomplete functionalisation are unlikely to affect the overall properties of the material.

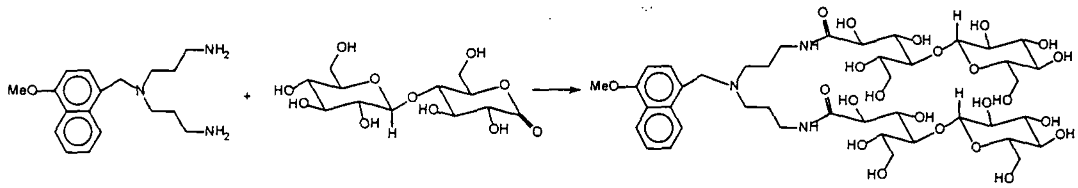
3.3 Experimental

3.3.1 Synthesis of *UV-dendr-(carb)$_1$*



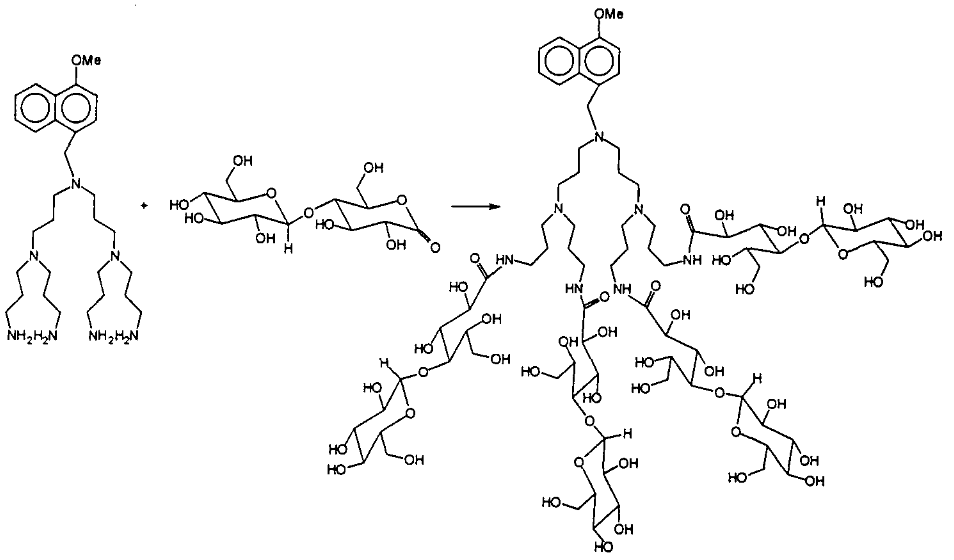
Lactobiono-lactone (0.61g, 1.79mmol.) was dissolved in methanol (150ml) with stirring in a 1-necked flask, fitted with a condenser. 4-Methoxy-1-aminomethyl naphthalene (0.99g, 5.28mmol.) was added and the mixture was refluxed for 24 hours. The solvent was removed using a rotary evaporator at water pump pressure, the residue was taken up in water (100ml) and the excess amine was extracted with dichloromethane (3x50ml). The water was removed using a rotary evaporator at water pump pressure and the residue was dissolved in methanol (500ml) at room temperature. The solution was left in a refrigerator (~5°C) and a white precipitate formed overnight. The solution was decanted off and the residue was washed with ice-cold methanol (2x50ml) and dried in a vacuum oven at room temperature to give *UV-dendr-(carb)$_1$*, (0.68g, 24%); found: C 55.06; H 6.51; N 2.92%, m/z M+Na$^+$ = 550 determined by MALDI-TOF Mass Spectrometry (Appendix 2.4); $C_{24}H_{32}O_{12}N$ requires: C 54.75; H 6.13; N 2.66%, m/z = 527. ^{13}C n.m.r. (100MHz, d_6-dimethyl sulfoxide) δ48.4 ($\underline{C}H_2NH$), δ55.6 ($\underline{C}H_3$), δ60.7 and δ62.4 ($\underline{C}H_2OH$), δ68.3-103.7 (carbohydrate O$\underline{C}$H), δ104.7-154.3 (aromatic C's), δ172.3 ($\underline{C}$=O) (Appendix 2.1). ^{1}H n.m.r. (400MHz, d_6-dimethyl sulfoxide) δ2.49 (dimethyl sulfoxide), δ3.17 (methanol), δ3.73 (2s, $C\underline{H}_2NH$), δ3.94 (3s, $OC\underline{H}_3$), δ3.3-5.3 (20m, carbohydrate H's), δ6.89 (1d, C-3 $\underline{H}$), δ7.42 (1D, C-2 $\underline{H}$), δ7.52 (2m, C-6 and C-7 $\underline{H}$), δ8.00 (1s, NHC=O), δ8.18 (2m, C-5 and C-8 $\underline{H}$) (Appendix 2.2). FTIR, ν_{max}/cm^{-1}: 3394.2 (OH stretch), 2932.4 (C-H stretch), 1651.8 (amide C=O stretch) (Appendix 2.3). CI Mass Spectrometry: m/z 42, 44, 56. UV spectroscopy: λ_{max} 296nm (Appendix 2.5).

3.3.2 Synthesis of *UV-dendr-(carb)$_2$*



Lactobiono-lactone (2.37g, 6.96mmol.) was dissolved in methanol (250ml) with stirring in a one-necked flask, fitted with a condenser. *UV-dendr-(NH$_2$)$_2$* (1.00g, 3.32mmol.) was added and the mixture was refluxed for 36 hours. The reaction mixture was allowed to cool to room temperature overnight. The solution was left in a refrigerator (~5°C) and a white precipitate formed after 72 hours. The solution was decanted off and the residue was washed with ice-cold methanol (2x50ml) and dried in a vacuum oven at room temperature to give *UV-dendr-(carb)*$_2$, (0.89g, 27%); found: C 51.06; H 7.01; N 4.32%, m/z M+Na$^+$ =1005 determined by MALDI-TOF Mass Spectrometry (Appendix 2.10); $C_{42}H_{67}O_{23}N_3$ requires: C 51.37; H 6.88; N 4.28%, m/z = 982. ^{13}C n.m.r. (100MHz, d$_6$-dimethyl sulfoxide) δ26.4 ($NCH_2\underline{C}H_2CH_2N$), δ37.0 ($NCH_2CH_2\underline{C}H_2NH$), δ50.8 ($N\underline{C}H_2CH_2CH_2NH$), δ55.0 ($\underline{C}H_3$), δ56.3 ($\underline{C}H_2NH$), δ60.7 and δ62.4 ($\underline{C}H_2OH$), δ68.2-104.7 (carbohydrate O$\underline{C}$H), δ106.3-155.8 (aromatic C's), δ172.1 ($\underline{C}$=O) (Appendices 2.6 and 2.7). ^{1}H n.m.r. (400MHz, d$_6$-dimethyl sulfoxide) δ1.60 (4m, $NCH_2C\underline{H}_2CH_2N$), δ2.06 (acetone), δ2.43 ($NC\underline{H}_2CH_2C\underline{H}_2N$), δ2.48 (dimethyl sulfoxide), δ3.14 (methanol), δ3.67 (2s, $C\underline{H}_2NH$), δ3.94 (3s, $OC\underline{H}_3$), δ3.3-5.3 (carbohydrate H's), δ6.90-δ8.22 (aromatic H's) (Appendix 2.8). FTIR, ν_{max}/cm^{-1}: 3379.5 (OH stretch), 2930.4 (C-H stretch), 1651.3 (amide C=O stretch) (Appendix 2.9). CI Mass Spectrometry: m/z 175, 328. EI Mass Spectrometry: m/z 174, 328. UV spectroscopy: λ_{max} 296nm (Appendix 2.11).

3.3.3 Synthesis of *UV-dendr-(carb)₄*



Lactobiono-lactone (2.61g, 7.68mmol.) was dissolved in methanol (200ml) with stirring in a one-necked flask, fitted with a condenser. *UV-dendr-(NH$_2$)$_4$* (0.87g, 1.64mmol.) was added and the mixture was refluxed for 72 hours. The solution was left to cool to room temperature overnight. The solution was left in a refrigerator (~5°C) and a white precipitate formed after 48 hours. The solution was decanted off and the residue was washed with ice-cold methanol (2x50ml) and dried in a vacuum oven at room temperature to give *UV-dendr-(carb)$_4$*, (0.91, 29%); found: C 50.03; H 7.33; N 5.05%, m/z M+Na$^+$ = 2010 determined by MALDI-TOF Mass Spectrometry. $C_{78}H_{131}O_{45}N_7$ requires: C 49.65; H 7.00; N 5.20%, m/z = 1887. ^{13}C n.m.r. (100MHz, D$_2$O) δ26.0 (NCH$_2$$\underline{C}H_2CH_2$N), δ36.8 (NCH$_2CH_2$$\underline{C}H_2$NH), δ50.2, δ50.9 (N$\underline{C}H_2CH_2CH_2$NH), δ55.3 ($\underline{C}H_3$), δ60.9 and δ60.9 ($\underline{C}H_2$OH), δ68.4-102.9 (carbohydrate O$\underline{C}$H), δ103.3-155.8 (aromatic C's), δ174.0 ($\underline{C}$=O) (Appendix 2.12). ^{1}H n.m.r. (400MHz, D$_2$O) δ1.62 (12m, NCH$_2$C$\underline{H_2}$CH$_2$N), δ2.44-δ3.2 (24m, NC$\underline{H_2}$CH$_2$C$\underline{H_2}$N), δ3.3-4.4 (81m, OCH$_3$, CH$_2$N and carbohydrate H's), δ6.76-δ8.21

(aromatic H's) (Appendix 2.13). FTIR, ν_{max}/cm^{-1}: 3375.9 (OH stretch), 2930.8 (C-H stretch), 1649.7 (amide C=O stretch) (Appendix 2.14). FAB Mass Spectrometry: m/z 171, 327. UV spectroscopy: λ_{max} 296nm (Appendix 2.15).

3.4 References

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CHAPTER 4

Adsorption Studies on Carbohydrate-Terminated Dendrimer Wedges

4. Adsorption Studies on Carbohydrate-Terminated Dendrimer Wedges

This chapter discusses the experimental study of adsorption of the molecules whose preparation was discussed in Chapters 2 and 3. The overall conclusions of the study are presented in Chapter 5.

4.1 Adsorption from solution at the solid/liquid interface

4.1.1 Adsorption isotherms

A molecule can adsorb onto a surface via chemical or physical processes or a combination of both.[1] Several types of bonding to a surface have been identified, and a generally accepted classification is given below:

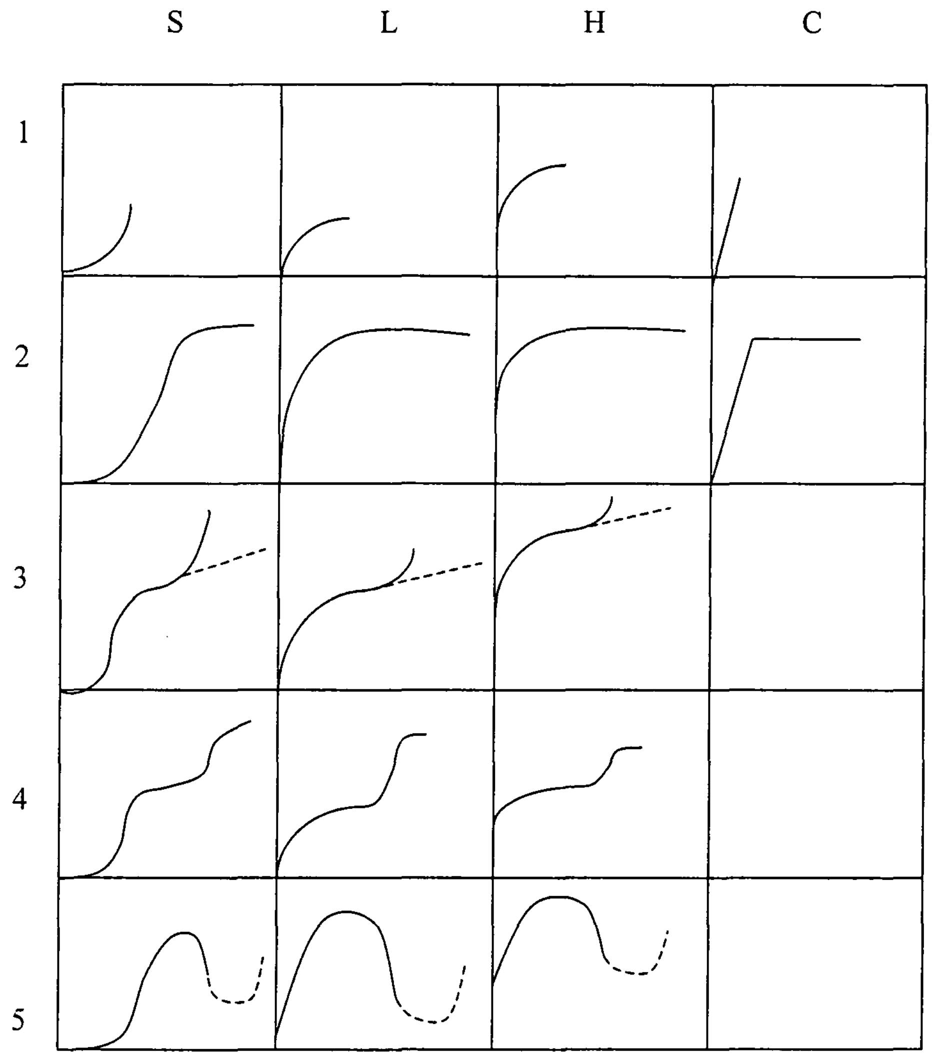
1. Chemical adsorption (chemisorption),
2. Hydrogen-bonding,
3. Hydrophobic-bonding,
4. van der Waals forces.

The actual mechanism of attraction to a surface may be a consequence of one or more of these interactions, depending on the chemical composition of the surface, the molecule to be adsorbed and the environment, e.g. solvent, temperature or pressure.

An *adsorption isotherm* is a plot of the amount of solute adsorbed per gram of substrate (Q), versus the equilibrium concentration of the solution (C), i.e. the concentration of solute in solution in equilibrium with the surface under study. Analysis of the characteristic adsorption isotherm for a particular system can provide insight into the method of adsorption of molecules onto surfaces. Important aspects to be taken into consideration when determining the mechanism of adsorption are:

(a) the shape of the isotherm,
(b) any plateau in the isotherm,
(c) the effect of temperature on the isotherm,
(d) whether the adsorption is monomolecular or extends over more than one layer,
(e) the orientation of the adsorbed molecules,
(f) the extent of solvent adsorption,
(g) the nature of the interaction between the adsorbate and adsorbent.[2]

There are various shapes of isotherm possible, but not all have been reported for adsorption from solution (Figure 4.1).[3] There are four distinct classes that are identified by the initial part of the isotherm that is shown in sub-group 1. These are termed the S, L, H, and C isotherms;[4] the S being an S-shaped curve, the L being the type studied extensively by Langmuir, the H being associated with high affinity and the C with constant partition.



x-axis: Equilibrium concentration; y-axis: Amount adsorbed.

Figure 4.1 Classification of isotherm shapes.

The sub-groups relate to the behaviour of the isotherm at higher concentrations. Sub-group 2 isotherms reach a plateau and further adsorption above this value gives a sub-group 3 isotherm, and if that reaches a second plateau it is designated a sub-group 4 isotherm. The fifth sub-group type shows a maximum and is related to the special case of solutes that associate in solution, e.g. certain dyes, and contain highly surface-active impurities since a maximum is not thermodynamically possible in a pure system. The curve can be rationalised if beyond a certain concentration the association of the solute in solution is more advantageous than adsorption.

The L curves are the best known, in fact, the L2 curve accounts for almost all cases of adsorption from dilute solution. An L2 curve is indicative of a solute molecule adsorbing onto a surface to form a monolayer via a Langmuir mechanism, i.e. adsorption does not proceed over more than one layer of adsorbed species.

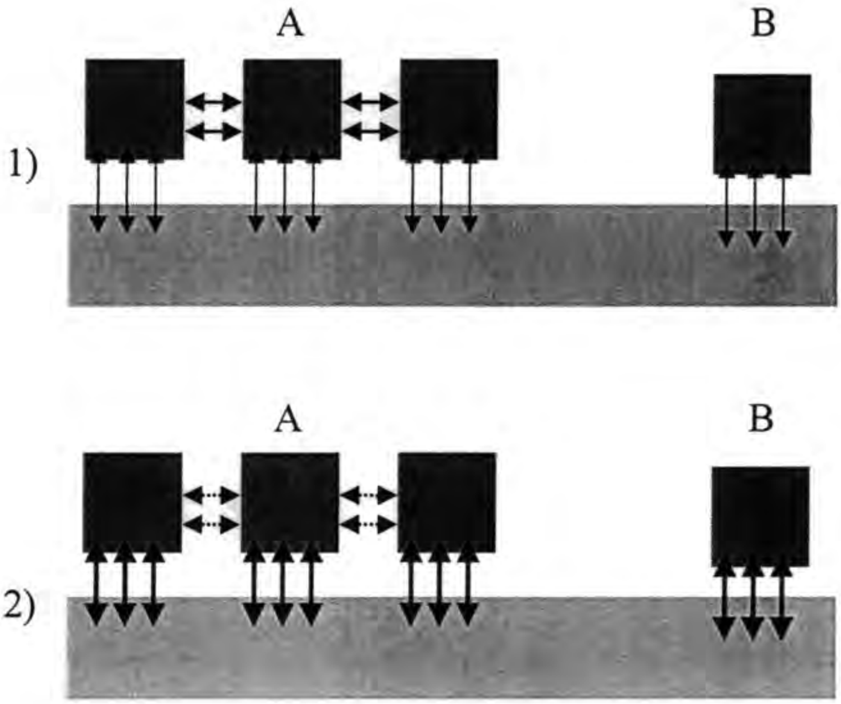
The initial slope of an adsorption isotherm depends on the rate of change of site availability with increase in solute adsorbed. As more solute is adsorbed, there is usually less chance for a subsequent solute molecule to find a suitable site for it to adsorb onto. This is the case for the L curves and for the latter stages of the S and H curves.

By contrast, in the initial part of the S curve, the opposite applies; the more solute already adsorbed, the easier it is for additional molecules to adsorb. This implies a side-by-side association between adsorbed molecules, helping them to hold to the surface and this is known as *co-operative adsorption.* Co-operative adsorption is most common when:

1. The solute molecule has a fairly large hydrophobic residue,
2. The solute molecule has a marked localisation of the forces of attraction for the substrate,
3. The solute molecule adsorbs as a single unit and not in the form of a micelle,

4. A solute molecule has moderate inter-molecular attraction with other solute molecules, causing it to pack vertically in regular array in the adsorbed layer,
5. The solute meets strong competition for substrate sites from solvent molecules.

This outline summary of the adsorption process is illustrated in Figure 4.2.



1) The solute-solute forces are strong compared to the solute-substrate forces. Therefore, a molecule would be more stable at A than B. This is known as co-operative adsorption and is characterised by S isotherms.

2) There are quite strong forces between solute molecules and the substrate, but very weak forces between solute molecules. Therefore, a molecule would be equally stable at B as at A producing an L (or H) isotherm.

Figure 4.2 Rationalisation of S and L isotherms.

The H curve is related to the L curve. In this case, the solute has such a high affinity for the substrate that in dilute solutions it is completely adsorbed, and the initial part of the isotherm is vertical. The H curves are associated with chemisorption or other strong interactions. The types of species that characteristically lead to H isotherms tend to be large, for example, ionic micelles and polymeric molecules.

In the case of C curves, the probability of a subsequent molecule finding a suitable site remains constant at all concentrations up to saturation. As sites are covered new sites appear, and the surface available expands proportionally to the amount of solute adsorbed and this occurs with microporous adsorbents resulting in a straight-line isotherm.

4.1.2 Theory of Langmuir adsorption

The theory of Langmuir adsorption assumes that every adsorption site is equivalent.[5] This means that the ability of a molecule to bind to a surface is independent of whether or not nearby sites are occupied. Molecules interact only with a site and not with each other, and adsorption is limited to a monolayer.

The adsorption process can be written as the equilibrium equation:

A (solute in solution) + B (adsorbed solvent) =

A (adsorbed solute) + B (solvent in solution)

With rate constants k_a for adsorption and k_d for desorption.

The rate of adsorption, r_a, is dependant on the concentration of the solution and the proportion of sites that are free, hence,

$$r_a = k_a \times C \times N\left(1 - \frac{Q}{N}\right)$$

Where Q is the amount of solute (in moles) adsorbed per gram of adsorbent, C is the equilibrium concentration and N is the total number of sites (in moles) per gram of adsorbent.

The rate of desorption is simply related to the amount of solute adsorbed, hence,

$$r_d = k_d \times Q$$

At equilibrium the rate of adsorption is equal to the rate of desorption, i.e. $r_a = r_d$, and this equation rearranges to give:

$$\frac{C}{Q} = \frac{1}{K_L N} + \frac{C}{N}$$

where $K_L = \frac{k_a}{k_d}$.

Therefore, a plot of $\frac{C}{Q}$ vs. C will give a straight line with gradient $\frac{1}{N}$, and intercept $\frac{1}{K_L N}$. N has units (mol. per gram of substrate) and K_L has units M^{-1}.

At low concentrations it can be assumed that the proportion of sites that are still free is approximately equal to the number of sites in total, i.e. $1-\frac{Q}{N}=1$ and hence,

$$Q = K_H C.$$

This is a version of Henry's Law and in this instance a plot of Q vs. C will give a straight line with gradient K_H which has units lg^{-1}, where g is grams of substrate.

4.2 Adsorption isotherm studies on carbohydrate-terminated dendrimers

4.2.1 Determination of extinction coefficients of *UV-dendr-(carb)$_1$*, *UV-dendr-(carb)$_2$* and *UV-dendr-(carb)$_4$*

The wavelength of maximum absorbance (λ_{max}) for each dendrimer in water was found to be 296nm (Appendices 2.5, 2.11 and 2.15), identical to that of 1-methoxy-naphthalene in methanol. A range of solutions of *UV-dendr-(carb)$_1$*, *UV-dendr-(carb)$_2$* and *UV-dendr-(carb)$_4$* at different concentrations were made up in distilled water and their absorbance at this wavelength, relative to their absorbance at a point on the baseline (400nm), were recorded at room temperature (20°C).

The Beer-Lambert law states that:

$$A = \varepsilon c l$$

Where A is absorbance, ε is the extinction coefficient, c is the concentration and l the path length.[6] Plotting absorbance at λ_{max} versus concentration produces a straight-line calibration curve with gradient εl (Figures 4.3, 4.4 and 4.5).

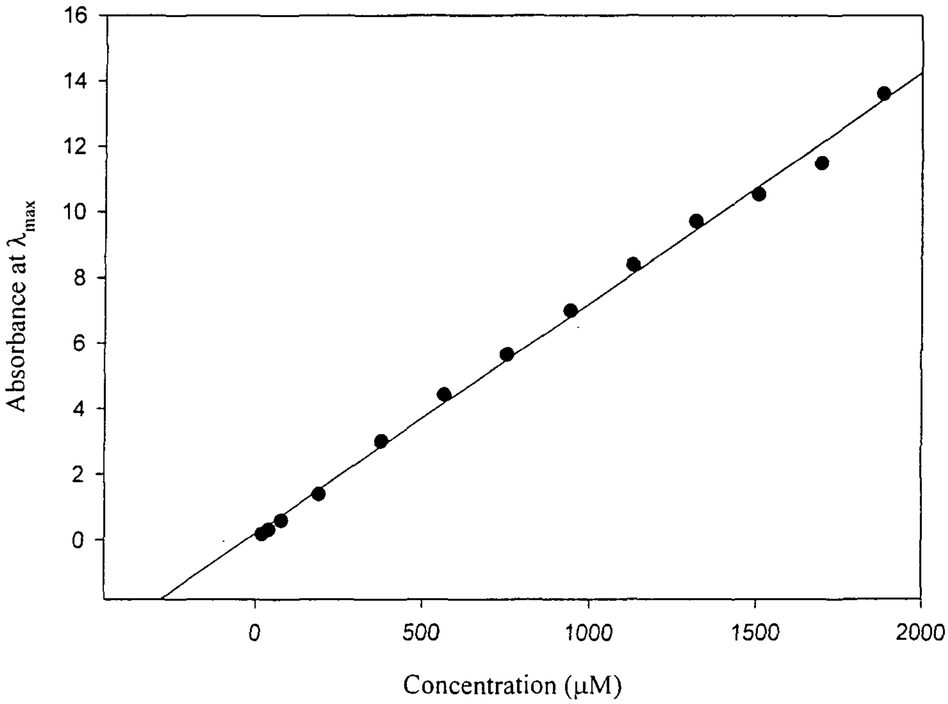


Figure 4.3 Calibration curve for *UV-dendr-(carb)*$_1$

Since the path length of the cell used was 1cm, the extinction coefficient for *UV-dendr-(carb)$_1$* = 7.2×10^3 M^{-1}cm^{-1} (Figure 4.3).

The extinction coefficient for *UV-dendr-(carb)$_2$* = 2.9×10^3 M^{-1}cm^{-1} (Figure 4.4), and for *UV-dendr-(carb)$_4$* = 1.6×10^3 M^{-1}cm^{-1} (Figure 4.5).

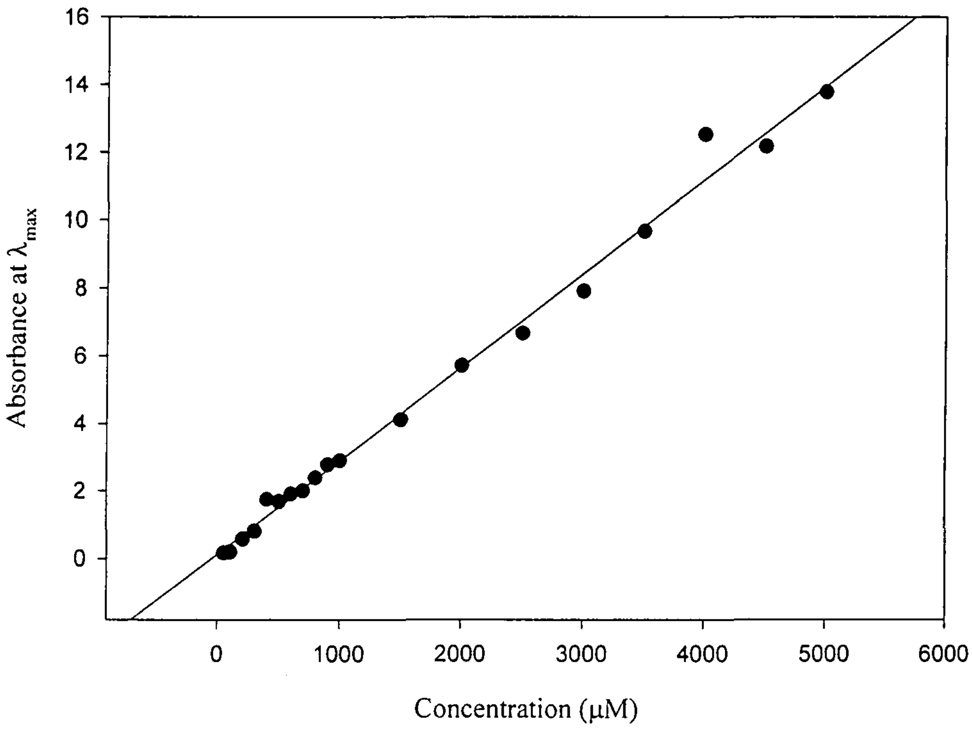


Figure 4.4 Calibration curve for *UV-dendr-(carb)$_2$*.

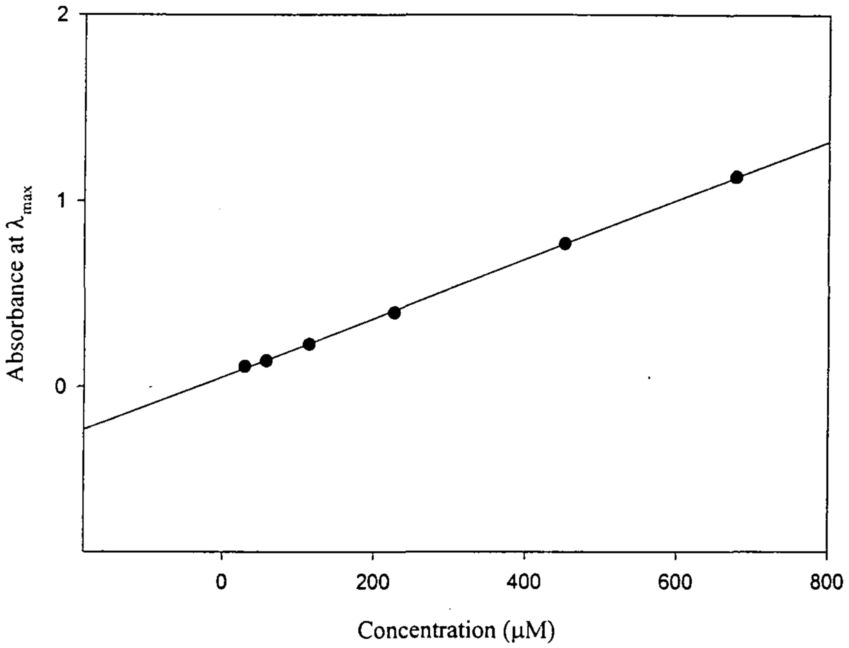


Figure 4.5 Calibration curve for *UV-dendr-(carb)$_4$*.

4.2.2 Experimental procedure

Experiments were carried out to determine the adsorption isotherm of each dendrimer adsorbing onto a cotton surface from aqueous solution. The type of cotton used was woven, unbleached, not dyed, and desized. Size is used to make the cotton easier to weave. Desizing involves washing the cotton at 95°C in Synperonic A7 (4g/l), which is a linear alcohol ethoxylate non-ionic surfactant, and sodium carbonate (4g/l), and then rinsing in demineralised water at 95°C. The cotton sample was a standard piece provided by Unilever Research Port Sunlight Laboratory.

A range of solutions of each dendrimer of known concentration was made-up in water and their absorbance at 296nm (λ_{max}) was measured, relative to a position on the baseline (400nm). To 4ml of each dendrimer solution was added a piece of cotton (0.50g) in a sample vial. These vials were placed on a Denley SPIRAMIX DS507 until the solution concentration had reached equilibrium at room temperature (293K); 4 hours was found to be sufficient for all solutions to reach equilibrium. The SPIRAMIX rotates at 50 rev/min and rocks the sample vials with a pitch of 10mm (Figure 4.6).

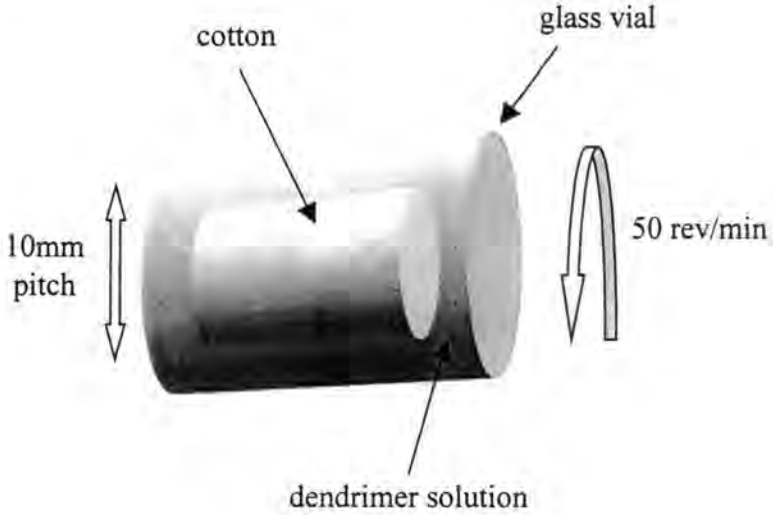


Figure 4.6 The mixing action of the Denley SPIRAMIX DS507.

After 4 hours, the absorbance of the solutions was measured in the same way, referenced to distilled water that had undergone an identical experimental process.

The dendrimer solutions, without cotton added, were also subjected to the same experimental process and there was found to be no changes in their absorbance.

4.2.3 Results

From the final absorbance, the equilibrium (final) concentration (*C*) can be calculated using the Beer-Lambert equation (Section 4.2.1). The amount adsorbed per gram of substrate (*Q*) can be calculated using the equation:

$$Q = \frac{\mathrm{d}A}{\varepsilon l} \times \frac{\text{volume of dendrimer solution}}{\text{mass of cotton}}$$

where d*A* is the change in adsorption of the solution during the experiment. The results are shown in Tables 4.1, 4.2 and 4.3.

The apparent phenomena of "negative adsorption" which is seen for *UV-dendr-(carb)*$_1$ and *UV-dendr-(carb)*$_4$ at very low concentrations (Table 4.1 and 4.3) can be rationalised since some UV active material, a contaminant on the cotton, may be washed off the cotton, and also the error of the experiment is large at very low solution concentrations and low levels of solute adsorption. Cotton threads suspended in the solutions may also affect readings, however, an attempt is made to limit this effect by measuring absorbance relative to distilled water that has undergone exactly the same treatment. The "oscillation" of *Q* values which is seen at high concentration for *UV-dendr-(carb)$_1$* (Table 4.1) occurs because these solutions are approaching saturation, and any error in the experiment is consequently increased.

Initial Absorbance at λ_{max}	Final Absorbance at λ_{max}	*C* (μM)	*Q* (μmol./gram of cotton)
0.18	0.29	39.7	-0.13
0.31	0.34	46.5	-0.03
0.59	0.64	89.2	-0.06
1.39	1.35	187.8	0.04
3.01	2.74	380.2	0.31
4.41	3.77	523.1	0.73
5.66	4.78	663.3	1.01
7.00	6.23	864.5	0.88
8.40	7.20	999.1	1.37
9.72	8.88	1232.2	0.96
10.54	9.41	1305.8	1.29
11.49	10.55	1464.0	1.07
13.61	12.00	1665.2	1.84

Table 4.1 Adsorption study results for *UV-dendr-(carb)$_1$*.

Initial Absorbance at λ_{max}	Final Absorbance at λ_{max}	C (μM)	Q (μmol./gram of cotton)
0.17	0.16	55.2	0.03
0.20	0.16	55.2	0.11
0.58	0.27	93.1	0.86
0.81	0.38	131.0	1.19
1.75	0.45	155.2	3.59
1.69	0.43	148.3	3.48
1.92	0.75	258.6	3.23
2.01	0.81	279.3	3.31
2.40	0.87	300.0	4.22
2.79	0.89	306.9	5.24
2.91	0.89	306.9	5.57
4.12	1.16	400.0	8.17
5.71	1.32	455.2	12.11
6.67	1.36	469.0	14.65
7.91	1.65	569.0	17.27
9.67	1.95	672.4	21.30
12.53	2.68	924.1	27.17
12.18	2.80	965.5	25.88
13.78	3.3	1137.9	28.91

Table 4.2 Adsorption study results for *UV-dendr-(carb)*$_2$.

Initial Absorbance at λ_{max}	Final Absorbance at λ_{max}	C (μM)	Q (μmol./gram of cotton)
0.11	0.14	87.5	-0.15
0.14	0.15	93.8	-0.05
0.23	0.16	100.0	0.35
0.40	0.20	125.0	1.00
0.77	0.30	187.5	2.35
1.13	0.39	234.8	3.70
2.02	0.55	343.8	7.35
2.34	0.65	406.3	8.45
2.78	0.78	487.5	10.00
3.05	0.89	556.3	10.80
3.43	1.02	637.5	12.05
3.68	1.15	718.8	12.65
4.33	1.26	787.5	15.35

Table 4.3 Adsorption study results for *UV-dendr-(carb)*$_4$.

4.2.4 Resulting adsorption isotherms for *UV-dendr-(carb)$_1$*, *UV-dendr-(carb)$_2$*, and *UV-dendr-(carb)$_4$*

Adsorption isotherms are gained for each dendrimer by plotting the amount of dendrimer adsorbed per gram of cotton (*Q*) versus the equilibrium concentration of the solution (*C*). *UV-dendr-(carb)$_1$* and *UV-dendr-(carb)$_2$* clearly adsorb in a co-operative manner since S isotherms are produced (Figures 4.7 and 4.8). *UV-dendr-(carb)$_4$* also adsorbs in a co-operative manner since adsorption begins when the equilibrium concentration is ca. 100μM and not at 0μM which would be expected if adsorption followed a Langmuir model (Figure 4.9).

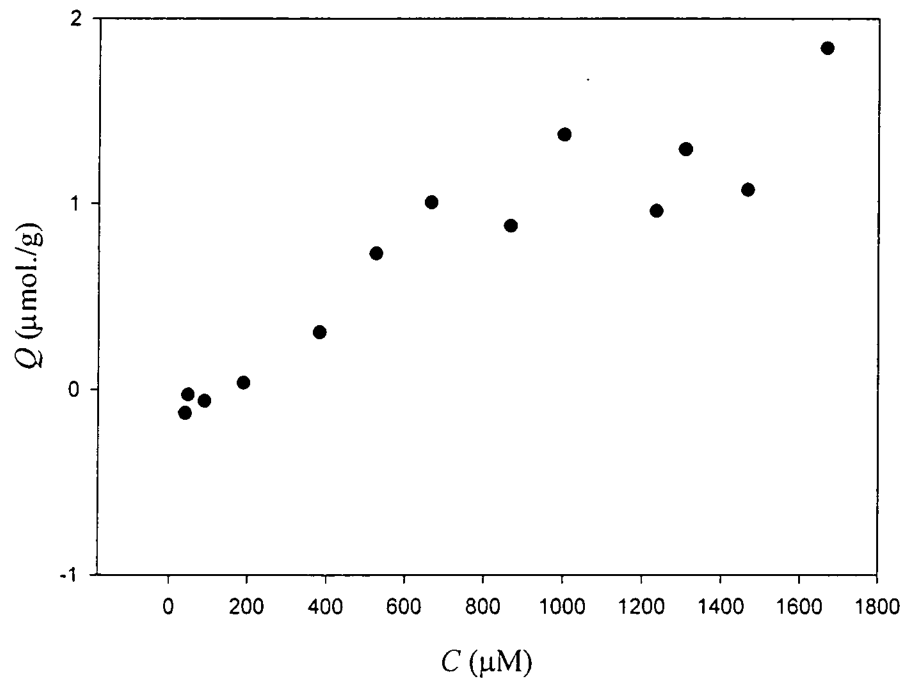


Figure 4.7 Adsorption isotherm for *UV-dendr-(carb)$_1$*.

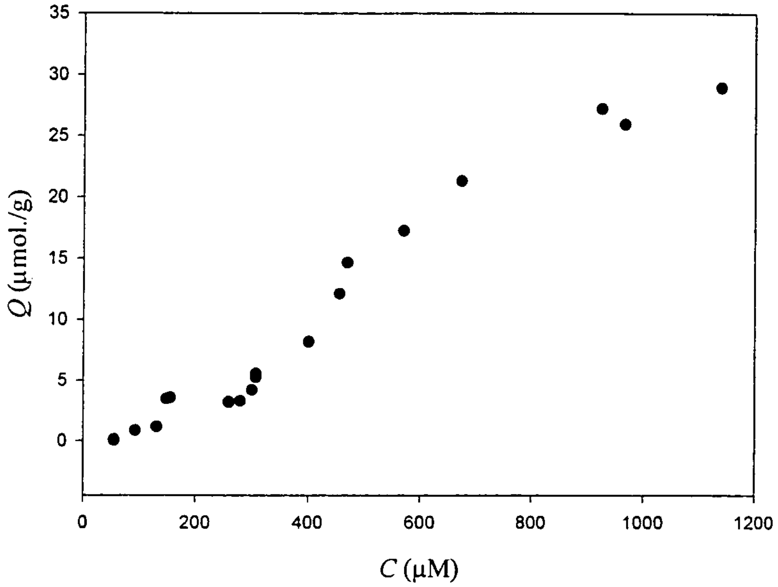


Figure 4.8 Adsorption isotherm for *UV-dendr-(carb)*$_2$.

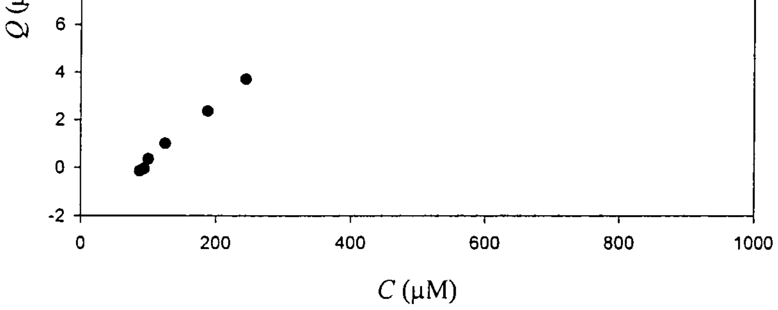


Figure 4.9 Adsorption isotherm for *UV-dendr-(carb)*$_4$.

Comparing the 3 isotherms, it can be seen that *UV-dendr-(carb)*$_1$ barely adsorbed onto the cotton surface at all (Figure 4.10) which is in good agreement with an almost identical system explored at Unilever Research Port Sunlight Laboratory. However, when the number of carbohydrate groups attached to the focus was increased to two, i.e. *UV-dendr-(carb)*$_2$, there was a very large increase, ca. twenty-fold, in the adsorption onto the cotton surface. An explanation for this observation could be the increased number and perhaps more effective orientation of the hydroxyl groups on *UV-dendr-(carb)*$_2$, which are capable of interaction with the cotton surface via hydrogen-bonding. *UV-dendr-(carb)*$_4$ also adsorbs very much better than *UV-dendr-(carb)*$_1$, ca. 10-15-fold, but not as well as *UV-dendr-(carb)*$_2$. The likely explanation of this observation is that the increased solubility of *UV-dendr-(carb)*$_4$ coupled with its extra steric bulk hinders its adsorption onto the cotton surface as compared to *UV-dendr-(carb)*$_2$. This result shows that *UV-dendr-(carb)*$_2$ contains the optimum number of cotton-recognising groups in this system which is advantageous to any possible technological application since the route to its synthesis is much shorter than that for *UV-dendr-(carb)*$_4$.

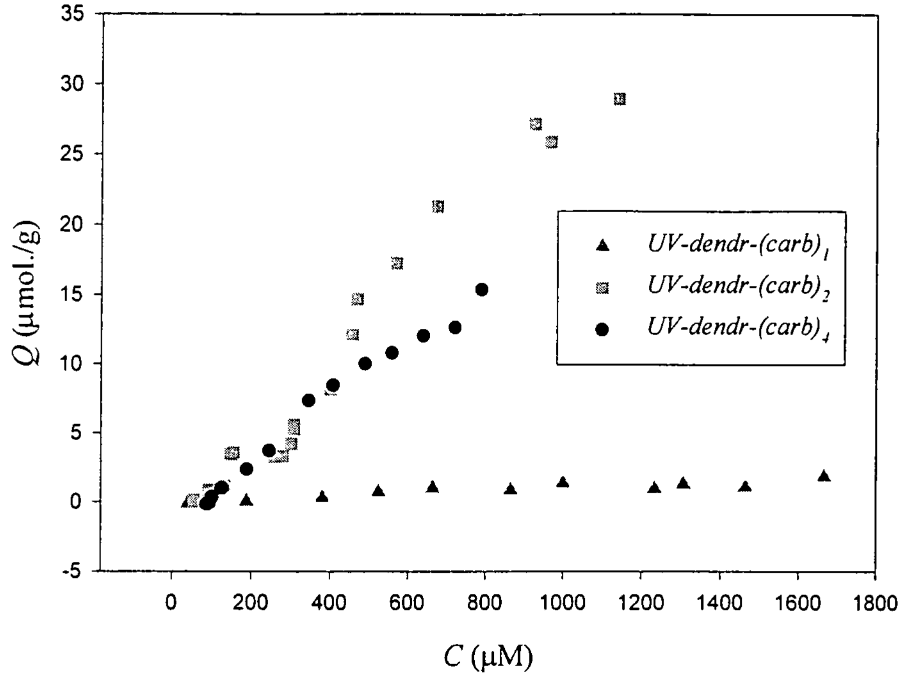


Figure 4.10 A comparison of the adsorption isotherms of *UV-dendr-(carb)*$_1$, *UV-dendr-(carb)*$_2$ and *UV-dendr-(carb)*$_4$.

4.2.5 Analysis of adsorption isotherms

Co-operative adsorption is very unusual for molecules adsorbing from solution at the solid/liquid interface, but it is not unexpected and is consistent with the conditions required for it to occur which were outlined in Section 4.1.1. The dendrimer molecules, *UV-dendr-(carb)*$_n$, have a hydrophobic portion, they are unlikely to form micelles but there will be moderate inter-molecular attraction via hydrogen-bonds, and the solute is likely to meet competition for substrate sites from water molecules. There are no theoretical models to analyse the whole isotherm when co-operative adsorption occurs; however, each adsorption isotherm obeys certain laws in regions of low and high concentration. At low concentrations Henry's Law is obeyed by each dendrimer (Figure 4.11, 4.12 and 4.13); a plot of Q versus C gives a straight line with gradient K_H.

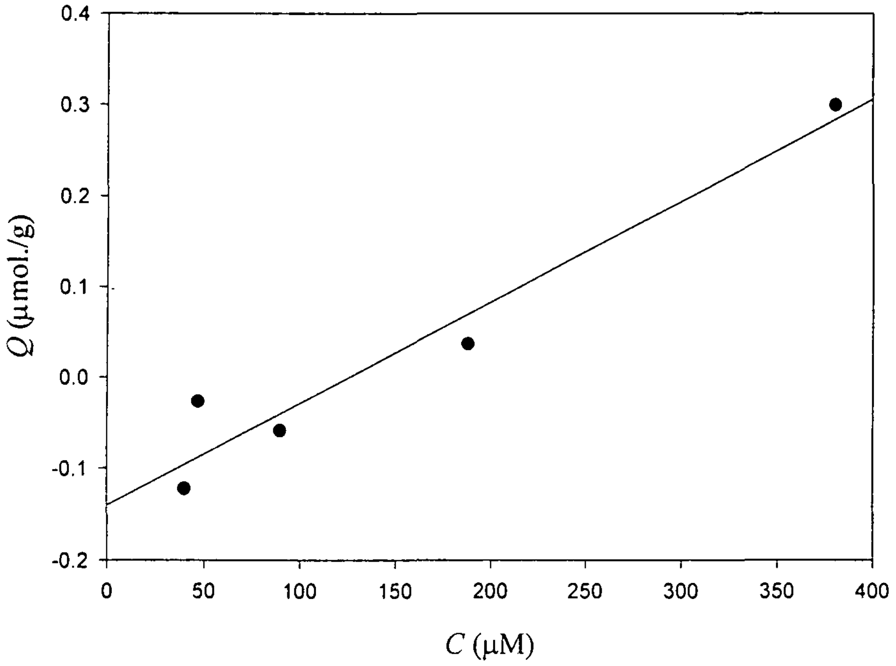


Figure 4.11 A plot of Q versus C for *UV-dendr-(carb)$_1$* at low concentrations.

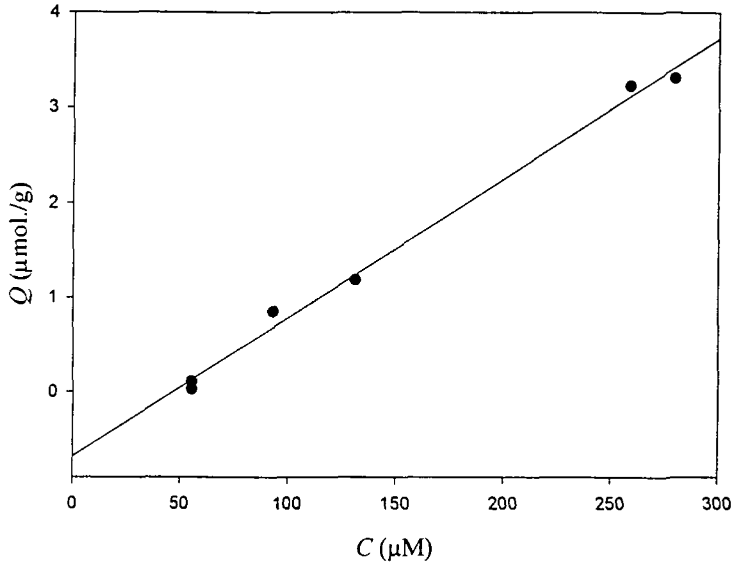


Figure 4.12 A plot of Q versus C for *UV-dendr-(carb)*$_2$ at low concentrations.

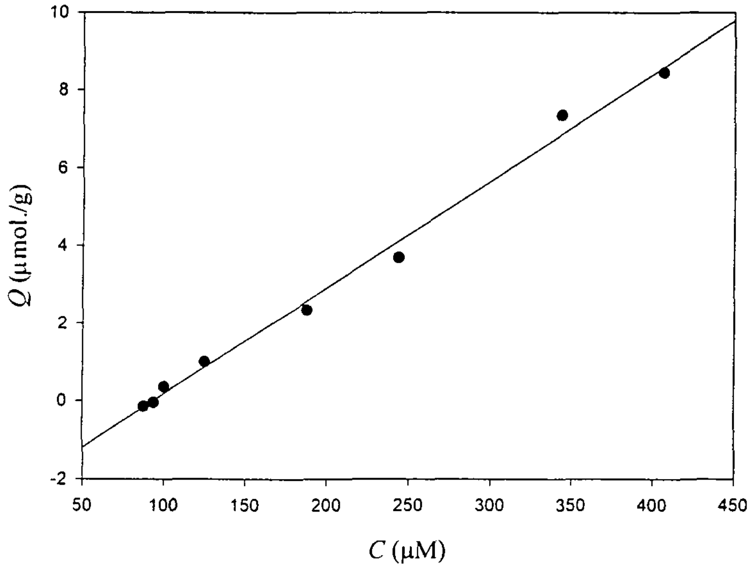


Figure 4.13 A plot of Q versus C for *UV-dendr-(carb)*$_4$ at low concentrations.

At higher concentrations, when the surface approaches saturation, Langmuir adsorption theory applies. Therefore, a plot of C/Q versus C gives a straight line (Figures 4.14, 4.15 and 4.16) with gradient $1/N$ and intercept on the y-axis $1/K_LN$.

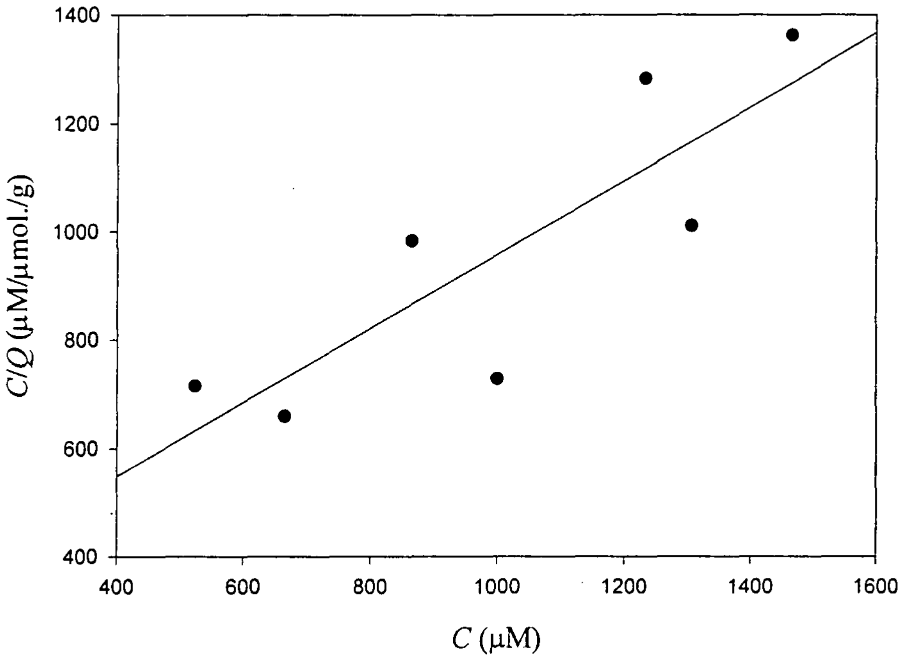


Figure 4.14 Langmuir adsorption analysis on *UV-dendr-(carb)$_I$* at high concentrations.

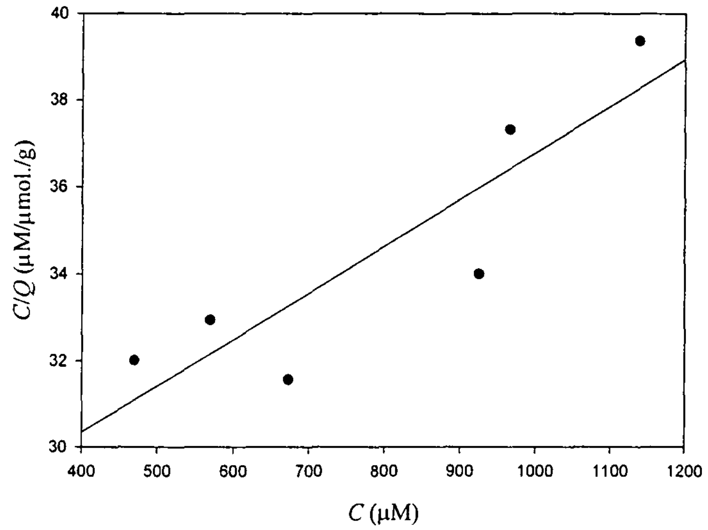


Figure 4.15 Langmuir adsorption analysis on *UV-dendr-(carb)*$_2$ at high concentrations.

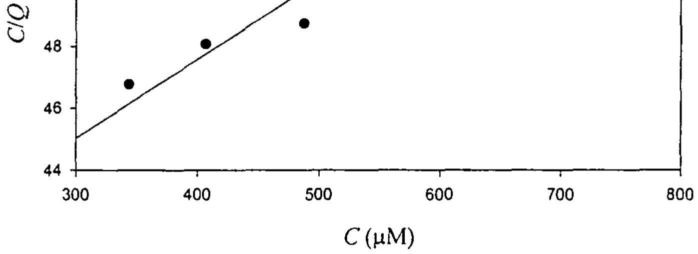


Figure 4.16 Langmuir adsorption analysis on *UV-dendr-(carb)*$_4$ at high concentrations.

The values of K and N that are obtained for each dendrimer using Henry's Law and the theory of Langmuir adsorption described in Section 4.1.2, are outlined in Table 4.4. Since neither model can provide an adequate description of adsorption that is true for the whole of the isotherm, these results have limited significance.

Dendrimer	Henry's Law	Langmuir Adsorption Theory		
	K_H (lg^{-1})	K_LN (lg^{-1})	N (mol.g^{-1})	K_L (M^{-1})
UV-dendr-(carb)$_1$	1.12×10^{-3}	3.63×10^{-3}	1.46×10^{-6}	2.48×10^{3}
UV-dendr-(carb)$_2$	14.70×10^{-3}	38.79×10^{-3}	93.11×10^{-6}	0.41×10^{3}
UV-dendr-(carb)$_4$	27.47×10^{-3}	26.79×10^{-3}	38.95×10^{-6}	0.69×10^{3}

Table 4.4 K and N values for *UV-dendr-(carb)$_1$*, *UV-dendr-(carb)$_2$* and *UV-dendr-(carb)$_4$* at 293K.

From these values of K_L and K_H the value of ΔG° can be determined. Since the units of K_L are in M^{-1} the equation below can be used:[6]

$$\Delta G^{\circ} = -RT\ln K_L$$

This gives values of ΔG° for *UV-dendr-(carb)*$_1$, *UV-dendr-(carb)*$_2$ and *UV-denr-(carb)*$_4$ as -19.04, -14.66 and -15.92kJmol^{-1} respectively, where T = 293K and R = 8.315JK^{-1}mol^{-1}.

However, the situation with K_H is more complicated since its units are l/g where g is grams of substrate (cotton). Therefore, K_H is a measure of how many litres of solution will contain the same amount of solute as that adsorbed onto 1g of cotton at equilibrium. It is more difficult to apply $\Delta G^{\circ} = -RT \ln K$ in this case. This equation can be expressed as:

$$\Delta G(x \text{ grams of cellulose per litre of water}) = -RT\ln(K/(\text{litre/g})) - RT\ln(x/(\text{g/litre}))$$

Therefore, if one were to have x grams of cotton per litre of water, the free energy difference between 1 mole of solute in 1 litre of solution and the same 1 mole adsorbed onto x grams of cotton, could be determined.

4.2.6 Effect of temperature on the adsorption isotherm of *UV-dendr-(carb)*$_2$

Adsorption studies on *UV-dendr-(carb)*$_2$ were performed at 3 different temperatures, 293, 313 and 333K. However, the mixing mechanism was somewhat different to that described in Section 4.2.2 since it was not possible to place the SPIRAMIX in environments of different temperature safely. Each sample vial was placed vertically in an oil bath at the required temperature, and the solutions were mixed using a magnetic stirrer for 4 hours. Therefore, these results are comparable to each other, but not to the results described in Sections 4.2.3 and 4.2.4. All other conditions were identical to previous adsorption study experiments, *Q* and *C* were calculated in the same way and the results are shown in Tables 4.4, 4.5 and 4.6.

Initial Absorbance at λ_{max}	Final Absorbance at λ_{max}	*C* (μM)	*Q* (μmol./gram of cotton)
0.33	0.21	73.1	0.33
0.63	0.27	93.4	0.99
0.92	0.29	99.3	1.74
1.22	0.30	102.4	2.55
1.52	0.32	109.0	3.33
2.11	0.37	126.9	4.81
2.74	0.42	146.2	6.39
3.48	0.50	173.4	8.21
4.01	0.57	195.2	9.50
4.40	0.62	212.1	10.44
5.38	0.68	235.9	12.95
5.82	0.79	272.4	13.88
7.01	0.88	302.8	16.91
7.20	0.93	320.7	17.30

Table 4.5 Adsorption study results for *UV-dendr-(carb)*$_2$ at 293K.

Initial Absorbance at λ_{max}	Final Absorbance at λ_{max}	C (μM)	Q (μmol./gram of cotton)
0.33	0.26	88.3	0.21
0.63	0.38	129.7	0.70
0.92	0.39	134.1	1.46
1.22	0.41	139.7	2.25
1.52	0.44	151.4	2.99
2.11	0.49	167.9	4.48
2.74	0.54	184.8	6.08
3.48	0.58	199.0	8.01
4.01	0.62	212.1	9.37
4.40	0.66	226.6	10.33
5.38	0.74	254.1	12.81
5.82	0.88	301.7	13.64
7.01	0.91	314.1	16.82
7.20	0.98	338.6	17.15

Table 4.6 Adsorption study results for *UV-dendr-(carb)*$_2$ at 313K.

Initial Absorbance at λ_{max}	Final Absorbance at λ_{max}	C (μM)	Q (μmol./gram of cotton)
0.33	0.31	105.2	0.07
0.63	0.40	136.2	0.65
0.92	0.43	149.0	1.34
1.22	0.48	166.9	2.04
1.52	0.44	150.3	3.00
1.92	0.50	173.1	3.91
2.01	0.56	193.4	4.00
2.40	0.61	209.0	4.95
2.79	0.64	221.7	5.92
3.68	0.74	254.5	8.12
4.35	0.80	276.9	9.78
7.40	0.99	340.0	17.69
8.51	1.15	397.6	20.30

Table 4.7 Adsorption study results for *UV-dendr-(carb)$_2$* at 333K.

Comparing the plots of Q versus C at each temperature (Figure 4.17) it can be seen that adsorption decreases with increasing temperature, i.e. the overall process is exothermic, confirming the results of ΔG° in Section 4.2.5. It is likely that the increased solubility of the solute at higher temperatures is the main factor in this observation. This experiment is consistent with the fact that adsorption is accompanied by a negative entropy change caused by molecules adsorbing onto the cotton surface. It is also noted that the isotherms merge at high concentration and this proves to be useful when calculating the isosteric enthalpy of adsorption, $\Delta H^{\circ}_{\text{ad}}$.

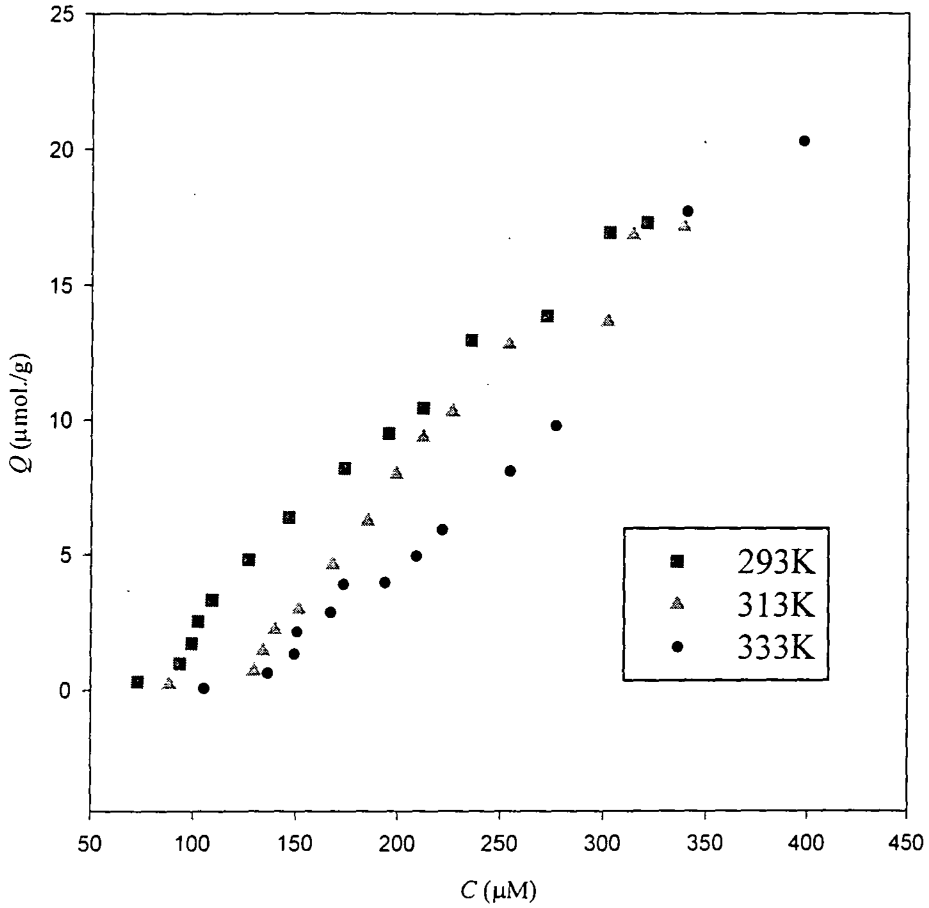


Figure 4.17 Adsorption isotherms for *UV-dendr-(carb)₂* at 20, 40 and 60°C.

4.2.7 Calculation of the isosteric enthalpy of adsorption for *UV-dendr-(carb)₂* onto cotton in water

The information gained from the adsorption isotherms for *UV-dendr-(carb)₂* at 293, 313 and 333K can be used to determine the isosteric enthalpy of adsorption, $\Delta H^{\ominus}_{\mathrm{ad}}$ (isosteric means at the same surface coverage) and this is achieved using the van't Hoff equation[6]:

$$\left(\frac{\partial \ln K}{\partial T}\right)_{\theta} = \frac{\Delta H^{\ominus}_{\mathrm{ad}}}{RT^2}$$

The Langmuir isotherm rearranges to:

$K_L C = \dfrac{\theta}{1-\theta}$, where θ is the fractional coverage of the substrate, $\left(\dfrac{Q}{N}\right)$.

However, the isotherms in Figure 4.17 merge at high concentration and this suggests that N is independent of temperature since the same amount of solute is causing saturation of the cotton surface at all temperatures.

Therefore, when Q is constant,

$$\ln K_L + \ln C = \text{constant}$$

Therefore, using the van't Hoff equation,

$$\left(\frac{\partial \ln C}{\partial T}\right)_{\theta} = -\left(\frac{\partial \ln K}{\partial T}\right)_{\theta} = \frac{-\Delta H^{\ominus}_{\mathrm{ad}}}{RT^2}$$

With $d(1/T)/dT = -1/T^2$ this expression rearranges to:

$$\left(\frac{\partial \ln C}{\partial(1/T)}\right)_\theta = \frac{\Delta H^\circ_{\text{ad}}}{R}$$

Hence, a plot of ln$C$ against $1/T$ (Table 4.8) gives a straight line of slope $\Delta H^\circ_{\text{ad}}/R$ (Figure 4.18) using the data in Figure 4.17.

Q = 4μmol. /gram of substrate		Q = 5μmol. /gram of substrate		Q = 6μmol. /gram of substrate	
$10^3/(T/\text{K})$	$\ln(C/\mu\text{M})$	$10^3/(T/\text{K})$	$\ln(C/\mu\text{M})$	$10^3/(T/\text{K})$	$\ln(C/\mu\text{M})$
3.41	4.73	3.41	4.87	3.41	5.01
3.20	5.01	3.20	5.14	3.20	5.27
3.00	5.19	3.00	5.30	3.00	5.39

Table 4.8 Data for the determination of the isosteric enthalpy of adsorption at 3 different values of Q.

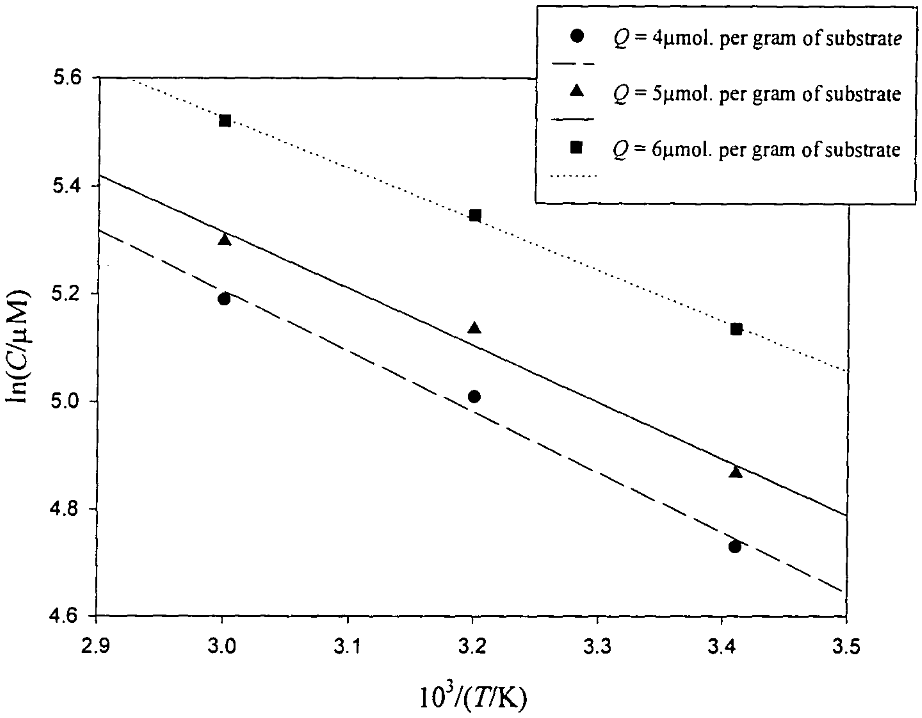


Figure 4.18 Plots of ln$C$ against $1/T$ at 3 different values of fractional surface coverage.

The above graph gives slope values of -1.12, -1.05 and -0.94×10^3 K for Q = 4, 5 and 6µmol./g respectively.

$R = 8.315 \mathrm{JK^{-1}mol^{-1}}$ and therefore $\Delta H^\circ_{\mathrm{ad}}$ = -9.34, -8.75 and -7.81kJmol^{-1}.

It would seem possible to now calculate the entropy change of the system for *UV-dendr-(carb)*$_2$ since $\Delta G^\ominus$ was calculated in Section 4.2.5. However, $\Delta H^\circ_{\mathrm{ad}}$ and $\Delta G^\ominus$ were calculated from slightly different parts of the isotherm and under different experimental conditions. Therefore, the result may have little meaning. However, using the values of $\Delta G^{\circ} =$ -14.66kJmol^{-1} at 293K and $\Delta H^{\circ}_{ad} =$ -8.75kJmol^{-1} it is found that $\Delta S^{\circ} = 20.17$JK^{-1}. This confirms the assumption that adsorption is accompanied by negative entropy which was discerned from Figure 4.17.

4.2.8 "Washing" properties of *UV-dendr-(carb)$_1$*, *UV-dendr-(carb)$_2$* and *UV-dendr-(carb)$_4$*.

The pieces of cotton used in the adsorption isotherm experiments for *UV-dendr-(carb)$_1$*, *UV-dendr-(carb)$_2$* and *UV-dendr-(carb)$_4$* (Section 4.2.2) were dried overnight in air at room temperature. These pieces of cotton were stirred on the SPIRAMIX, in distilled water (4ml), under conditions identical to the original adsorption experiments described in Section 4.2.2. This has been termed a washing experiment.

The absorbance of the solutions was measured after 4 hours and the amount of each dendrimer desorbed per gram of cotton was calculated as before, see Section 4.2.3. However, there is a substantial error to be taken into account when considering the results. The cotton would not only have contained dendrimer which had adsorbed onto the cotton surface during the adsorption experiments, but also dendrimer which would have been left on the surface as the wet cotton had dried out. Consequently, the results for *UV-dendr-(carb)*$_1$ are meaningless since so little dendrimer adsorbed onto the surface initially, compared to the amount left on as the cotton dried out.

The amount of *UV-dendr-(carb)*$_2$ and *UV-dendr-(carb)*$_4$ desorbed after washing compared to the amount adsorbed onto the cotton before washing is shown, without a correction for the phenomena described above, in Tables 4.9 and 4.10. It can be seen that almost twice as much of *UV-dendr-(carb)*$_4$ has been washed off compared to *UV-dendr-(carb)*$_2$. Not only does this experiment shows that adsorption is reversible but it is very pleasing to note that, not only does *UV-dendr-(carb)*$_2$ adsorb onto the cotton in much larger amounts initially, compared to *UV-dendr-(carb)*$_4$, but it also remains on the cotton surface after washing to a much greater extent.

Final absorbance at λ_{max} after washing	Amount desorbed after washing (μmol./gram of cotton)	Amount adsorbed before washing (μmol./gram of cotton)
0.21	0.59	0.03
0.26	0.71	0.11
0.26	0.71	0.86
0.36	0.98	1.19
0.36	1.00	3.59
0.33	0.92	3.48
0.40	1.10	3.23
0.43	1.18	3.31
0.39	1.08	4.22
0.49	1.35	5.24
0.47	1.30	5.57
0.52	1.42	8.17
0.60	1.64	12.11
0.73	2.02	14.65
0.82	2.26	17.27
0.84	2.3	21.30
1.15	3.17	27.17
1.05	2.89	25.88
1.18	3.27	28.91

Table 4.9 Results for *UV-dendr-(carb)*$_2$.

Final absorbance at λ_{max} after washing	Amount desorbed after washing (μmol./gram of cotton)	Amount adsorbed before washing (μmol./gram of cotton)
0.21	1.05	-0.15
0.22	1.10	-0.05
0.20	1.01	0.35
0.24	1.22	1.00
0.25	1.23	2.35
0.33	1.67	3.70
0.45	2.27	7.35
0.52	2.61	8.45
0.55	2.74	10.00
0.60	3.01	10.80
0.64	3.18	12.05
0.66	3.31	12.65
0.77	3.83	15.35

Table 4.10 Results for *UV-dendr-(carb)$_4$*.

4.3 References

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CHAPTER 5

Conclusions and Ideas for Future Work

5. Conclusions and Ideas for Future Work

5.1 Conclusions

The synthesis of poly(propylene imine) dendrimer wedges from various foci has been performed. It has been found that aryl and sterically hindered primary amines are not as suitable nucleophiles for the Michael reaction as compared to alkyl amines. It has also been found to be either very difficult or impossible to perform the Michael reaction on commercially available dyes and this is due to the low nucleophilicity of their aryl amine groups. The reduction of cyano groups in the iterative procedure to poly(propylene imine) dendrimers was best performed using Raney nickel but this was not completely ideal since the product sometimes proved difficult to extract from the basic water layer and distillation was required in order to remove some impurities. However, Raney nickel proved to be a far superior catalyst for large-scale reduction than either sodium borohydride or diisobutylaluminum hydride.

The attachment of a carbohydrate, lactobiono-lactone, onto poly(propylene imine) dendrimers possessing a UV-absorbing focus proceeded satisfactorily, although traces of mono-, di- and tri-functionalised molecules were detected by MALDI-TOF mass spectrometry in *UV-dendr-*$(NH_2)_4$. The products were found to be soluble in water with a wavelength of maximum absorbance (λ_{max}) of 296nm and suitable extinction coefficients for surface adsorption studies to be possible. Adsorption experiments were performed using a standard cotton surface in water and it was found that each carbohydrate-terminated dendrimer was characterised by an S-shaped adsorption isotherm, thus, it was determined that the dendrimer wedges adsorb onto cotton in a co-operative manner. In other words, there is a side-by-side association between dendrimer molecules on the cotton surface which occurs via hydrogen-bonding, and this helps them to adsorb onto the cotton surface more strongly.

It is noted that *UV-dendr-(carb)*$_1$ adsorbs onto the cotton in only very small amounts and this is in good agreement with results obtained from Unilever Research Port Sunlight Laboratory. At Unilever, the same carbohydrate, lactobiono-lactone, was attached to a different species that absorbs in the UV region and there was found to be negligible adsorption of this species onto an identical cotton surface. However, *UV-dendr-(carb)*$_2$ adsorbs very much more strongly onto the cotton surface than *UV-dendr-(carb)*$_1$. One explanation for this observation could be the increased number and perhaps more effective orientation of the molecule's hydroxyl groups, which are capable of interaction with the cotton surface via hydrogen-bonding. *UV-dendr-(carb)*$_4$ also adsorbs very strongly onto cotton in water, but not as strongly as *UV-dendr-(carb)*$_2$ and this is likely to be a consequence of its larger size, i.e. site availability is decreased, and its increased solubility in water.

Each isotherm was found to obey Henry's Law at low concentrations and Langmuir adsorption theory at high concentrations. From this, the equilibrium constant for the adsorption process and hence the free energy of adsorption was calculated.

The adsorption experiments on *UV-dendr-(carb)*$_2$ were repeated at different temperatures and adsorption was found to be accompanied by a negative entropy change due to molecules leaving the solution and adsorbing onto the surface. The isosteric enthalpy of adsorption was also calculated.

The samples of cotton used for the initial adsorption experiments were "washed" in distilled water and approximately twice as much of *UV-dendr-(carb)*$_4$ was washed off as compared to *UV-dendr-(carb)*$_2$.

In conclusion, *UV-dendr-(carb)*$_2$ has the optimum number of cotton recognising groups and is the surface-active species of choice which is a very satisfactory result since much fewer steps are required to synthesise *UV-dendr-(carb)*$_2$ as compared to *UV-dendr-(carb)*$_4$.

5.2 Ideas for future work

The synthesis of poly(propylene imine) dendrimers using Raney cobalt as the reduction catalyst could be attempted to ascertain whether this would further improve experimental yields and purity. With Raney cobalt, it might also be possible to synthesise *UV-dendr-*$(NH_2)_8$ to a high degree of purity although, in view of the superior properties of *UV-dendr-(carb)*$_2$, this would be of only academic interest.

It might also be interesting to attach a larger carbohydrate (Figure 5.1) to the periphery of the dendrimer wedge and ascertain whether such a species might adsorb onto cotton more readily than those discussed in this work.

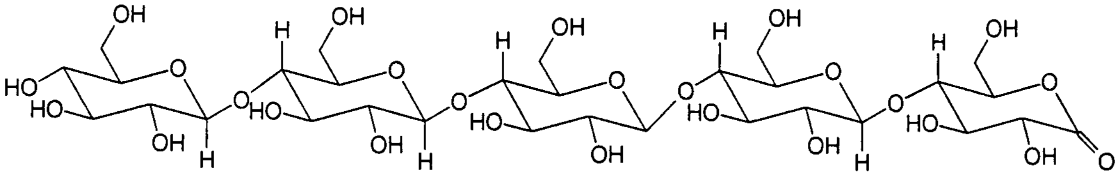
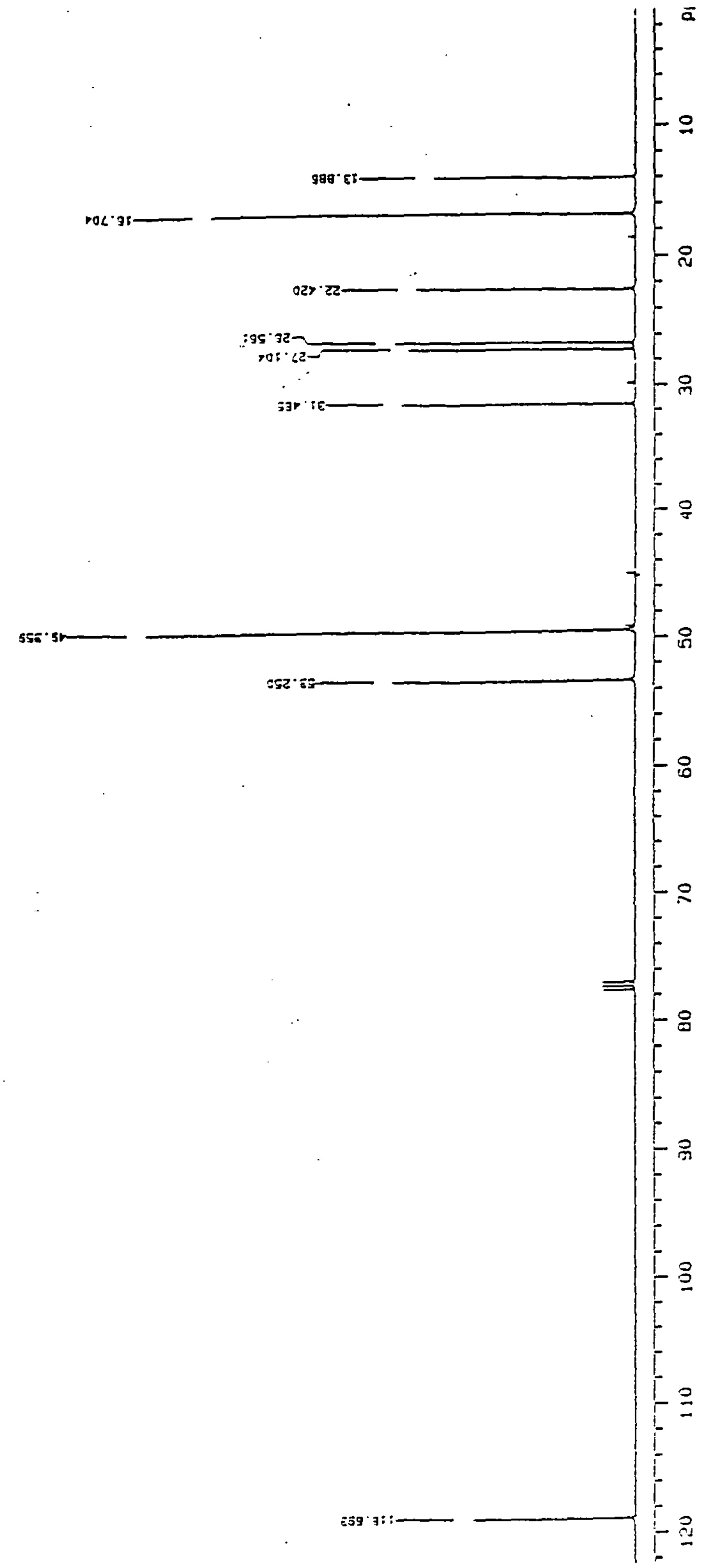


Figure 5.1 A commercially available lactone with 5 glucosyl repeat units.

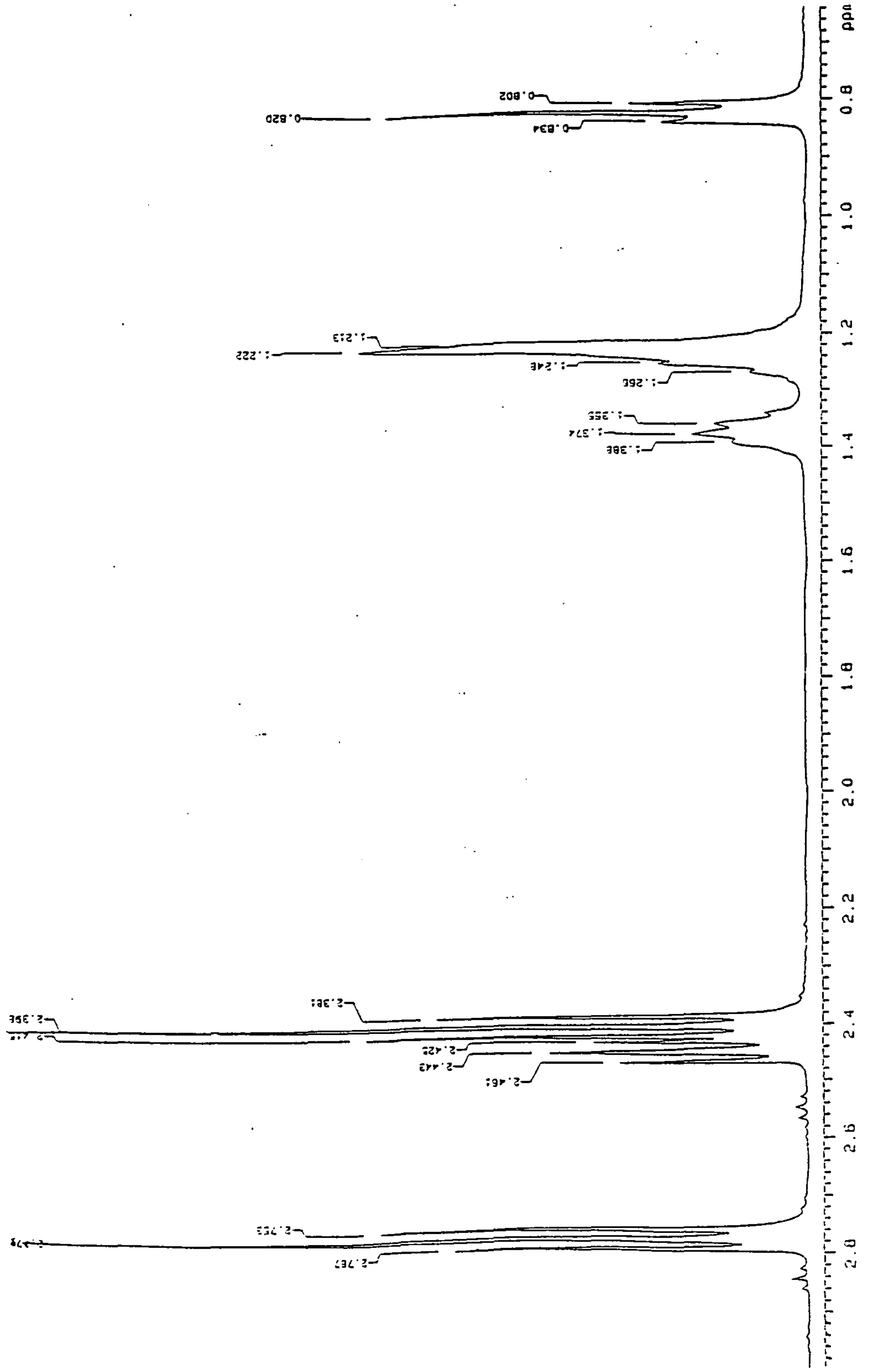
Adsorption experiments could be carried out on different substrates, either different cellulose surfaces, or surfaces such as wood which contain a high proportion of cellulose and modelling of the dendrimers in solution and the adsorption process might prove useful in understanding the results in this work.

APPENDIX 1

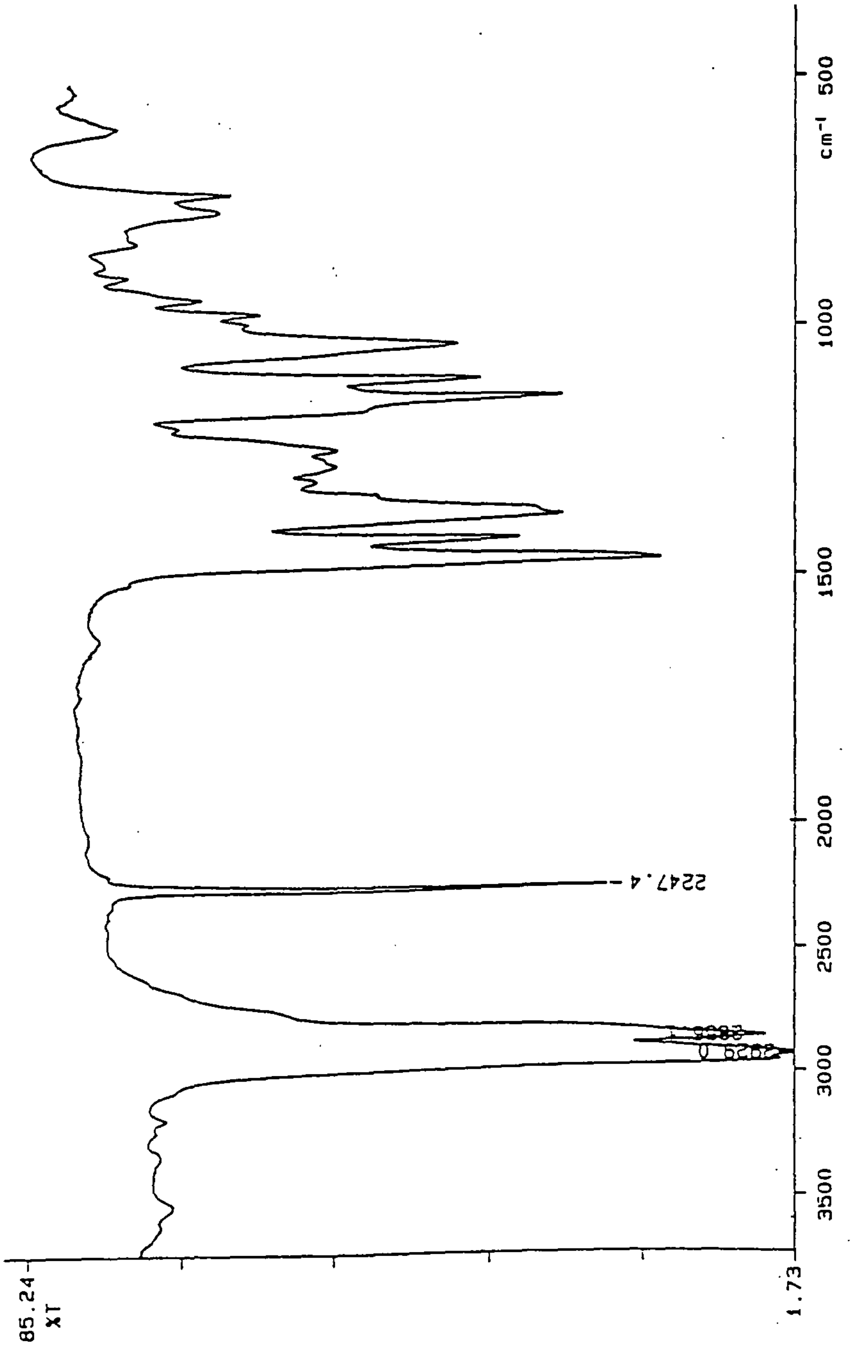
Characterisation Data for Chapter 2



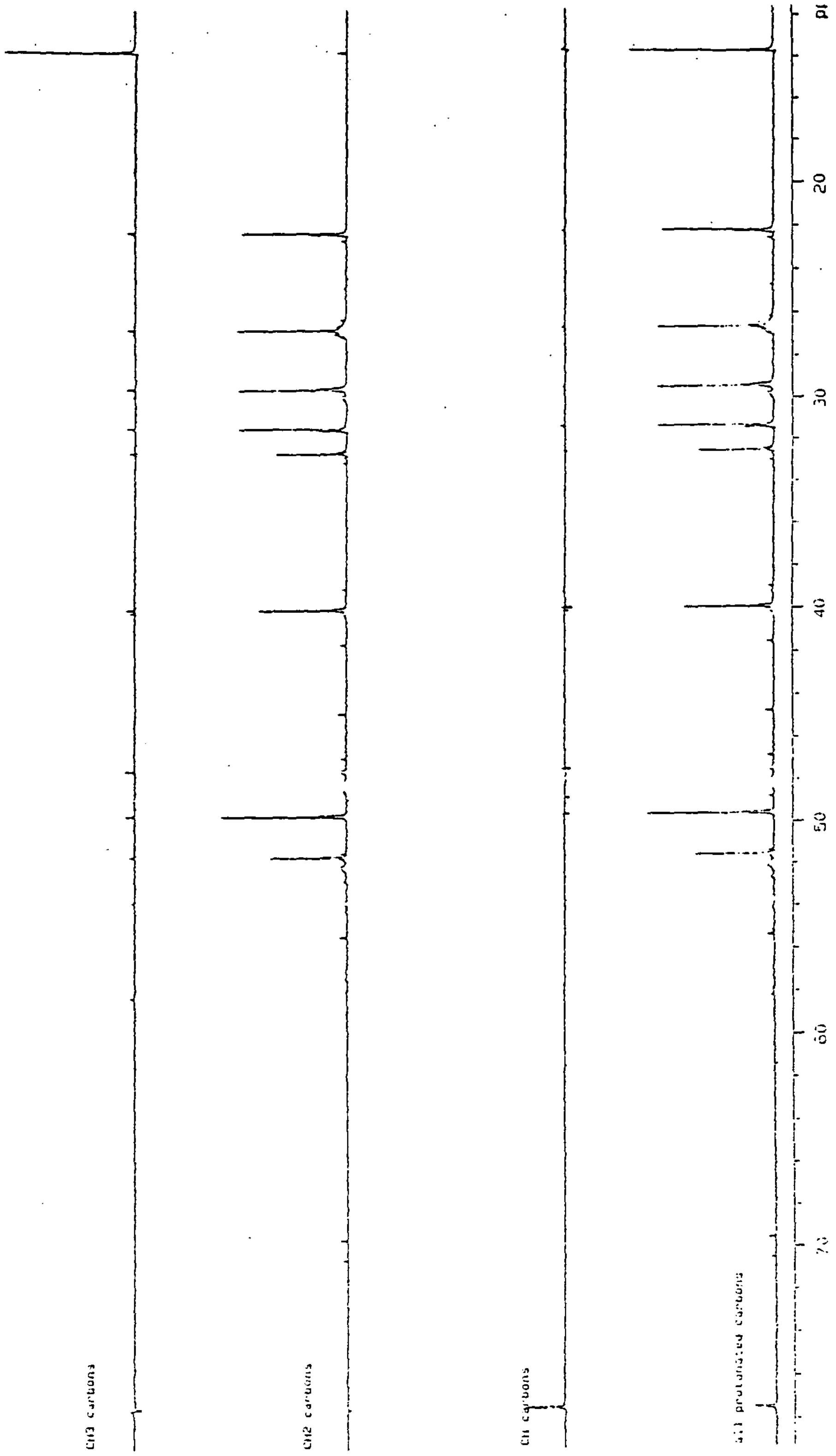
Appendix 1.1 ^{13}C n.m.r. ($CDCl_3$, 100MHz) spectrum of *Hex-dendr-(CN)*$_2$.



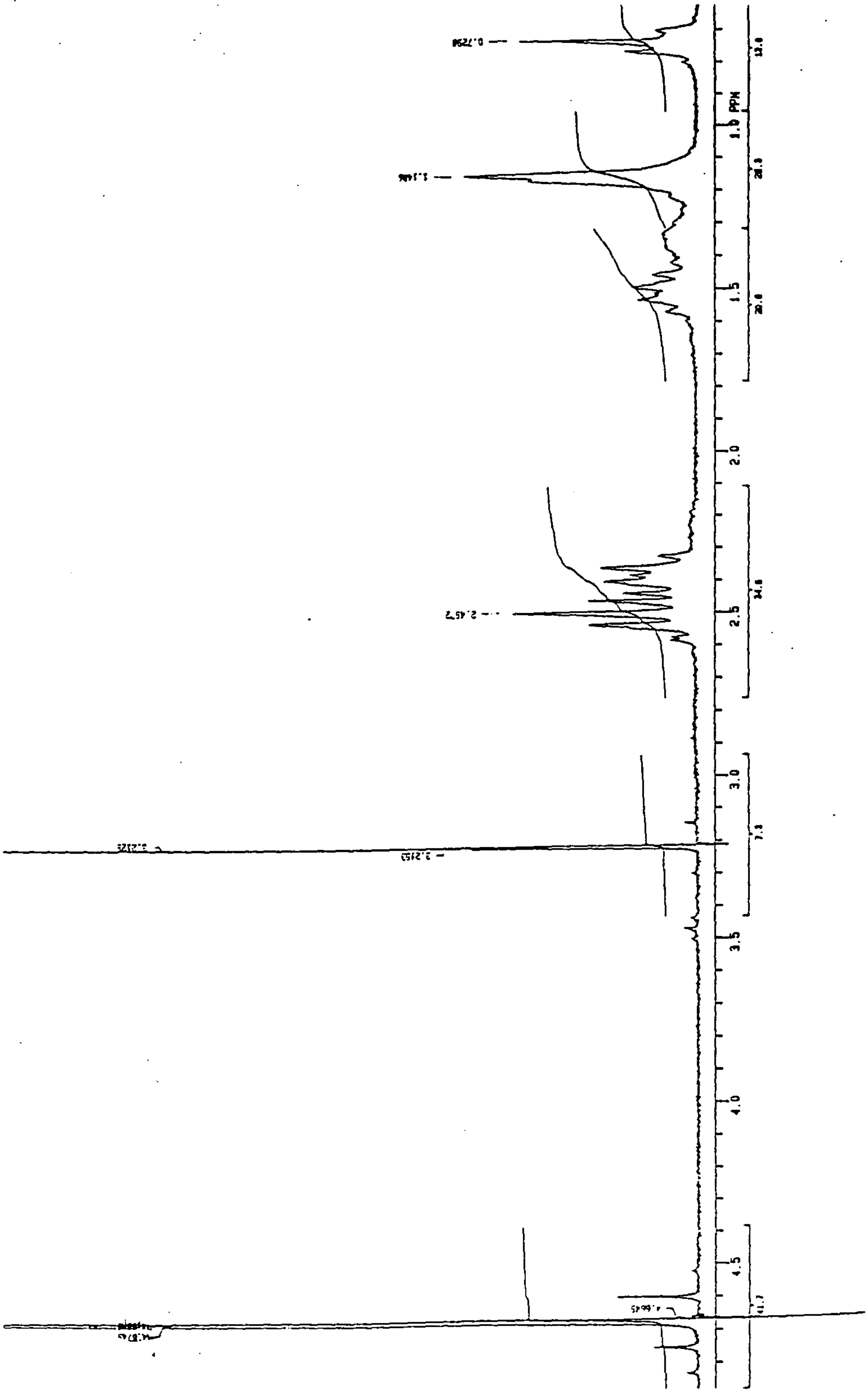
Appendix 1.2 ^{1}H n.m.r. ($CDCl_3$, 400MHz) spectrum of *Hex-dendr-(CN)$_2$*.



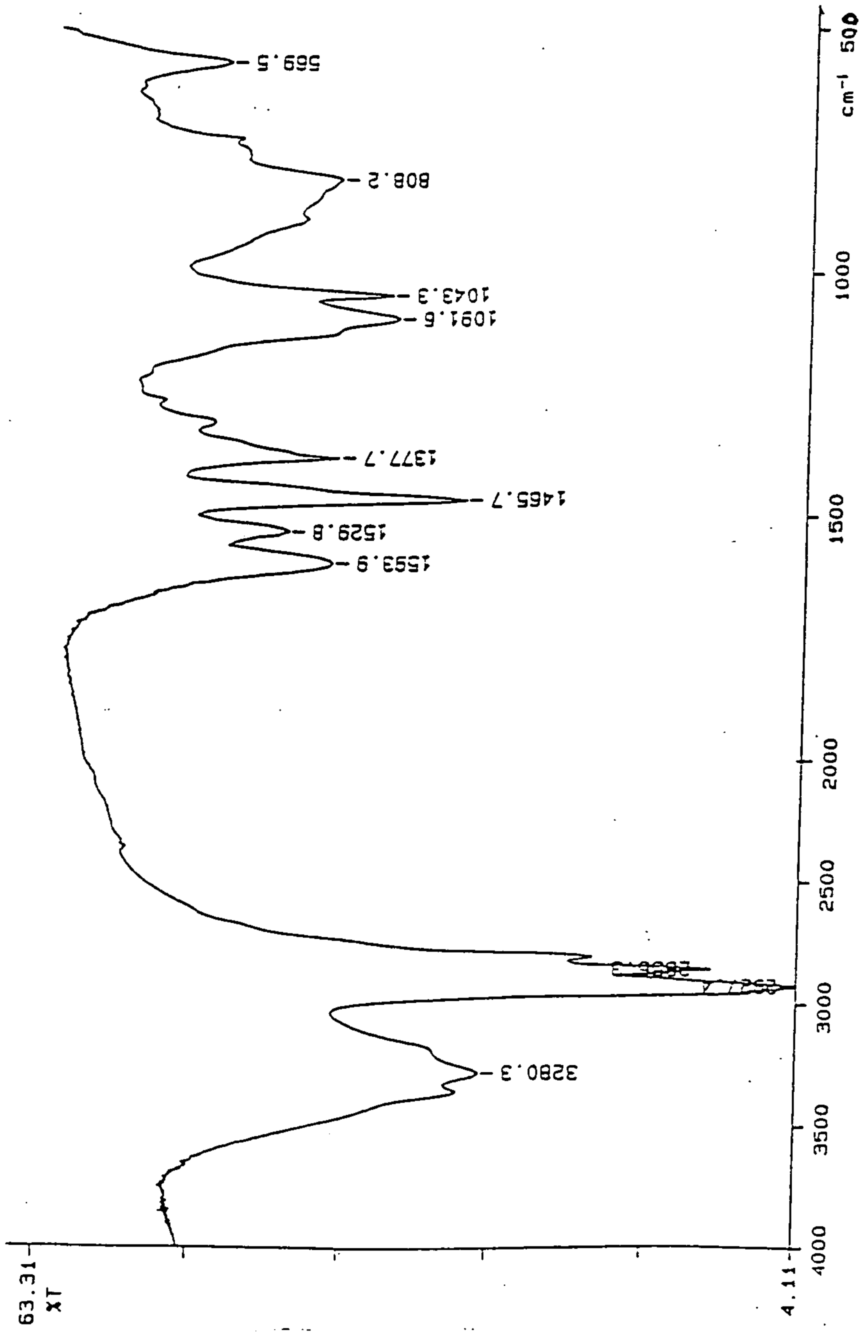
Appendix 1.3 FTIR spectrum of *Hex-dendr-(CN)*$_2$.



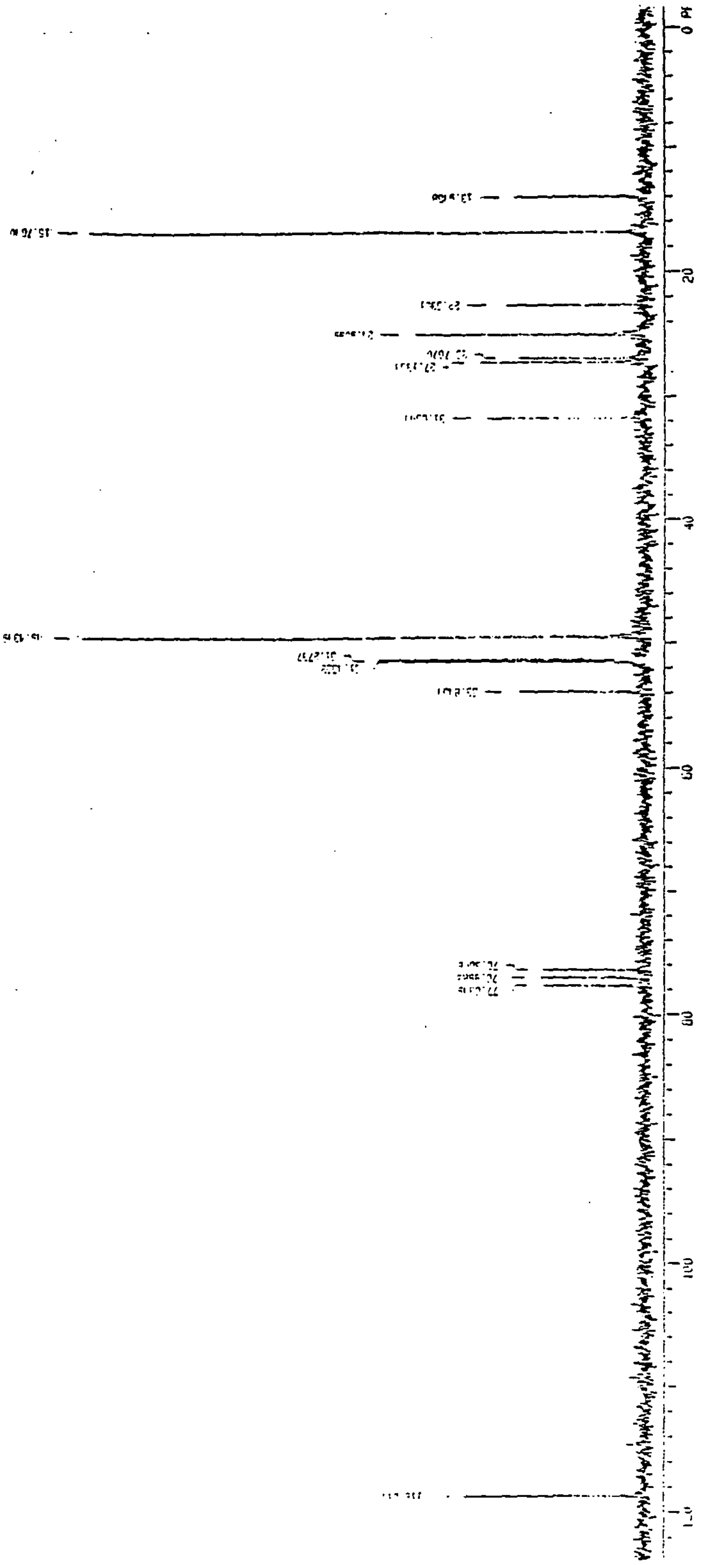
Appendix 1.4 ^{13}C n.m.r. ($CDCl_3$, 100MHz) D.E.P.T. spectrum of *Hex-dendr-(NH$_2$)$_2$*.



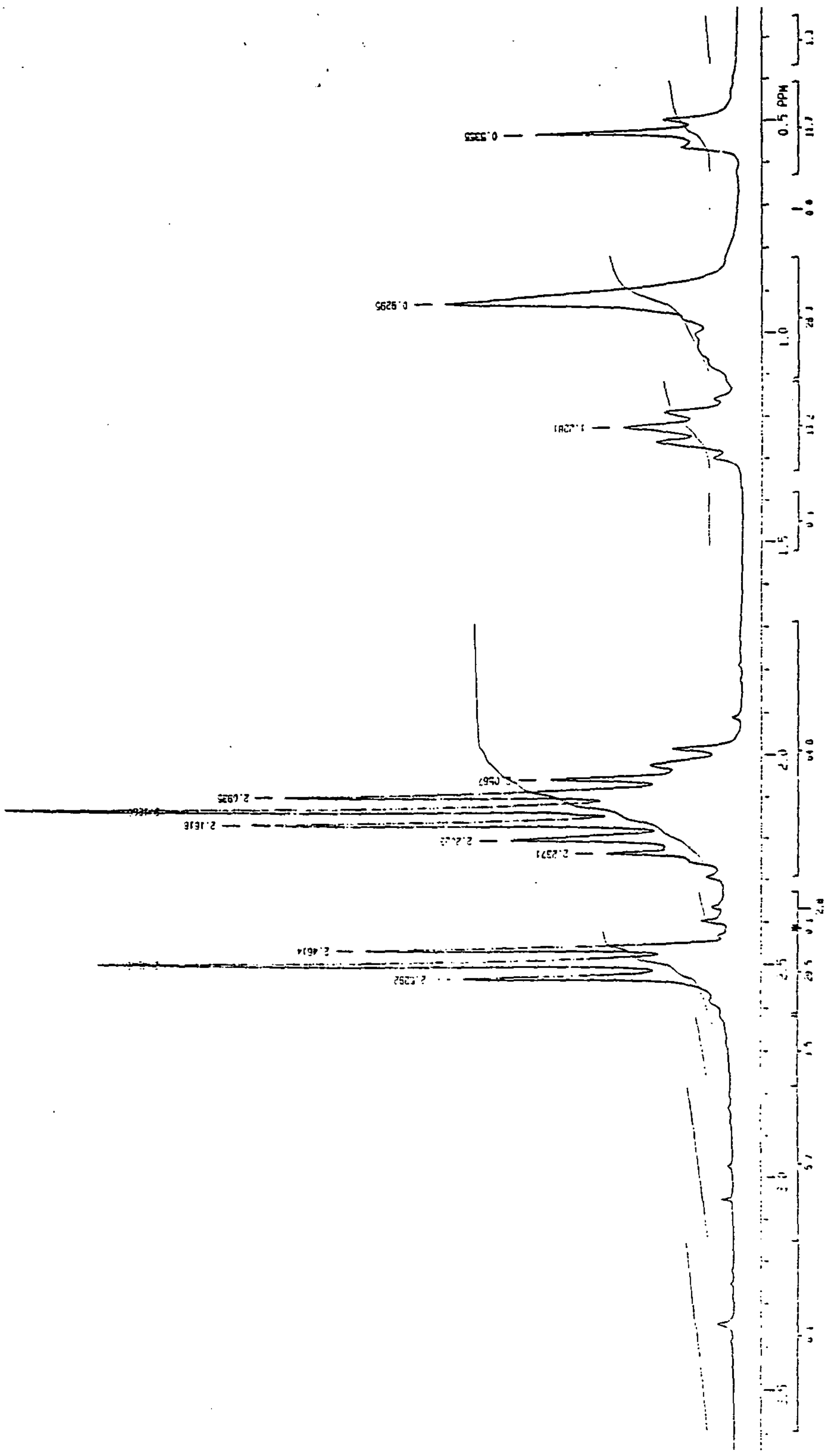
Appendix 1.5 ^{1}H n.m.r. ($CDCl_3$, 400MHz) spectrum of *Hex-dendr-$(NH_2)_2$*.



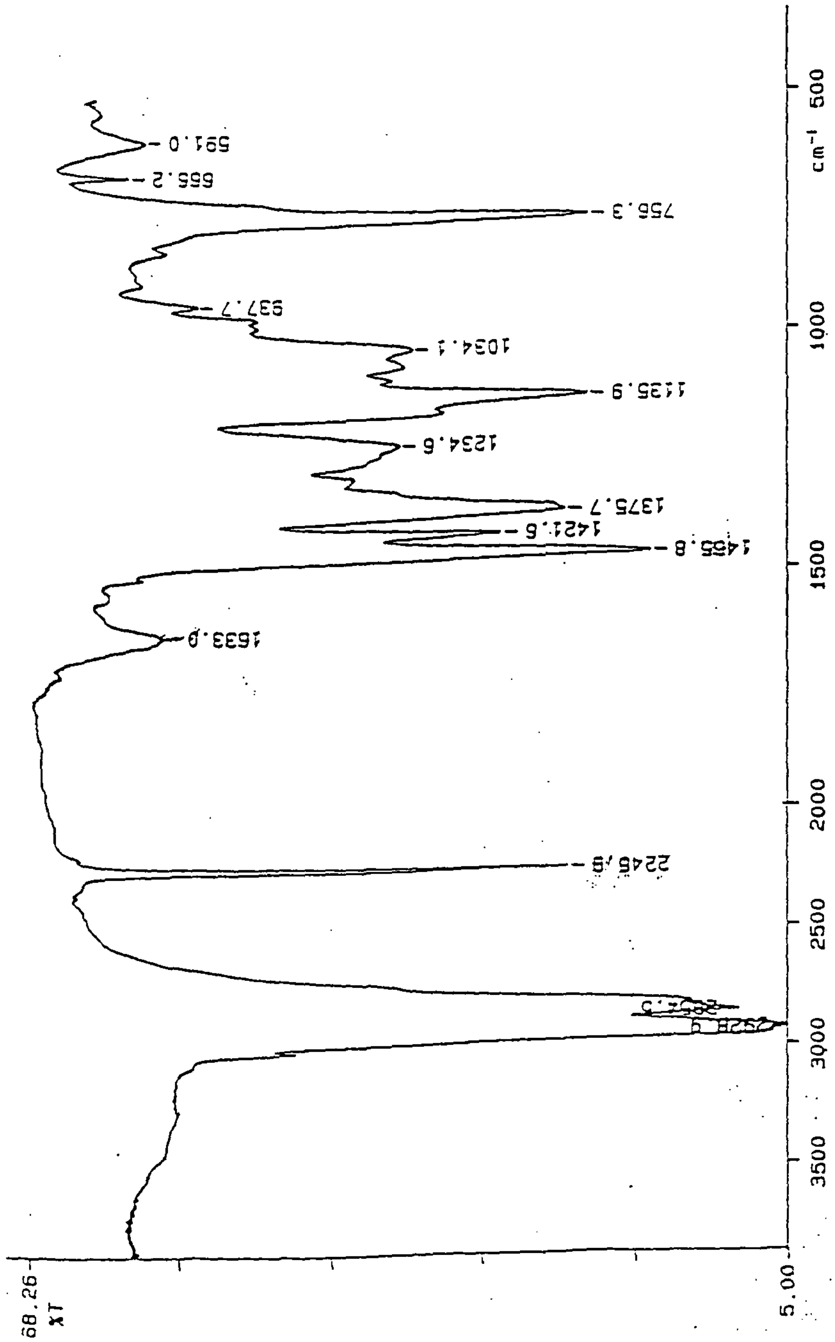
Appendix 1.6 FTIR spectrum of *Hex-dendr-*$(NH_2)_2$.



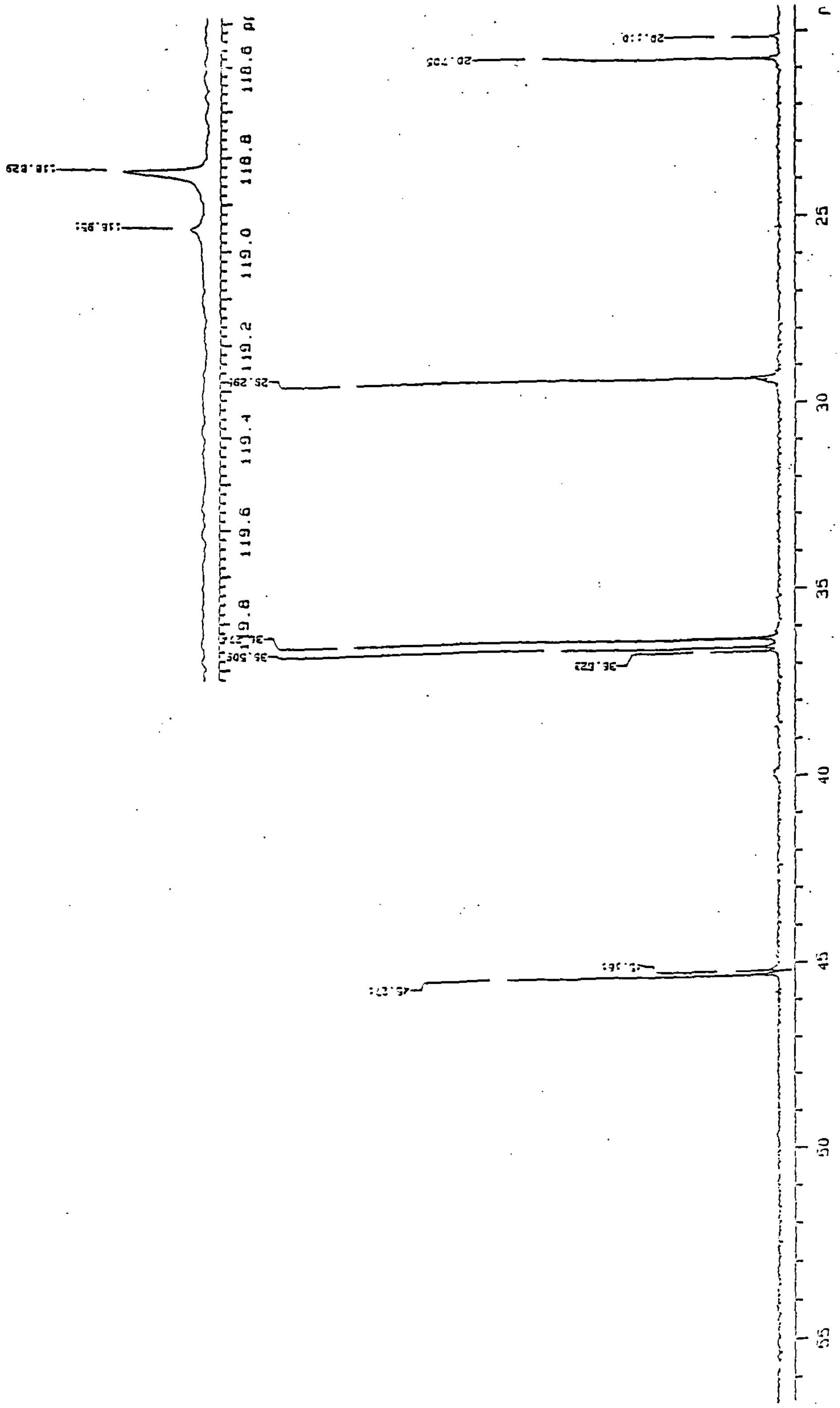
Appendix 1.7 ^{13}C n.m.r. (CDCl$_3$, 100MHz) spectrum of *Hex-dendr-(CN)$_4$*.



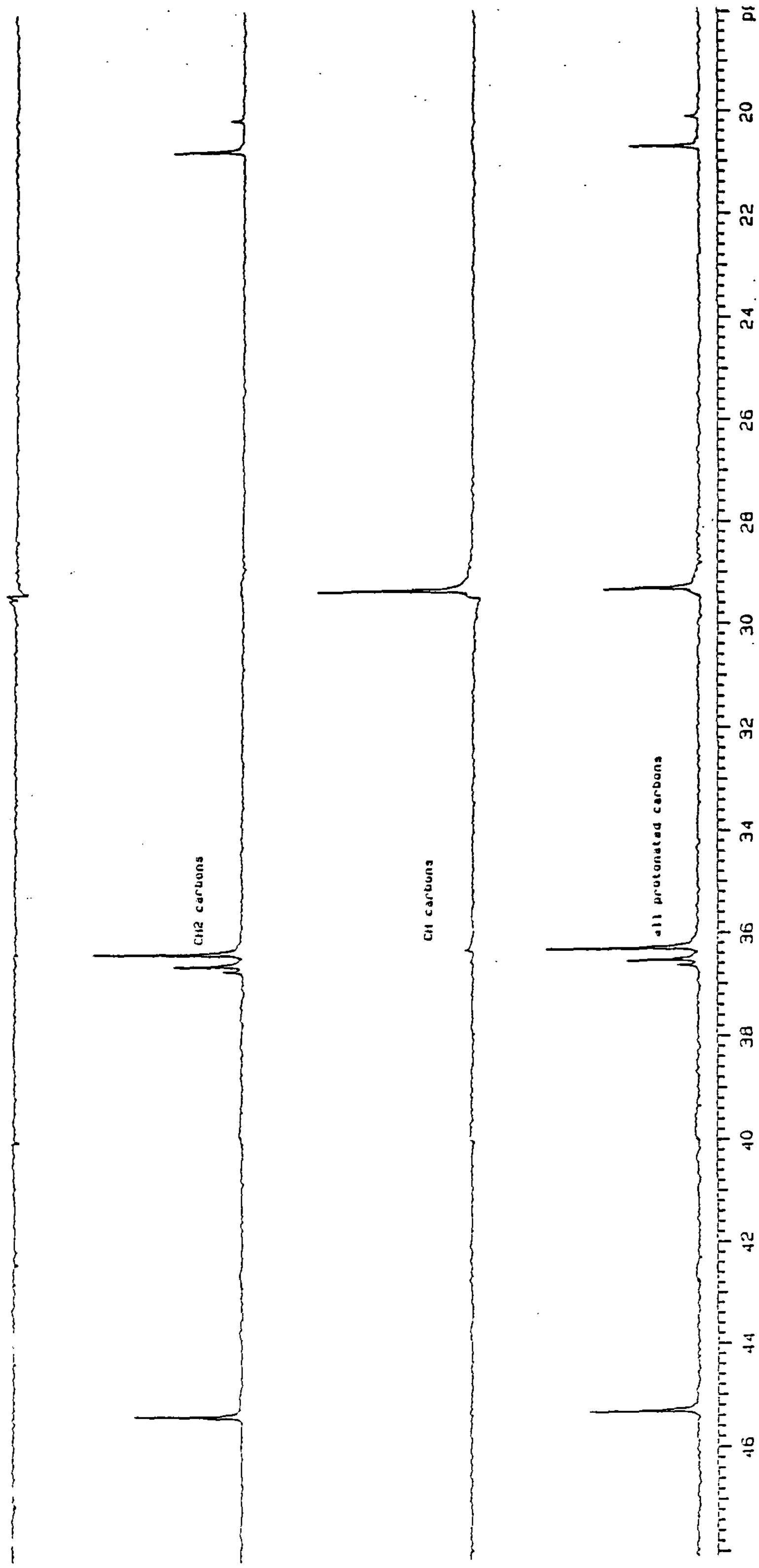
Appendix 1.8 ^{1}H n.m.r. ($CDCl_3$, 400MHz) spectrum of *Hex-dendr-(CN)₄*.



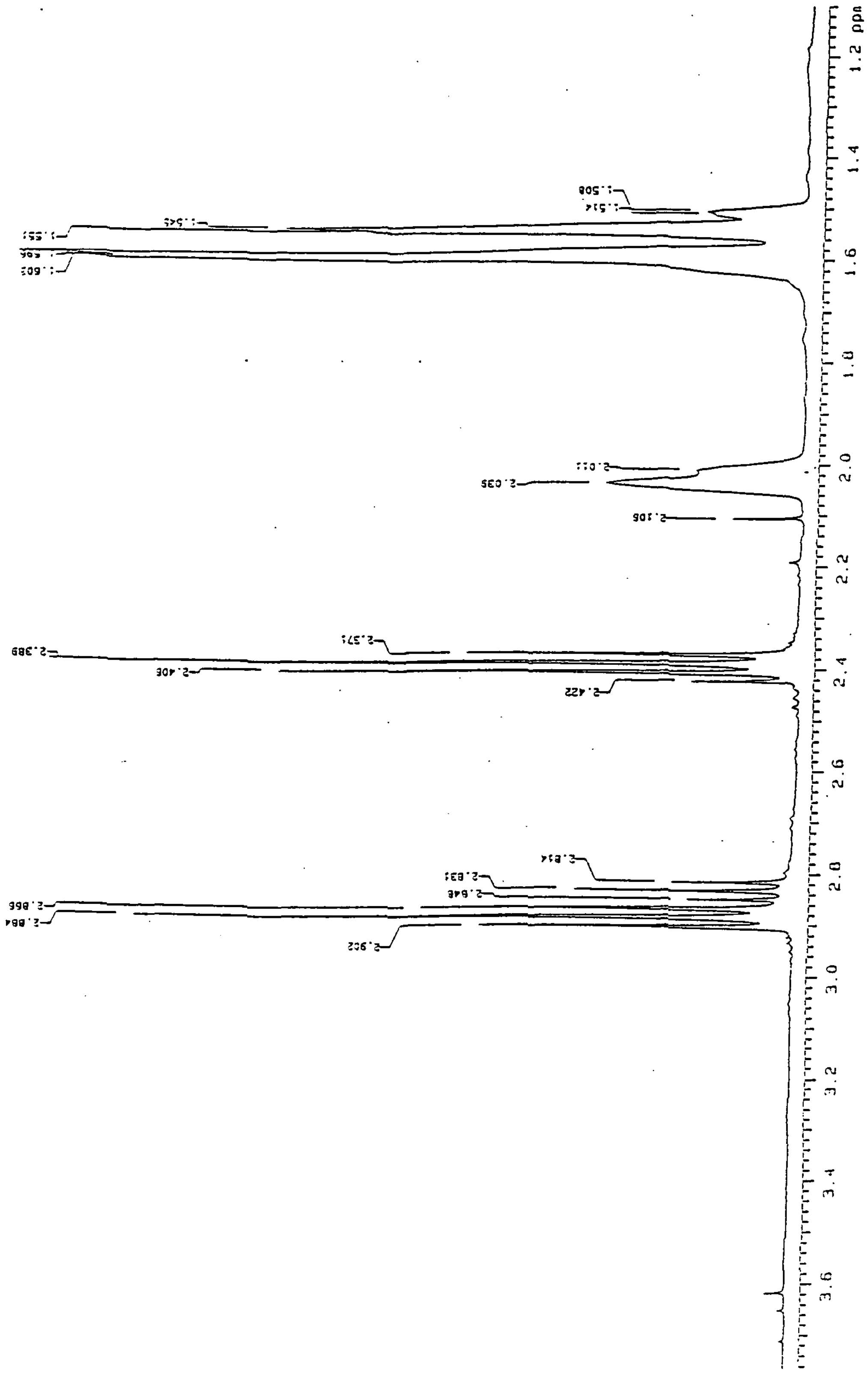
Appendix 1.9 FTIR spectrum of *Hex-dendr-(CN)₄*.



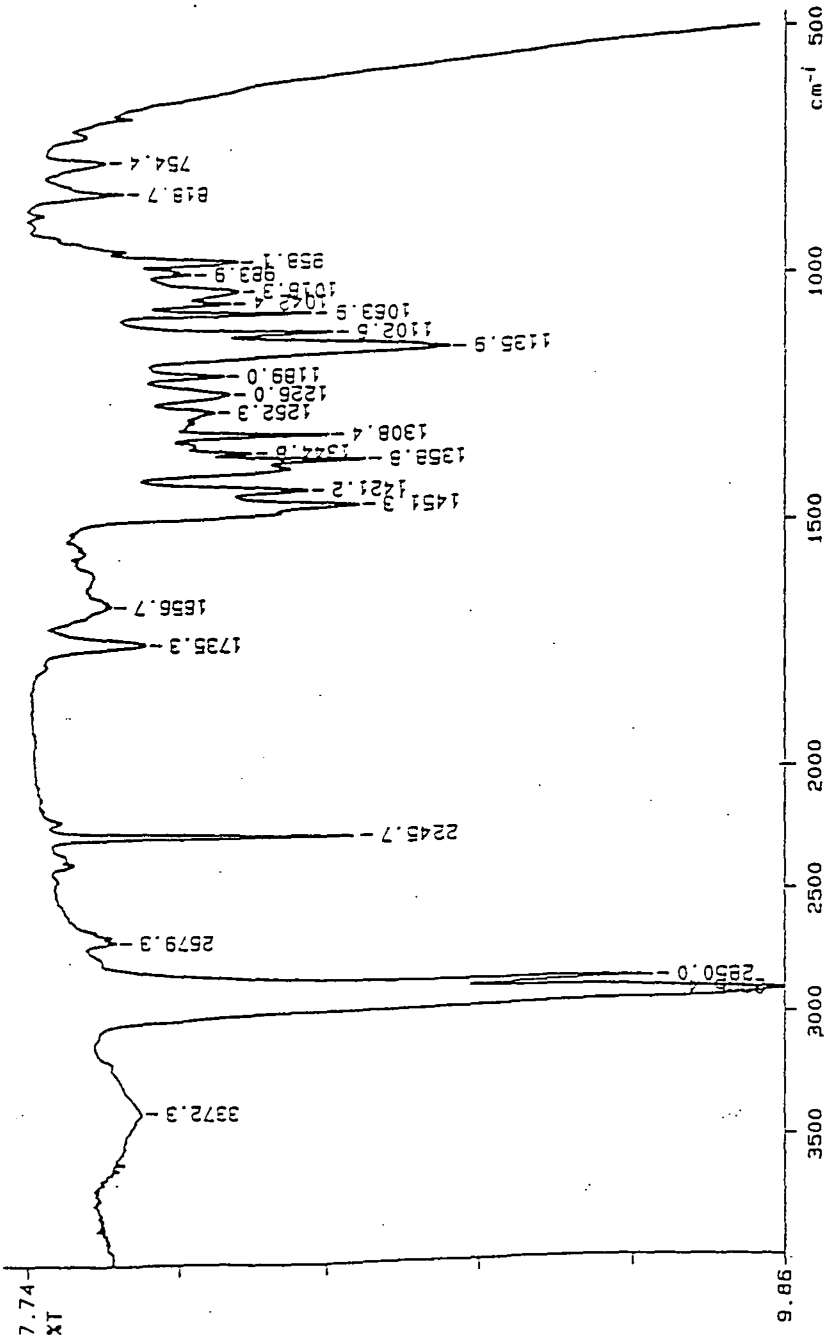
Appendix 1.10 ^{13}C n.m.r. (CDCl$_3$, 100MHz) spectrum of *Ad-dendr-(CN)$_2$*.



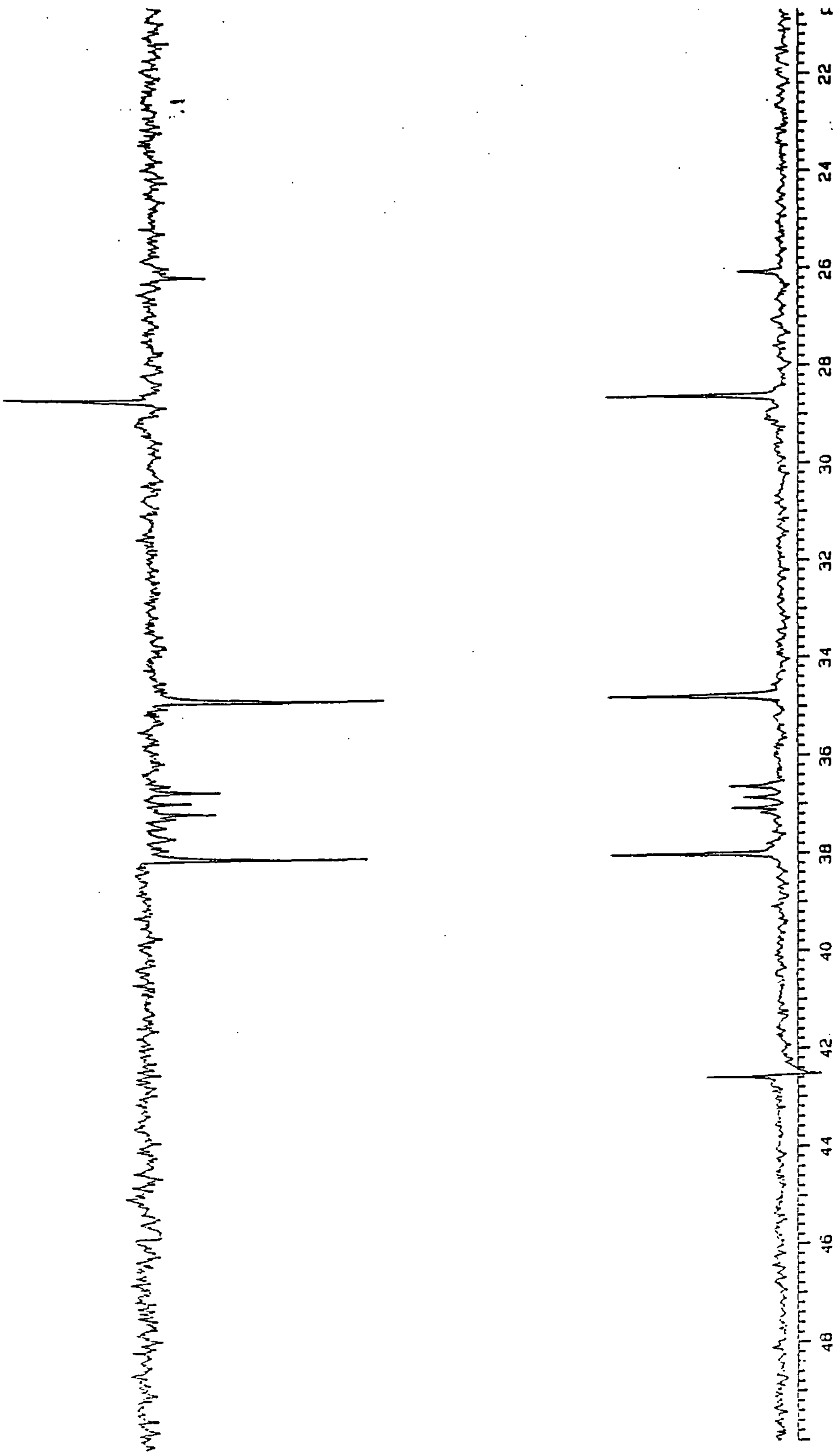
Appendix 1.11 ^{13}C n.m.r. ($CDCl_3$, 100MHz) D.E.P.T. spectrum of *Ad-dendr-(CN)$_2$*.



Appendix 1.12 ^{1}H n.m.r. ($CDCl_3$, 400MHz) spectrum of *Ad-dendr-(CN)$_2$*.

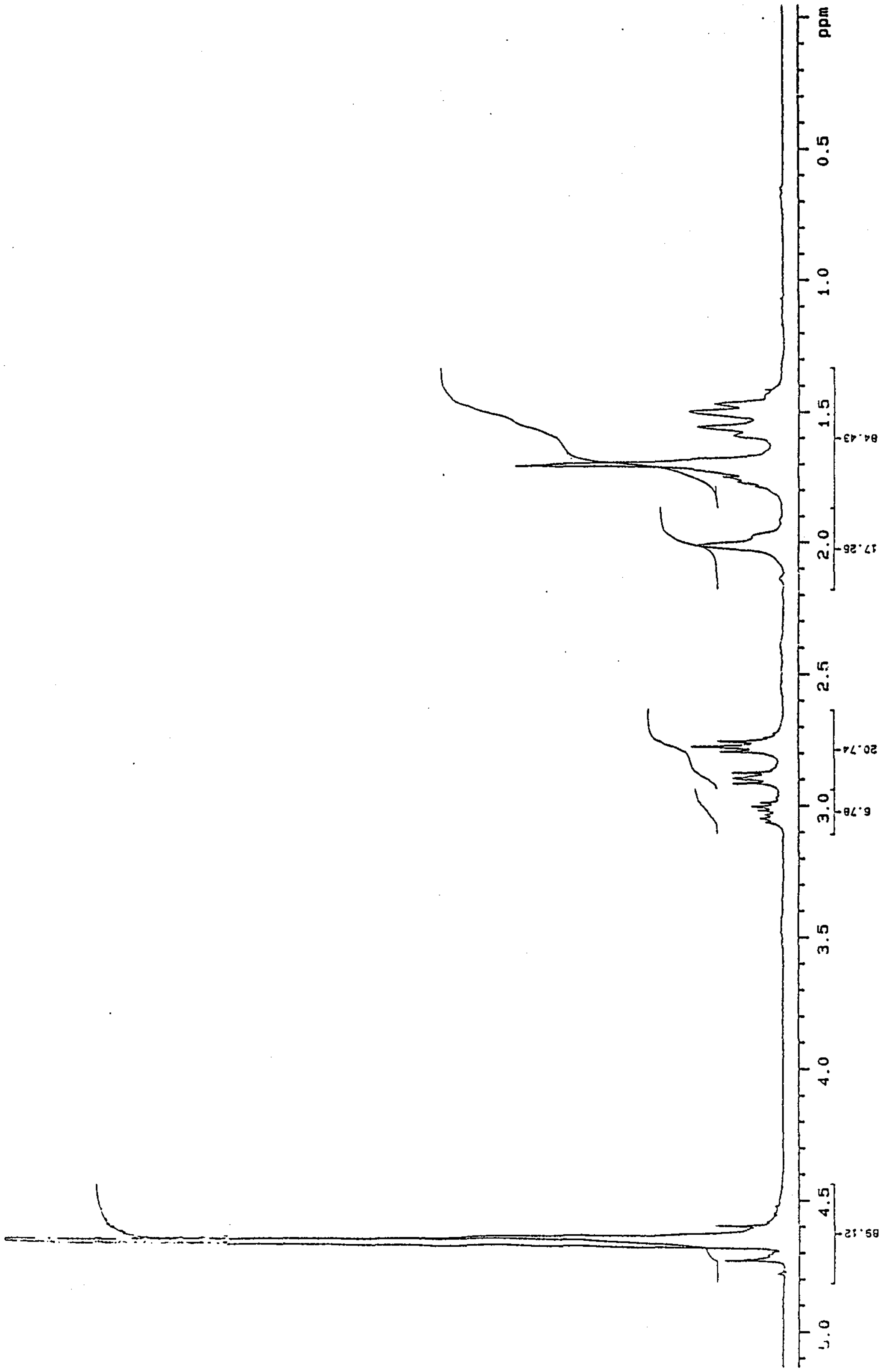


Appendix 1.13 FTIR spectrum of *Ad-dendr-(CN)*$_2$.

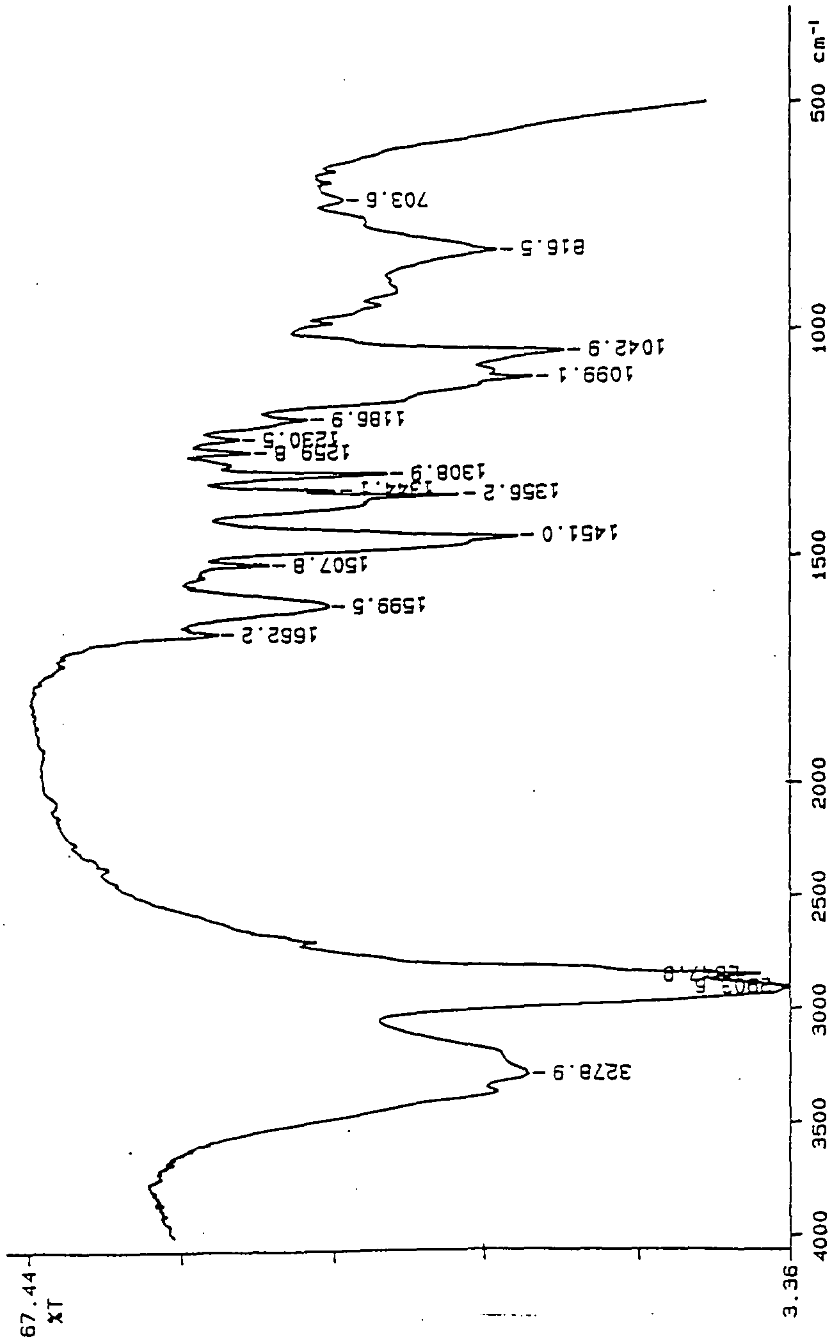


Appendix 1.14 ^{13}C n.m.r. ($CDCl_3$, 100MHz) D.E.P.T. spectrum of *Ad-dendr-*

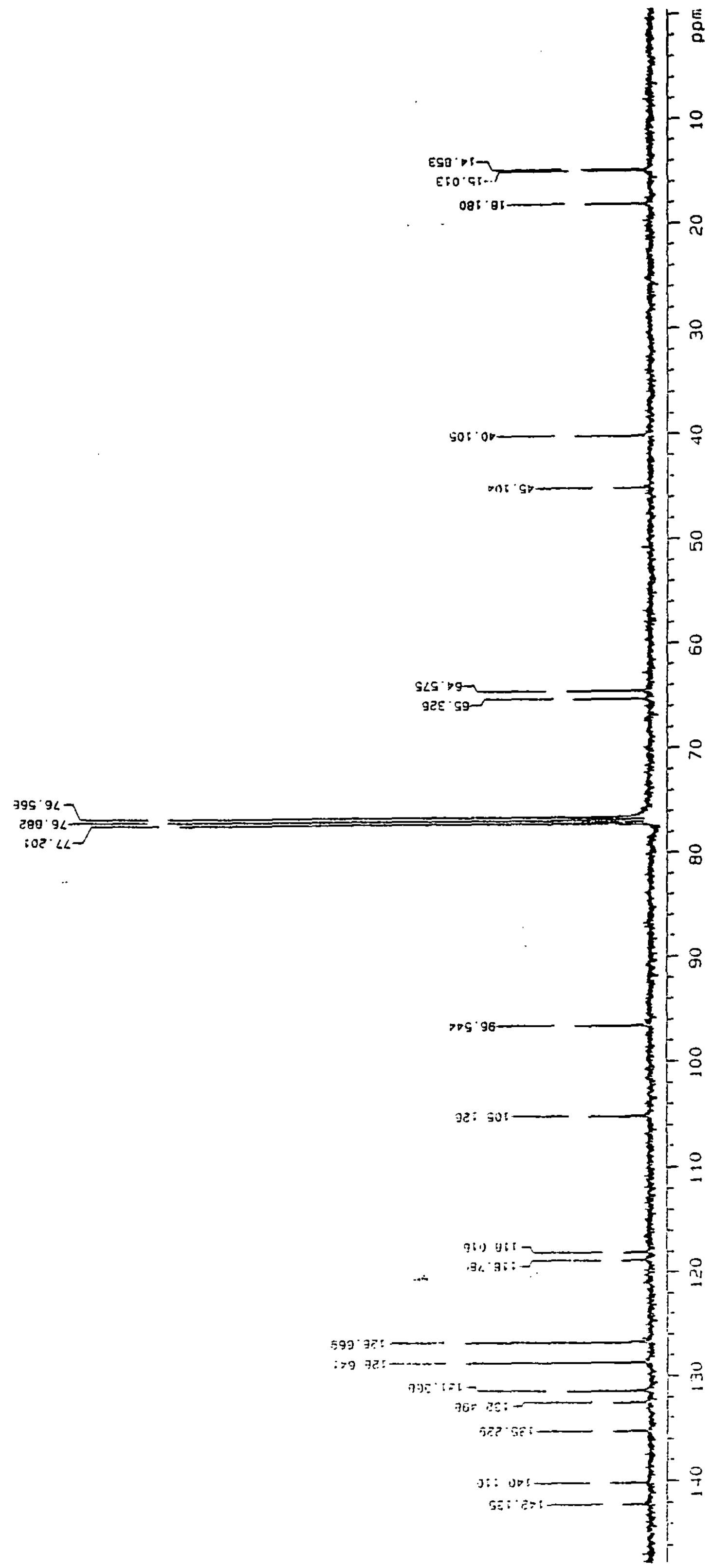
(NH_2)$_2$.



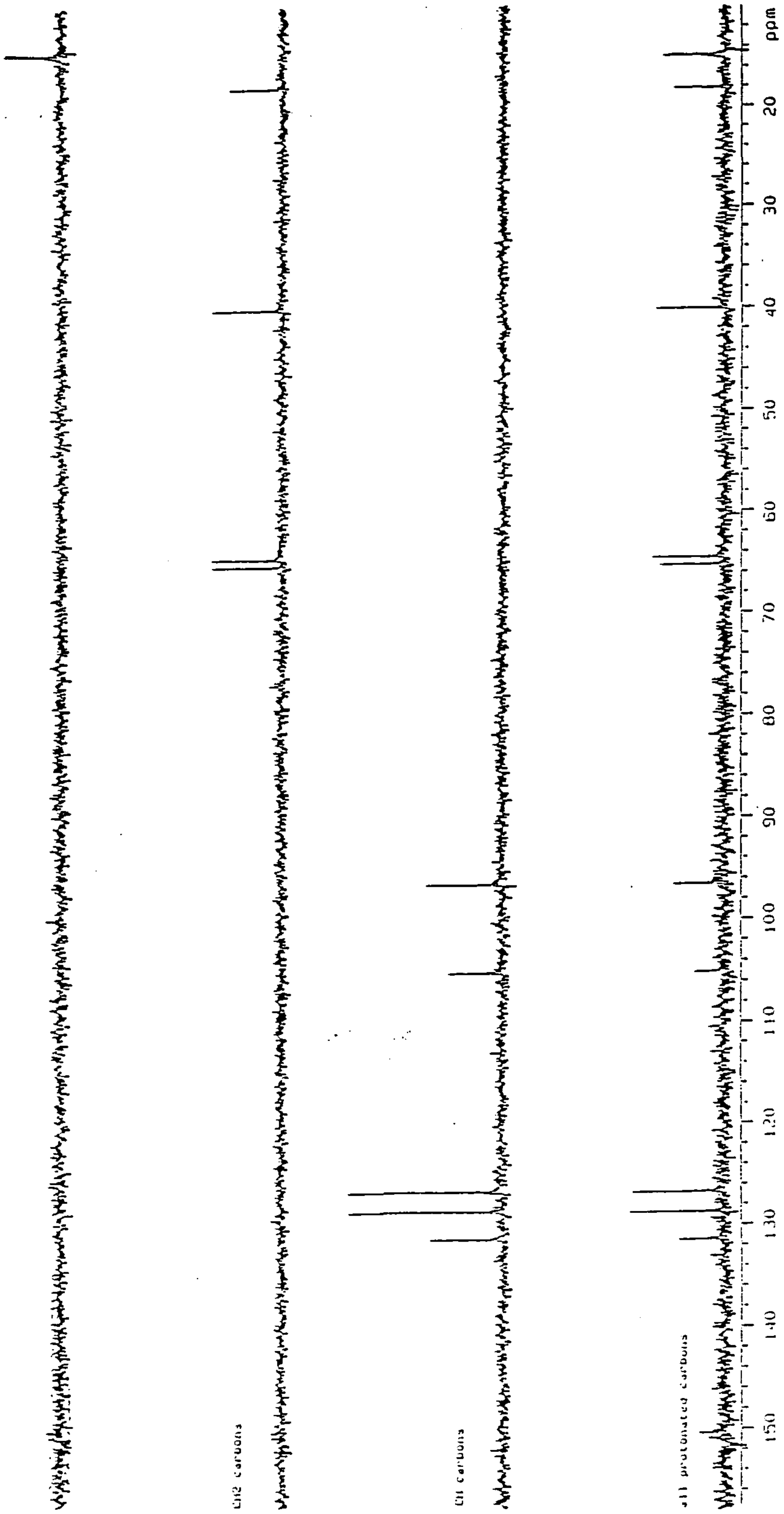
Appendix 1.15 ^{1}H n.m.r. ($CDCl_3$, 400MHz) spectrum of *Ad-dendr-*$(NH_2)_2$.



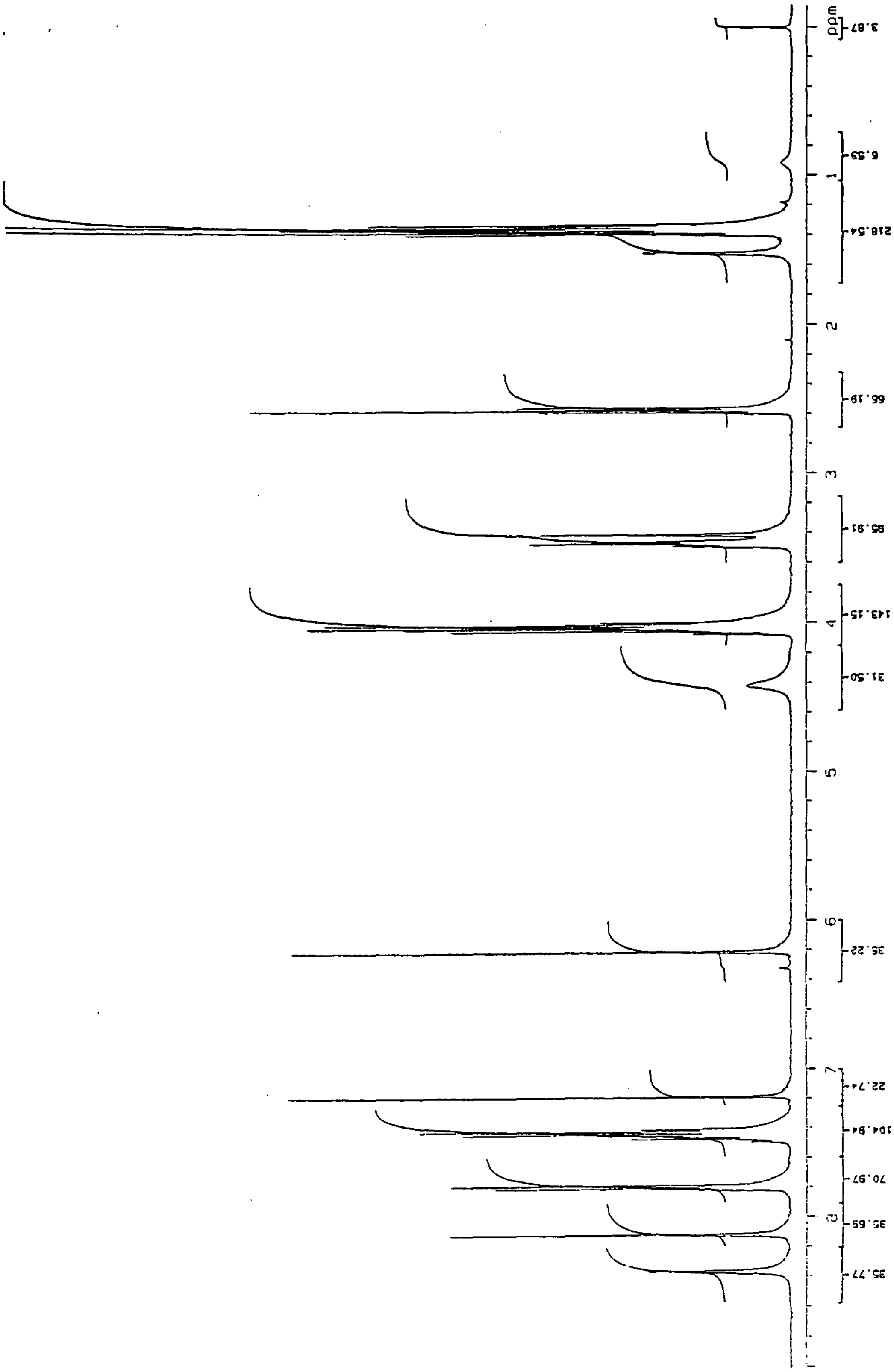
Appendix 1.16 FTIR spectrum of *Ad-dendr-(NH$_2$)$_2$*.



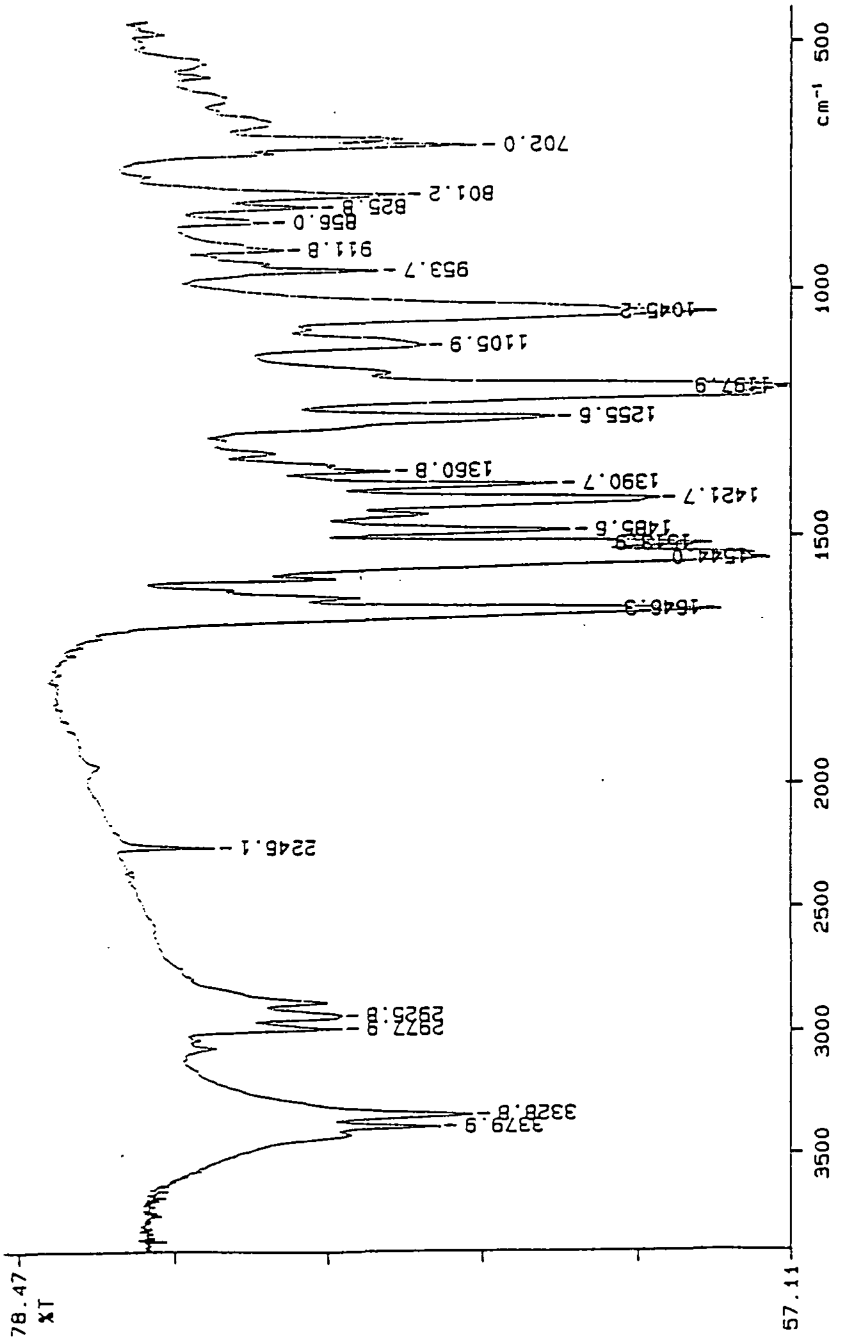
Appendix 1.17 ^{13}C n.m.r. ($CDCl_3$, 100MHz) spectrum of *FB-dendr-(CN)$_1$*.



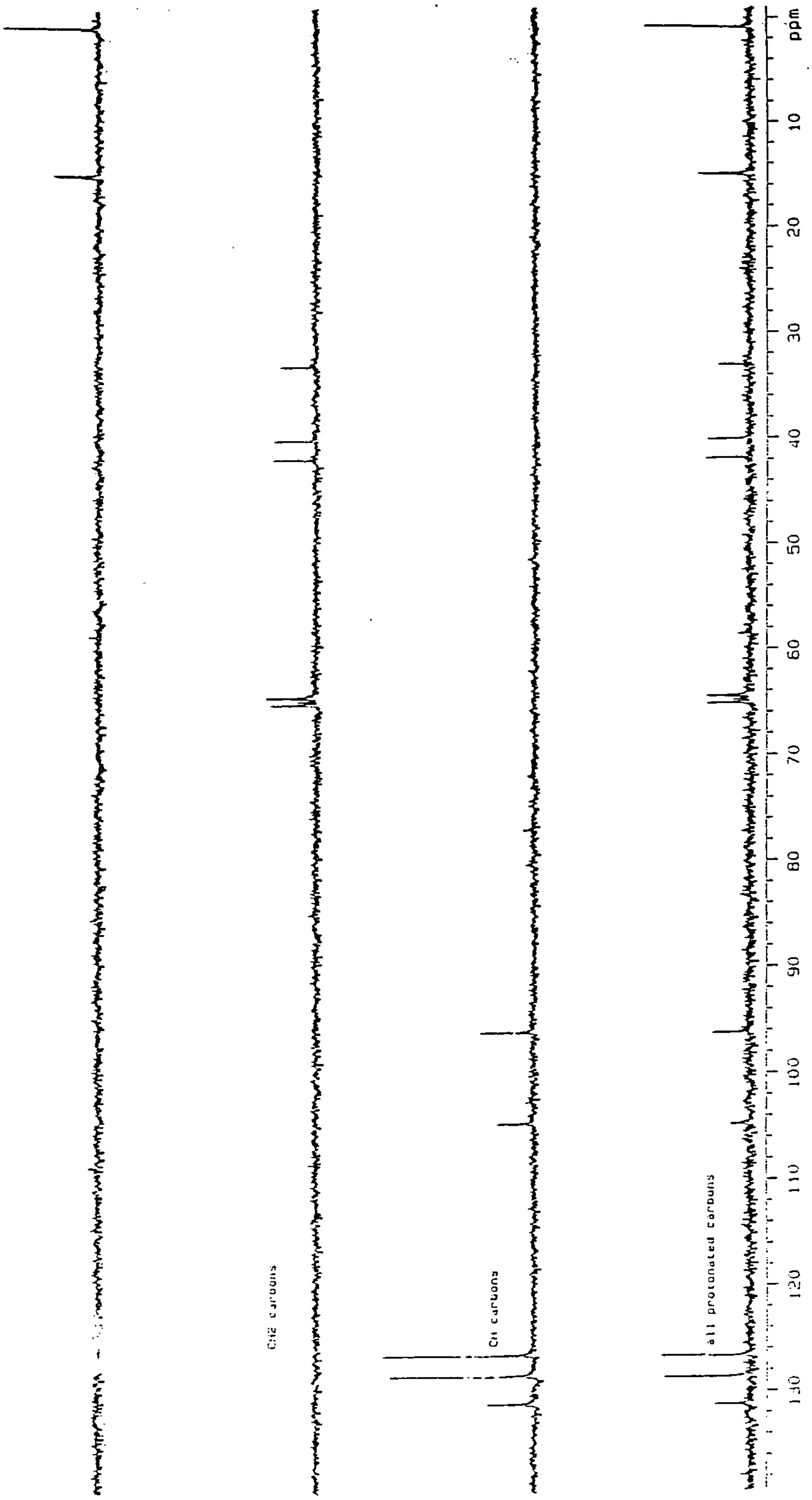
Appendix 1.18 ^{13}C n.m.r. (CDCl$_3$, 100MHz) D.E.P.T. spectrum of *FB-dendr-(CN)$_1$*.



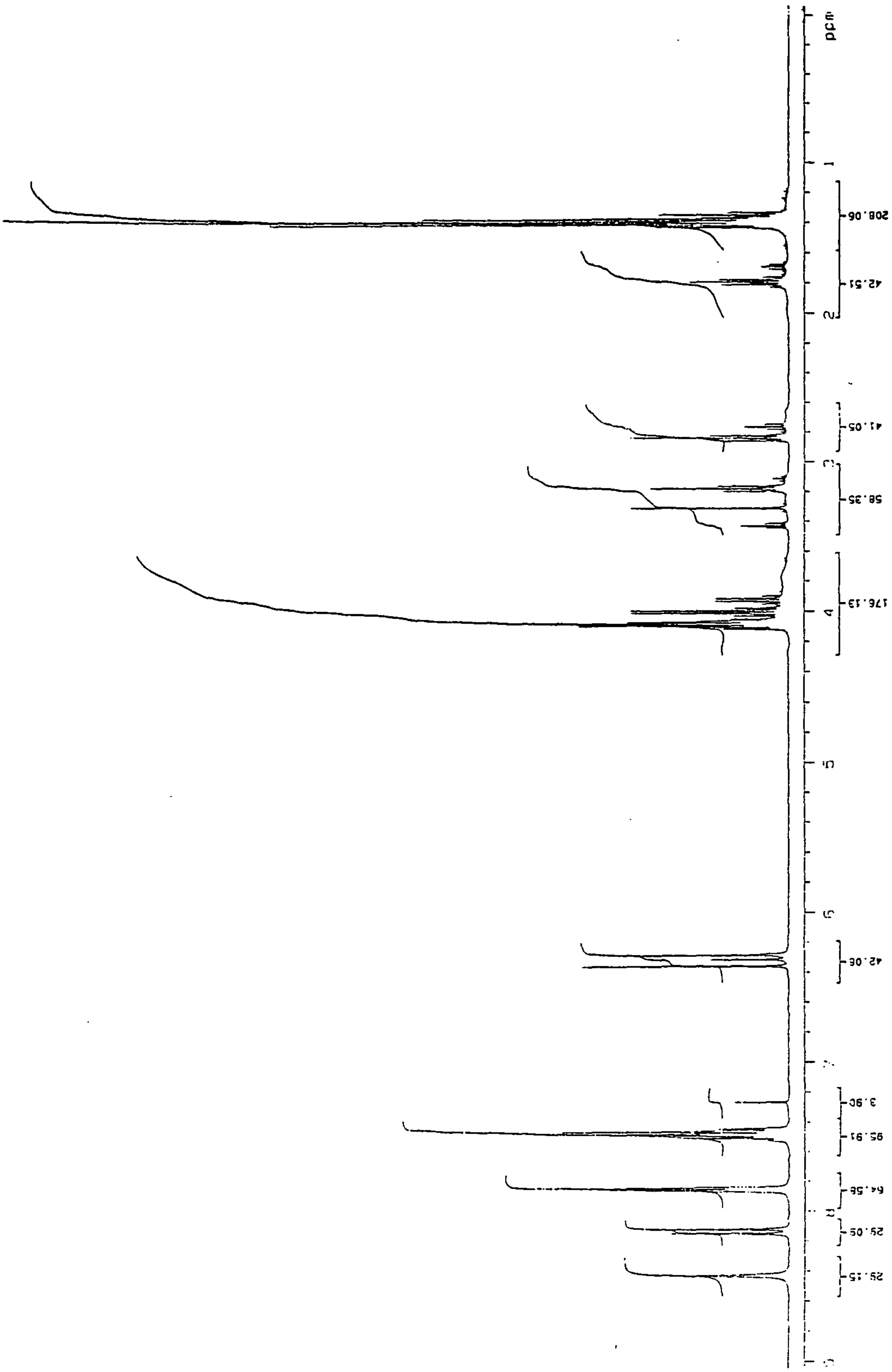
Appendix 1.19 ^{1}H n.m.r. ($CDCl_3$, 400MHz) spectrum of *FB-dendr-(CN)$_1$*.



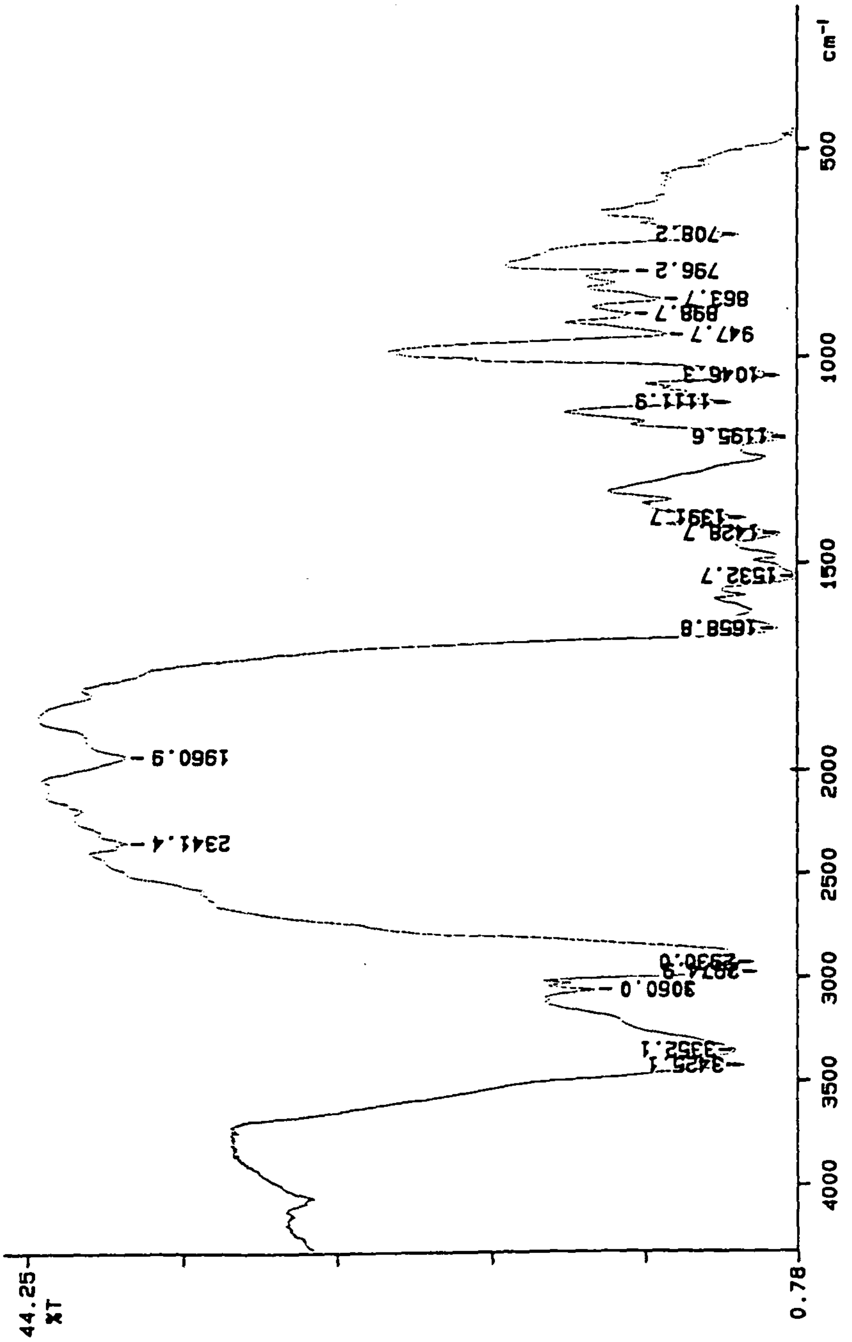
Appendix 1.20 FTIR spectrum of *FB-dendr-(CN)₁*.



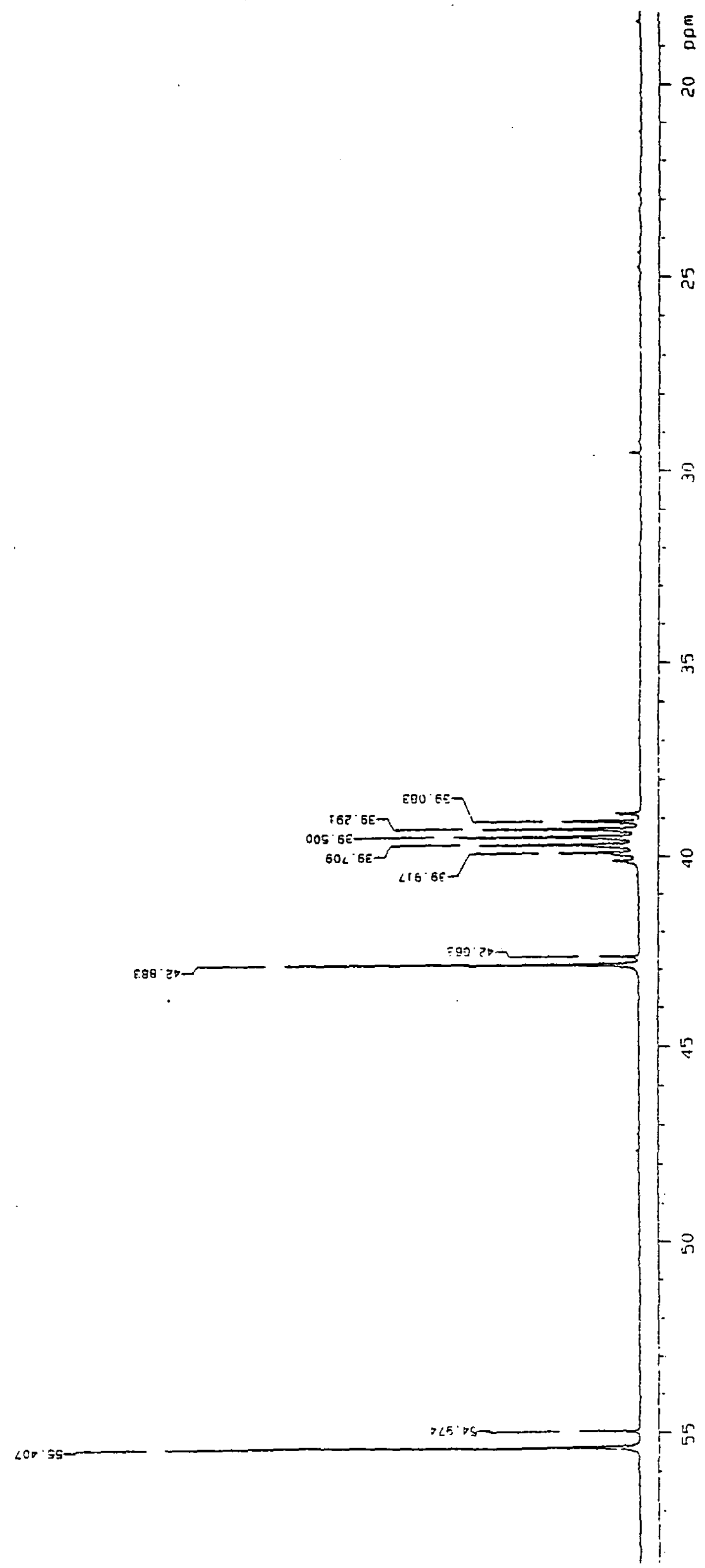
Appendix 1.21 ^{13}C n.m.r. (CDCl$_3$, 100MHz) D.E.P.T. spectrum of *FB-dendr-(NH$_2$)$_1$*.



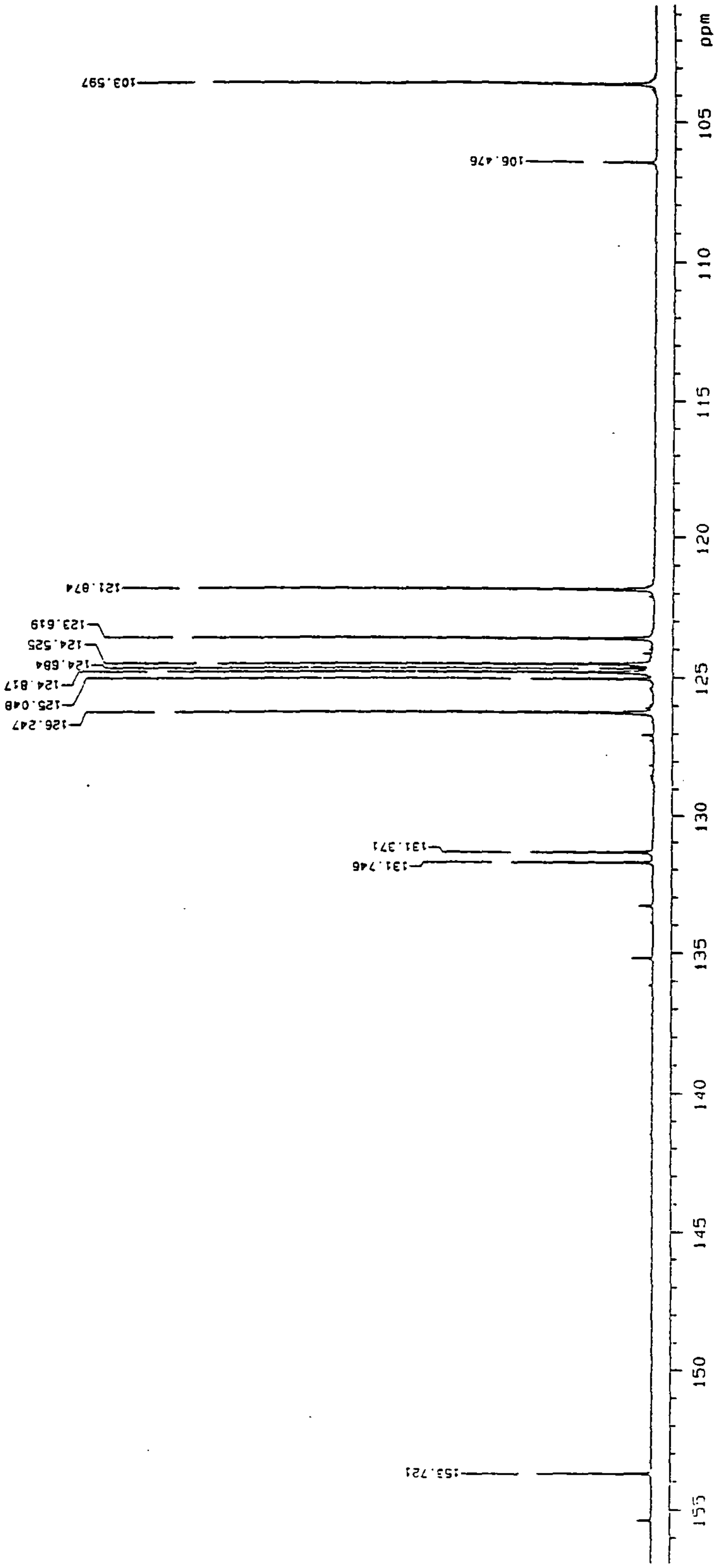
Appendix 1.22 ^{1}H n.m.r. ($CDCl_3$, 400MHz) spectrum of *FB-dendr-*$(NH_2)_1$.



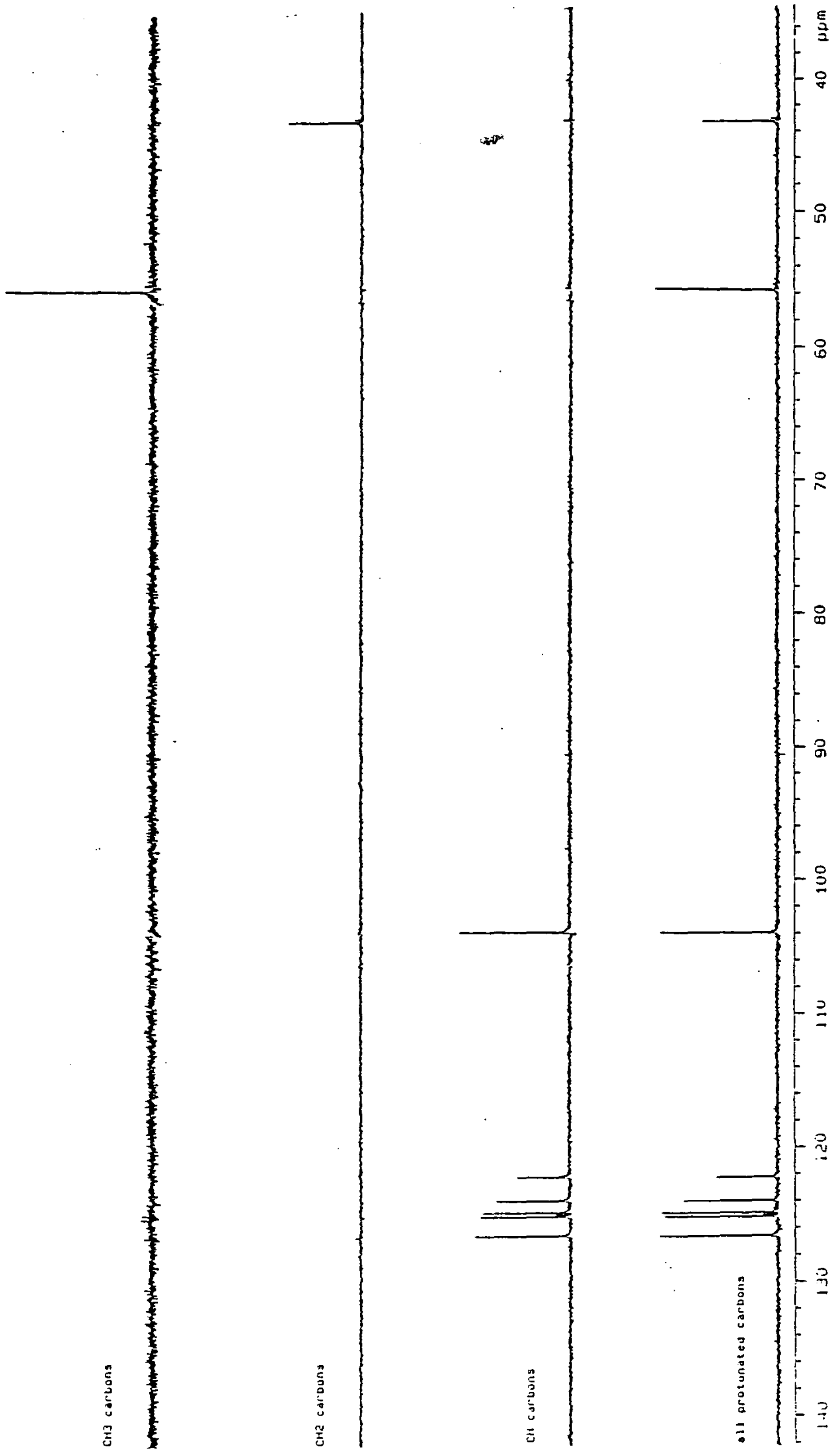
Appendix 1.23 FTIR spectrum of *FB-dendr-*$(NH_2)_1$.



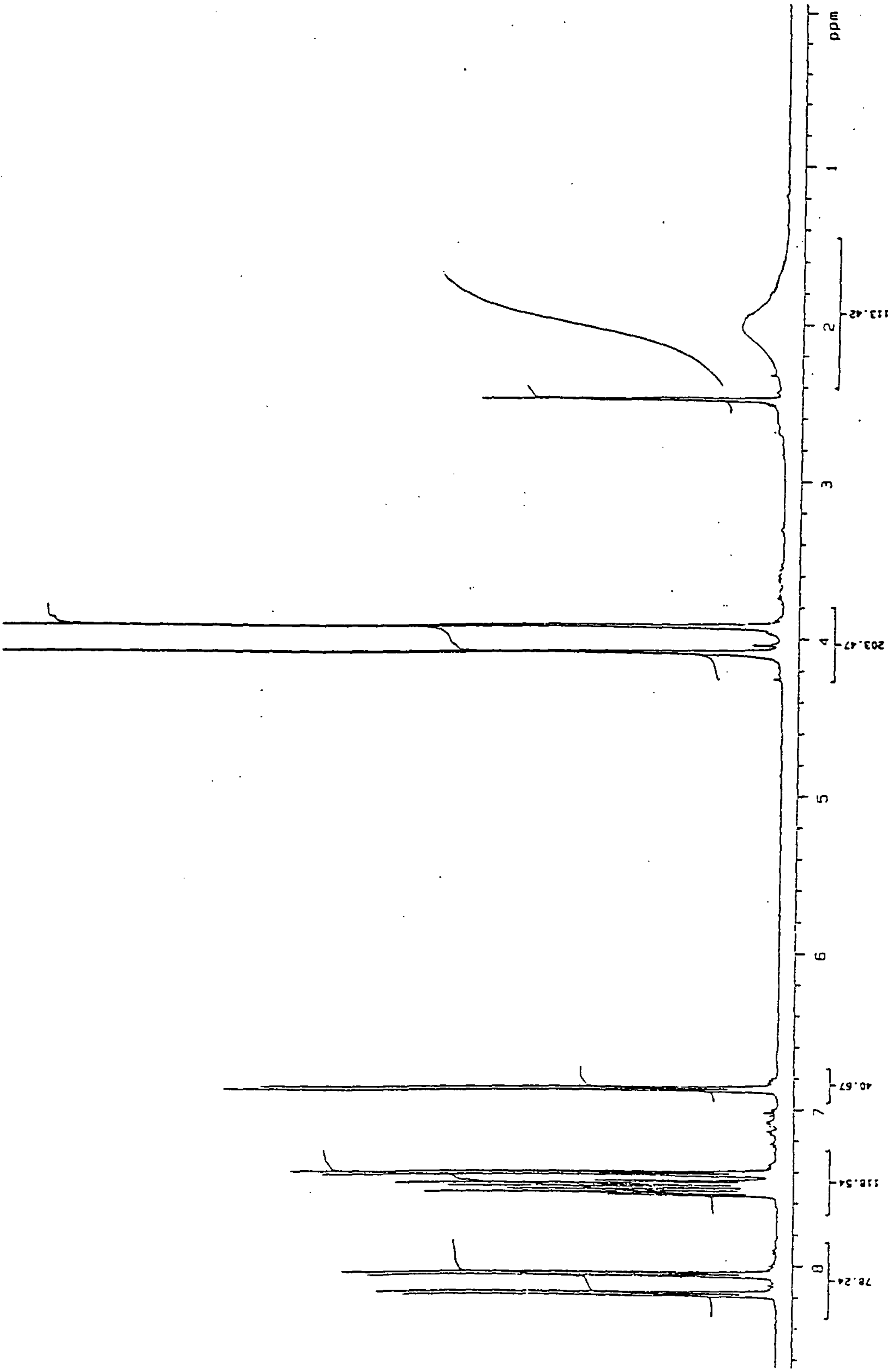
Appendix 1.24.a ^{13}C n.m.r. (100MHz, d_6-methyl sulfoxide) spectrum of 1-aminomethyl, 4-methoxy-naphthalene.



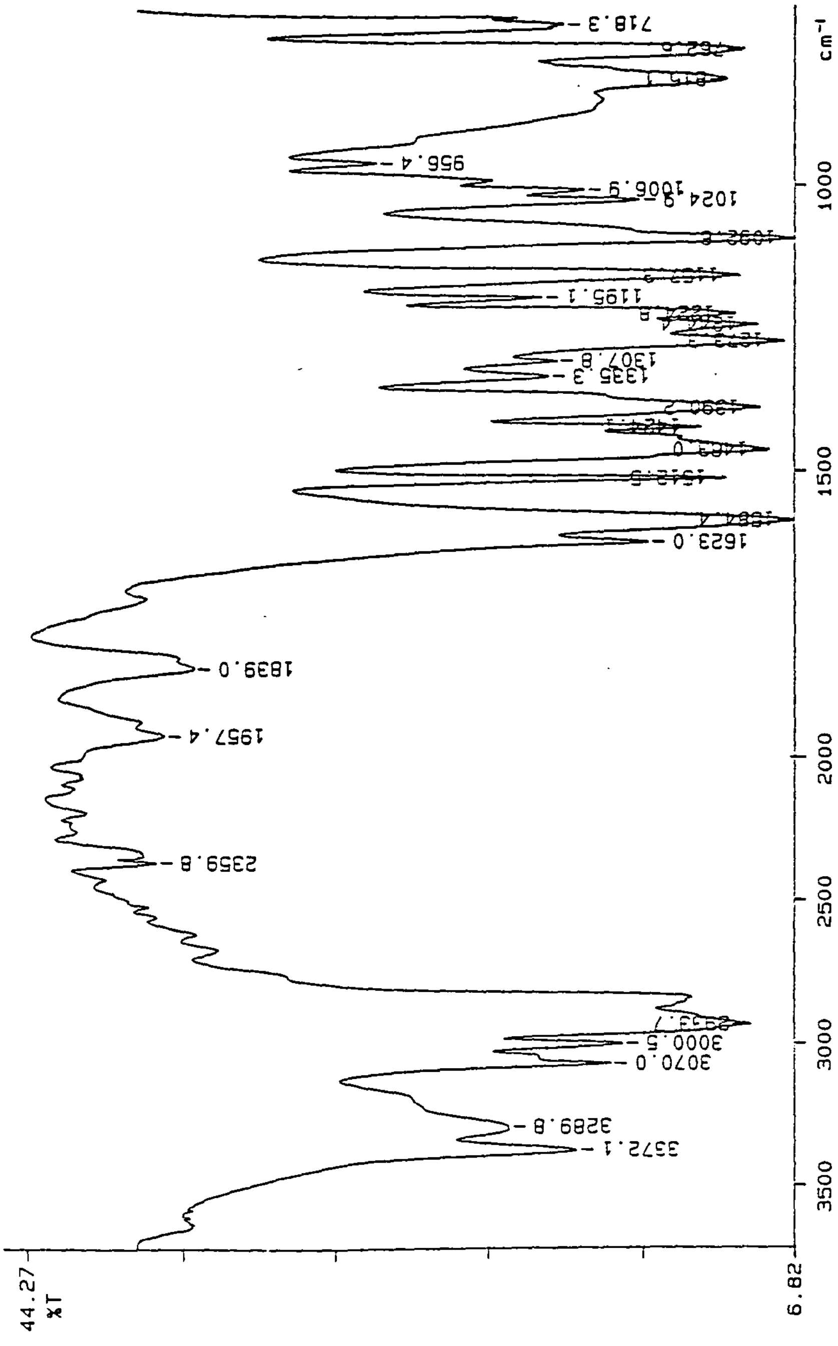
Appendix 1.24.b ^{13}C n.m.r. (100MHz, d_6-methyl sulfoxide) spectrum of 1-aminomethyl, 4-methoxy-naphthalene.



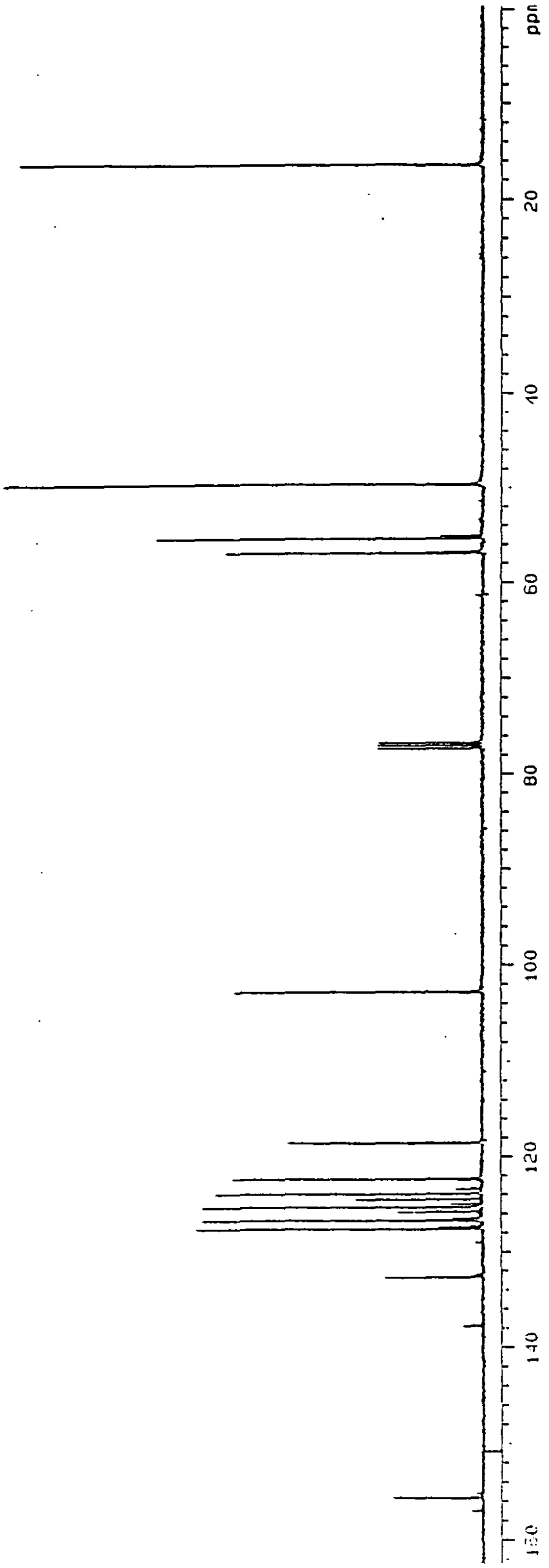
Appendix 1.25 ^{13}C n.m.r. (100MHz, d_6-methyl sulfoxide) D.E.P.T. spectrum of 1-aminomethyl, 4-methoxy-naphthalene.



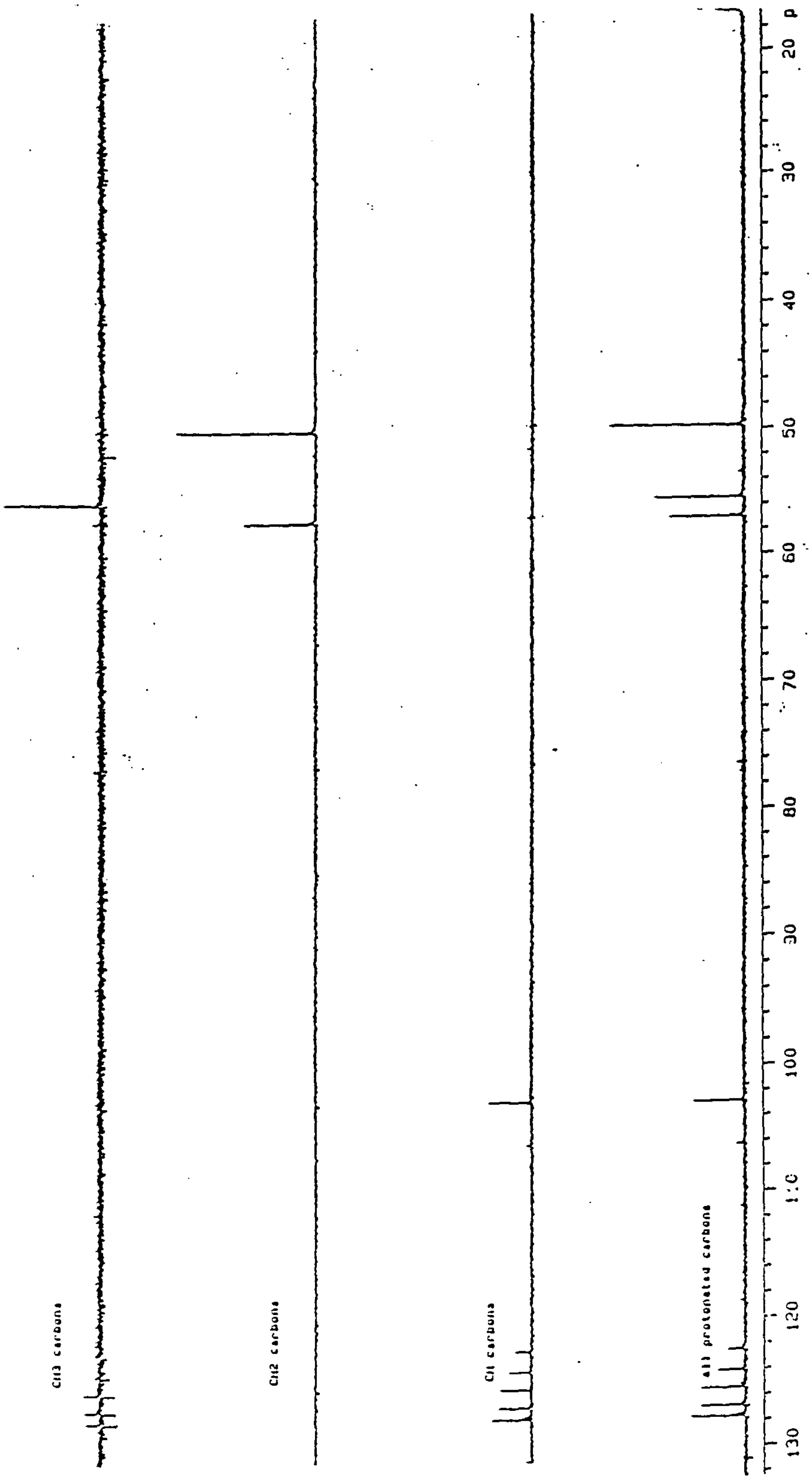
Appendix 1.26 ^{1}H n.m.r. (400MHz, d_6-methyl sulfoxide) of 1-aminomethyl, 4-methoxy-naphthalene.



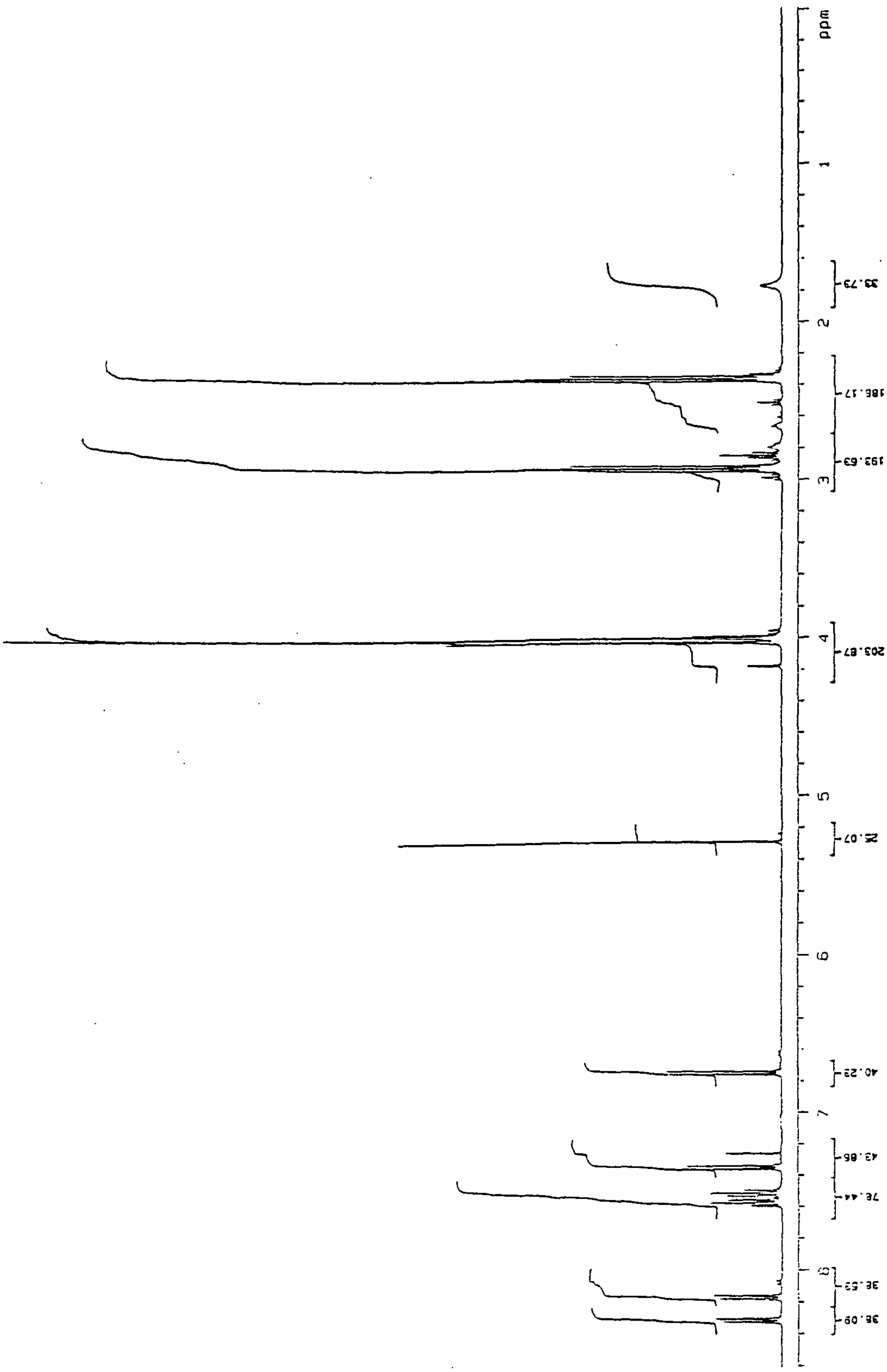
Appendix 1.27 FTIR spectrum of 1-aminomethyl, 4-methoxy-naphthalene.



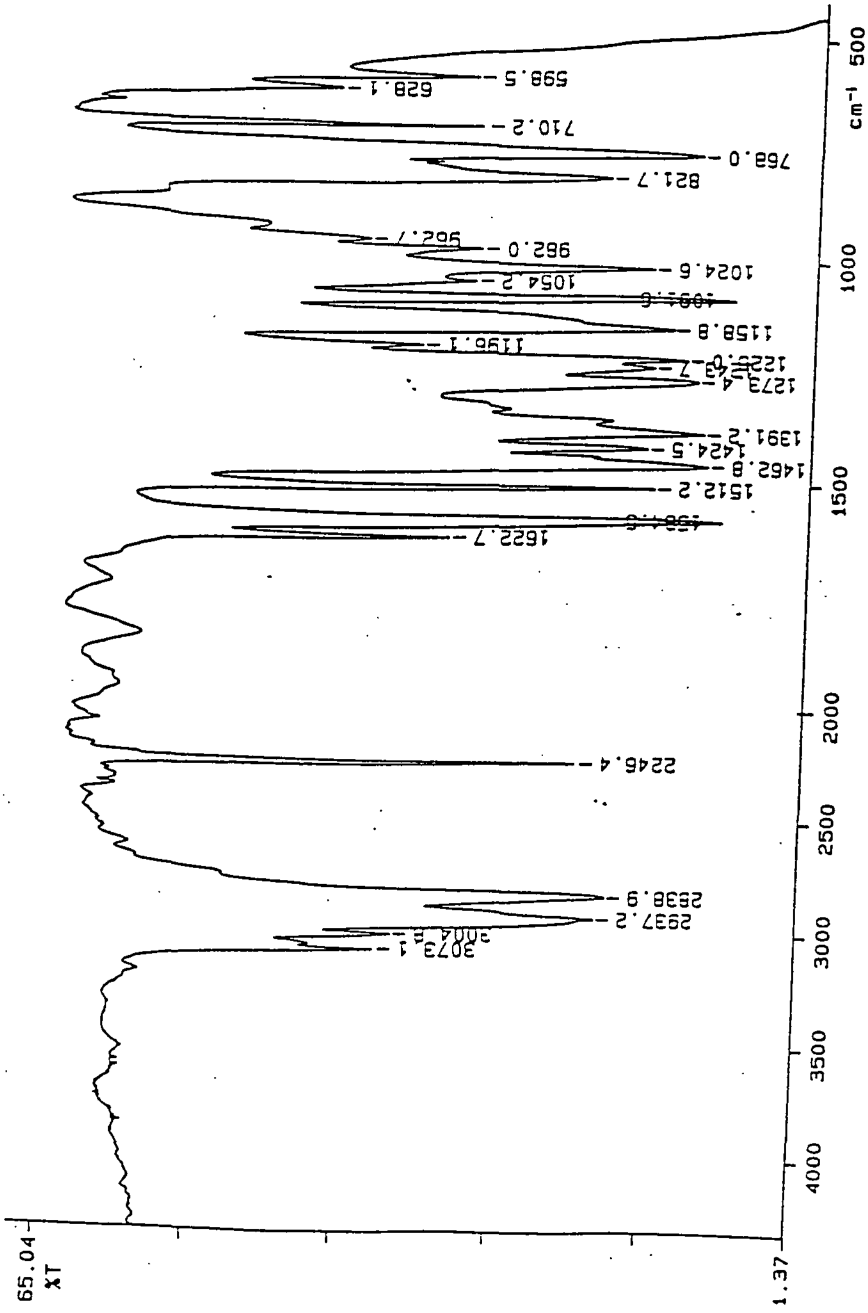
Appendix 1.28 ^{13}C n.m.r. (100MHz, $CDCl_3$) spectrum of *UV-dendr-(CN)*$_2$.



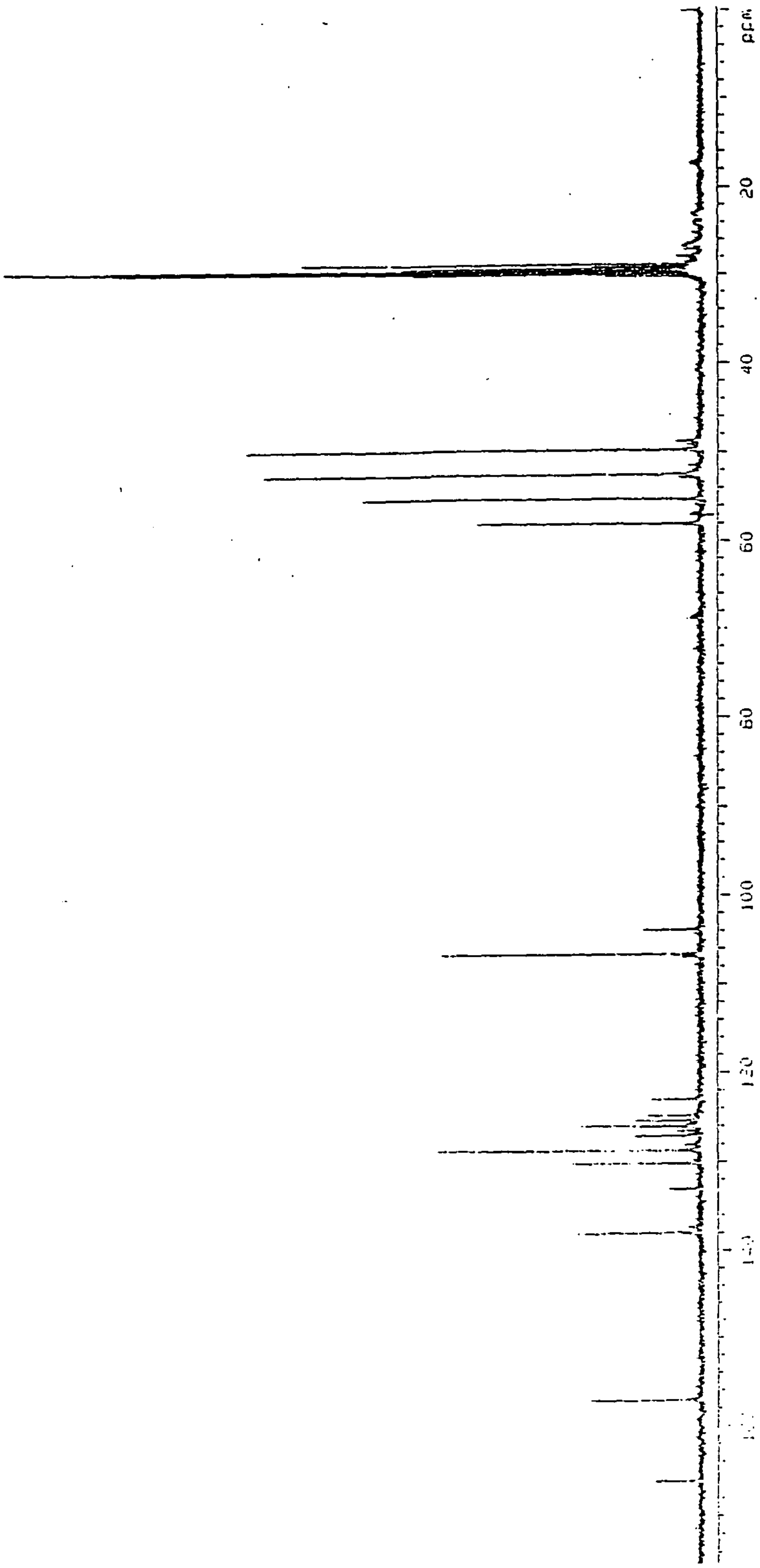
Appendix 1.29 ^{13}C n.m.r. (100MHz, $CDCl_3$) D.E.P.T. spectrum of *UV-dendr-(CN)$_2$*.



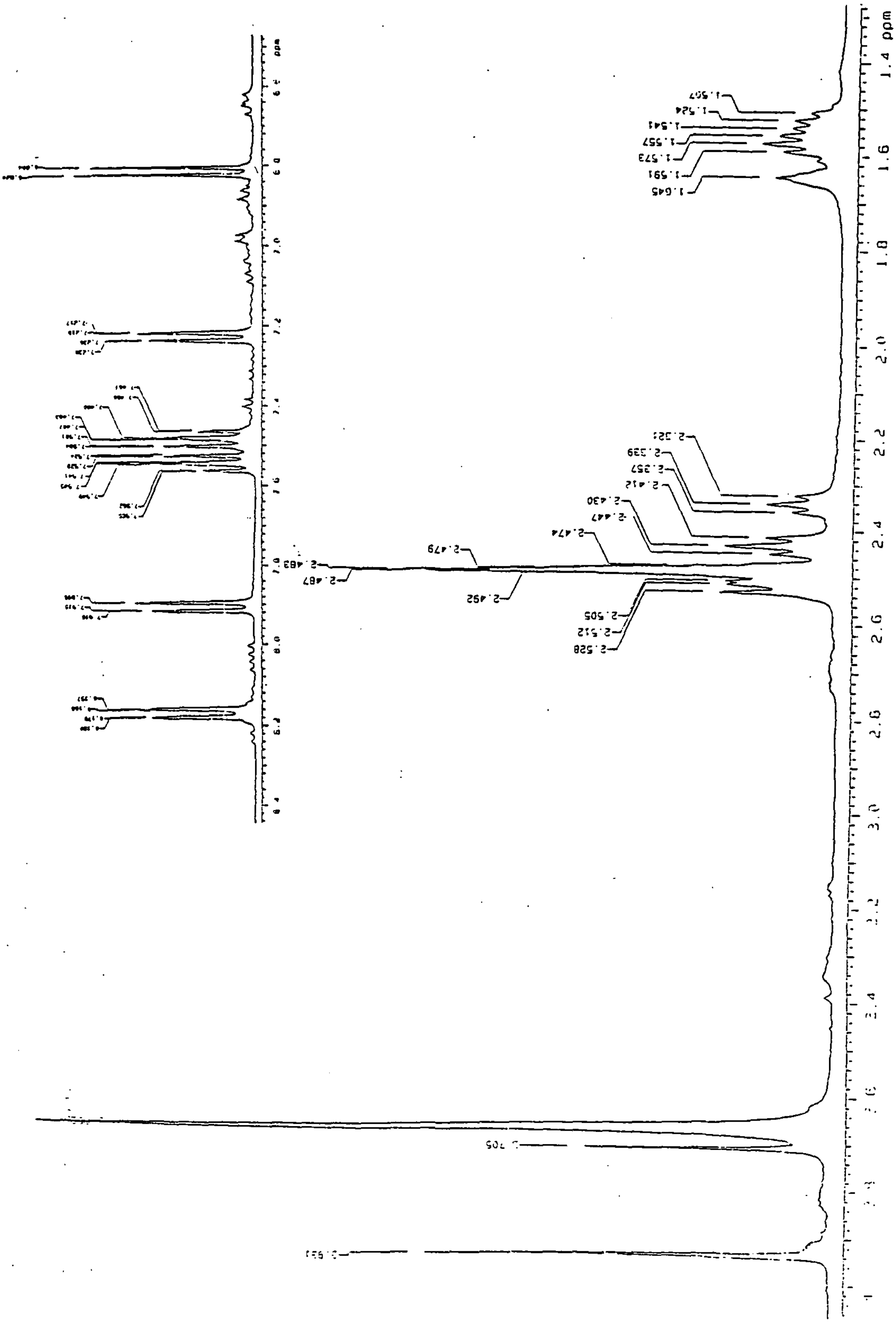
Appendix 1.30 ^{1}H n.m.r. (400MHz, $CDCl_3$) spectrum of *UV-dendr-(CN)*$_2$.



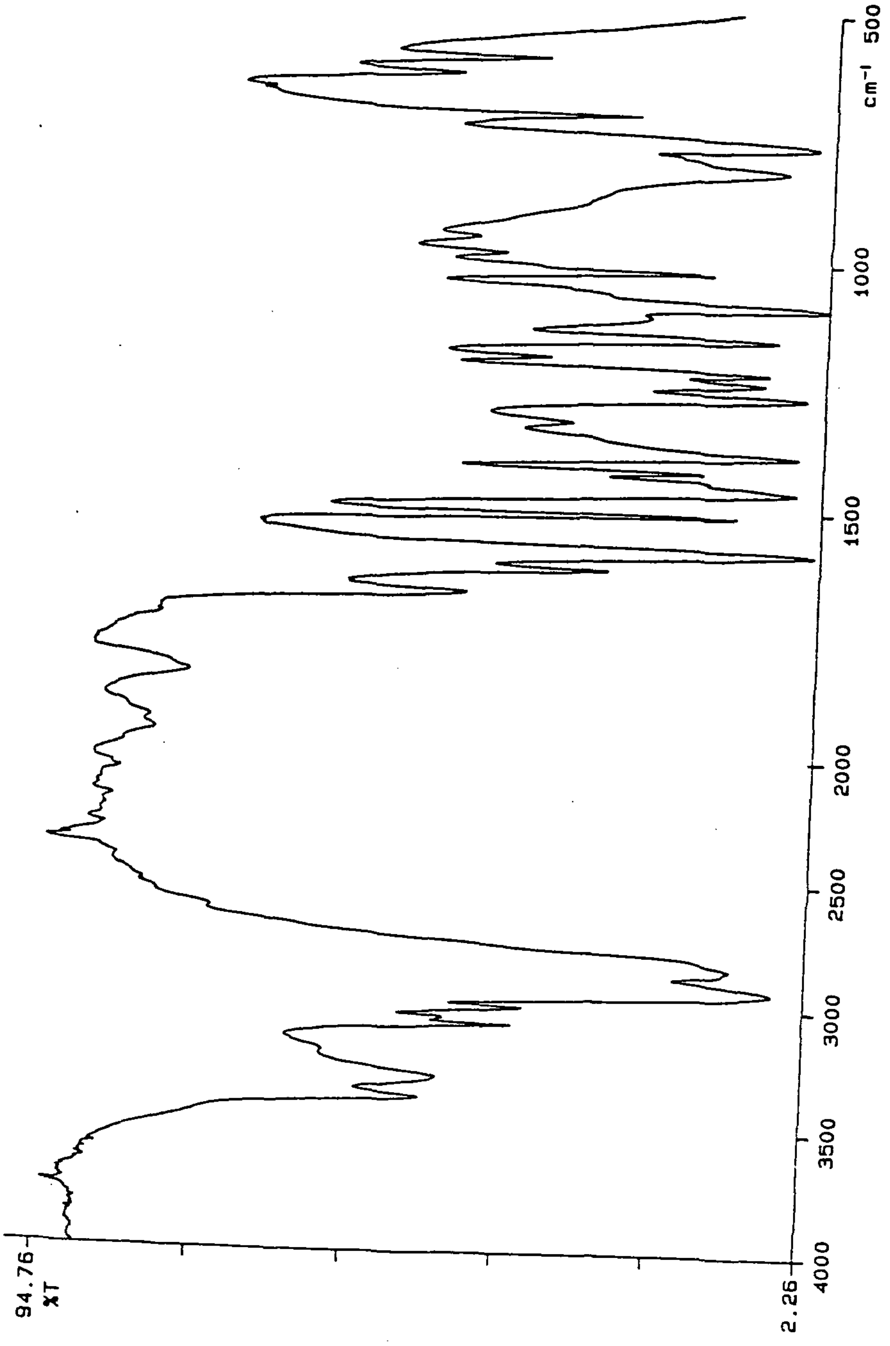
Appendix 1.31 FTIR spectrum of *UV-dendr-(CN)*$_2$.



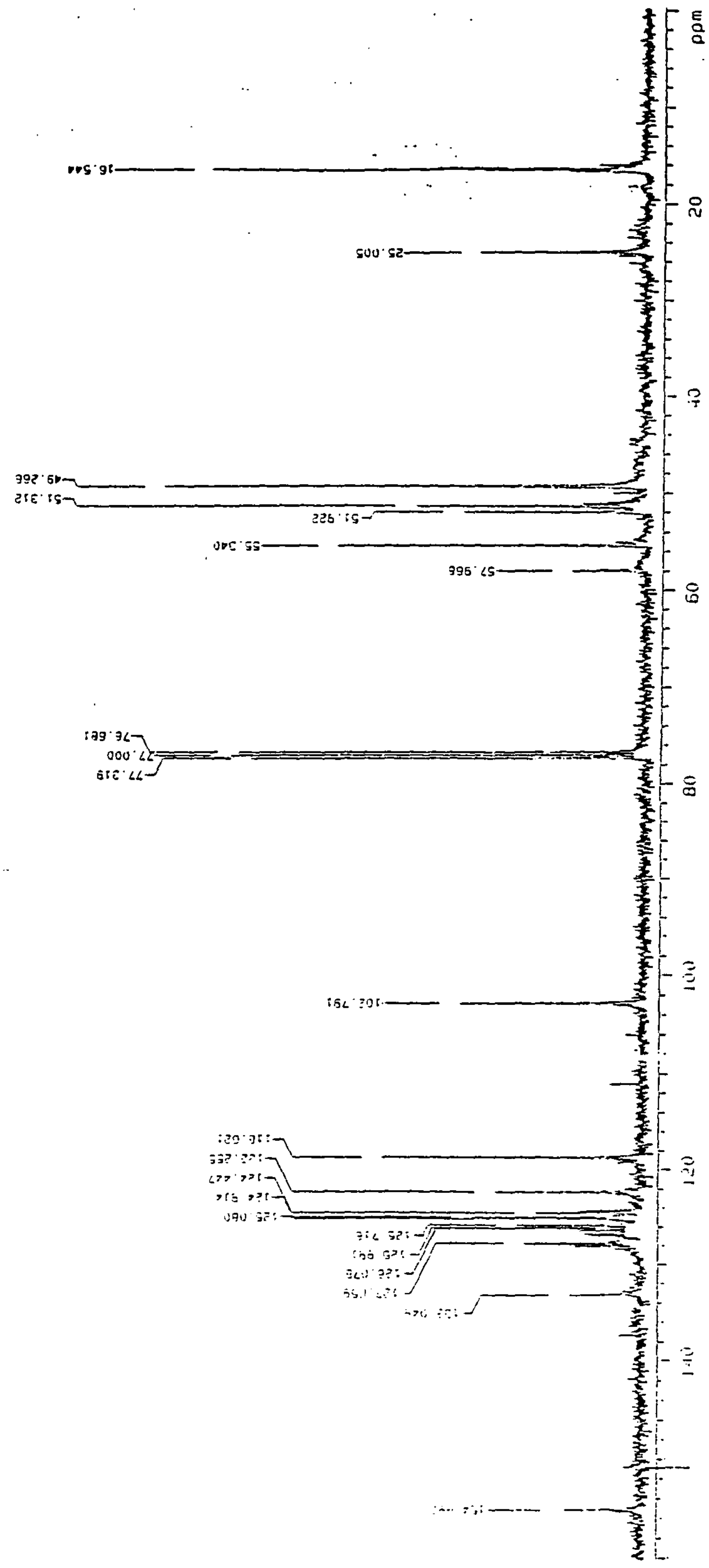
Appendix 1.32 ^{13}C n.m.r. (100MHz, CDCl$_3$) spectrum of *UV-dendr-(NH$_2$)$_2$*.



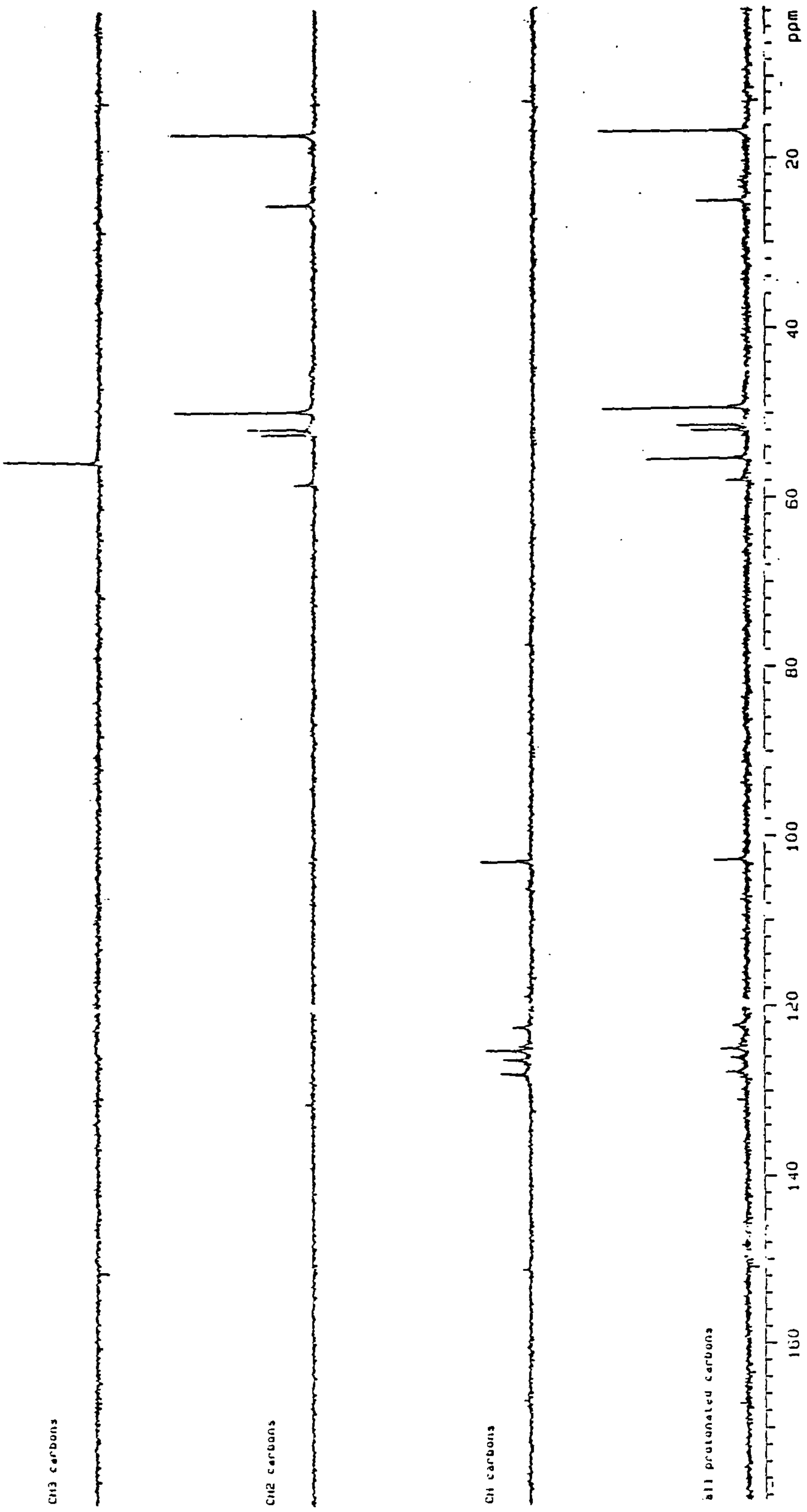
Appendix 1.33 ^{1}H n.m.r. (400MHz, $CDCl_3$) spectrum of *UV-dendr-*$(NH_2)_2$.



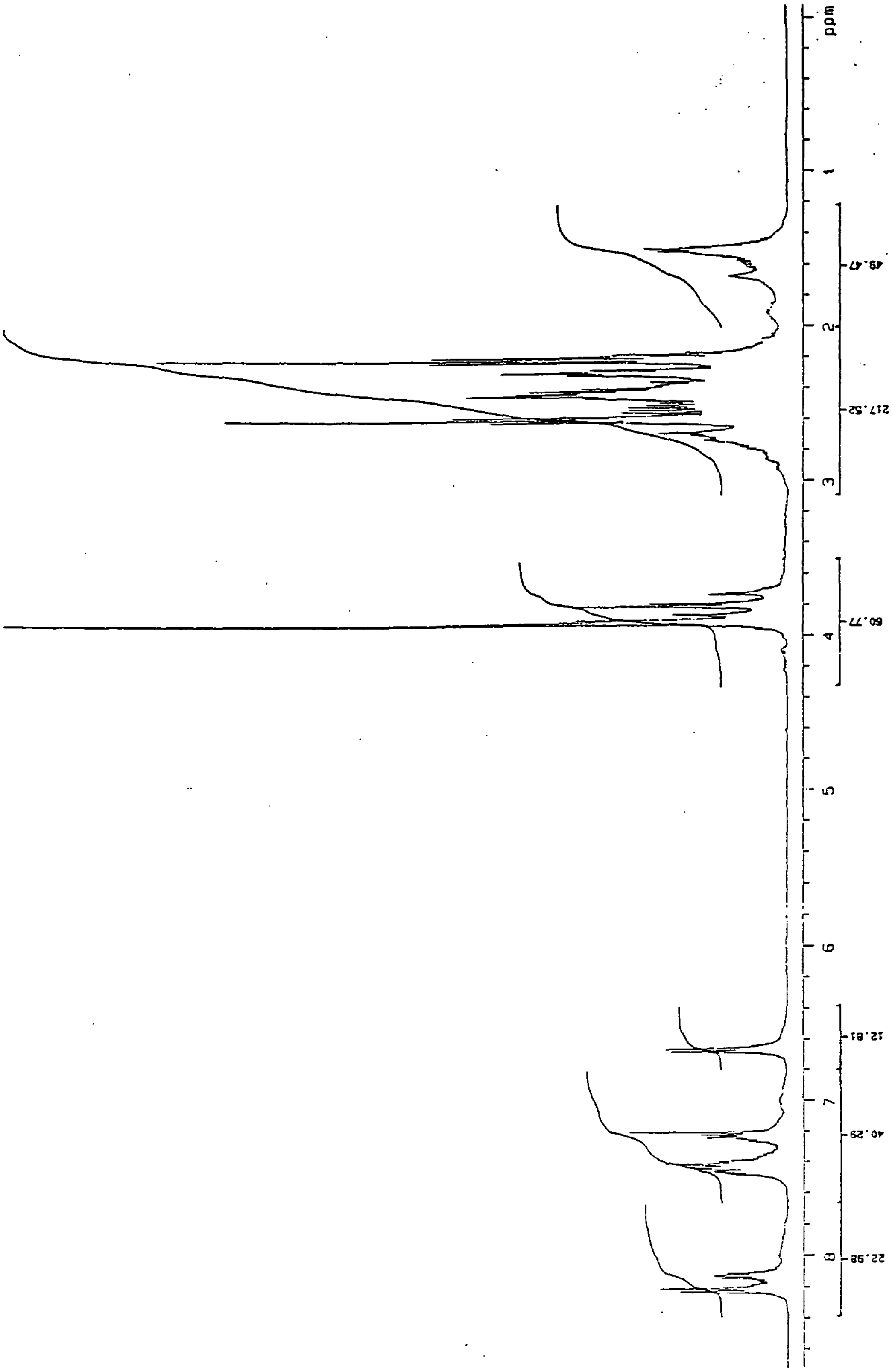
Appendix 1.34 FTIR spectrum of *UV-dendr-(NH$_2$)$_2$*.



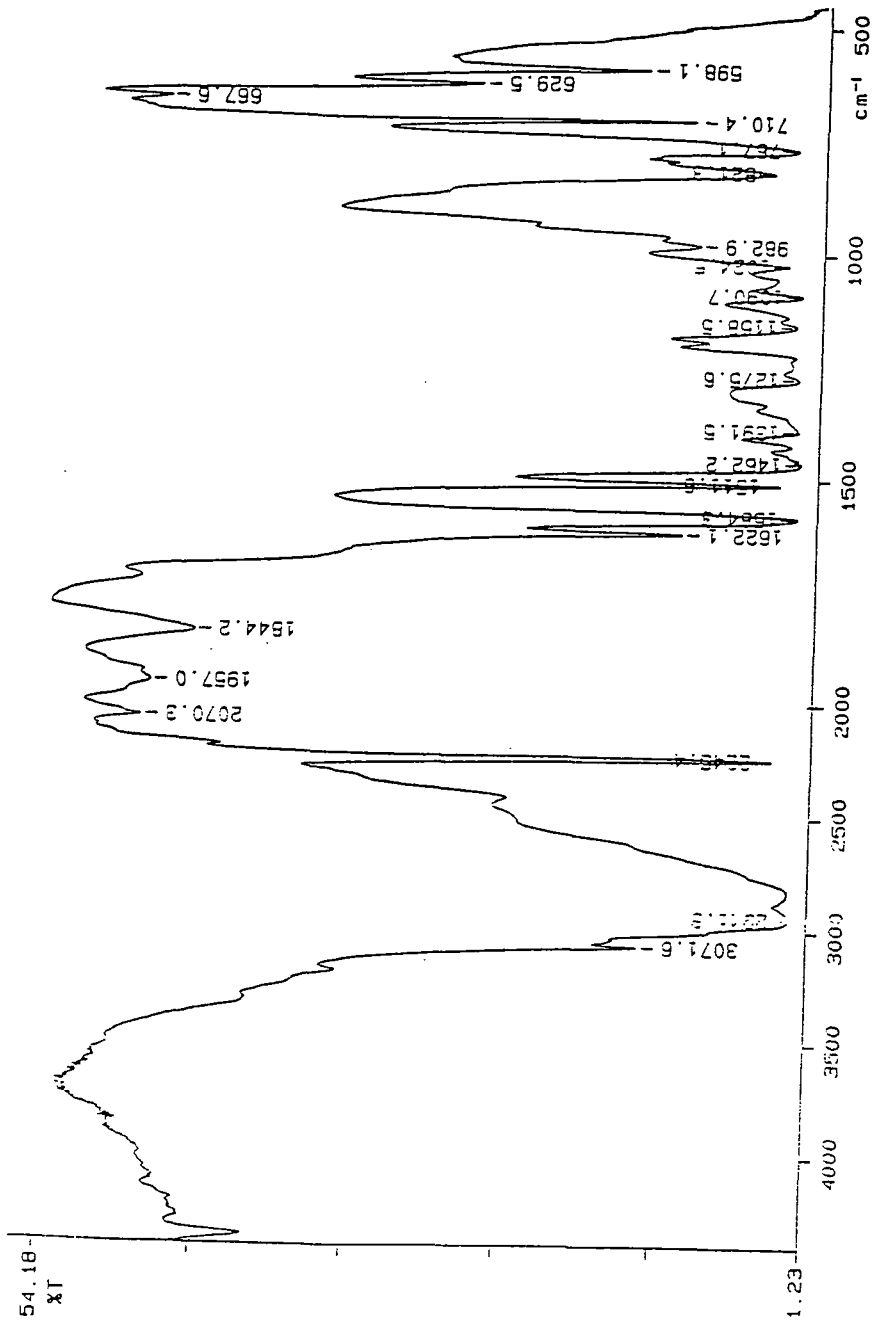
Appendix 1.35 ^{13}C n.m.r. (100MHz, CDCl$_3$) spectrum of *UV-dendr-(CN)$_4$*.



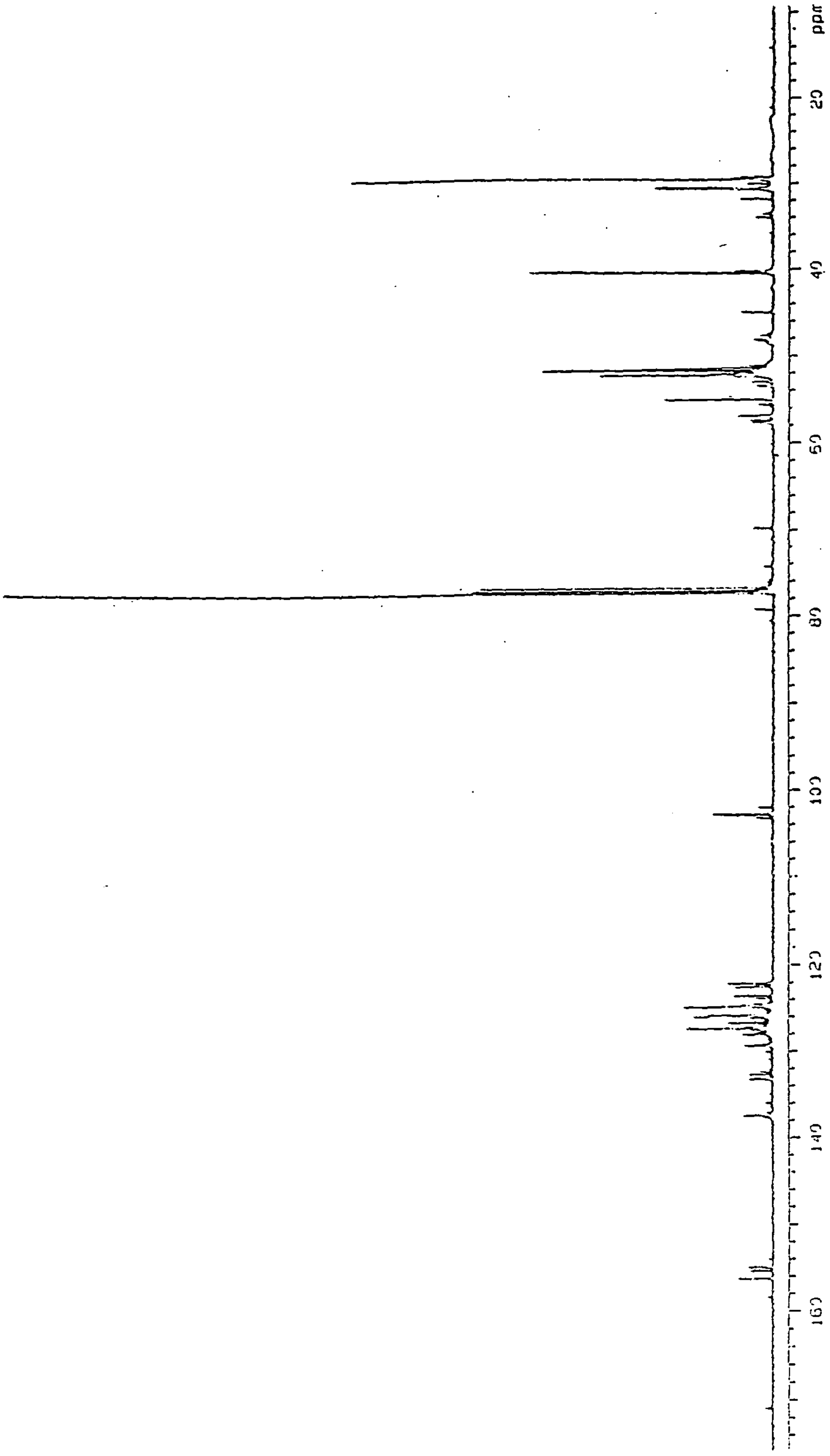
Appendix 1.36 ^{13}C n.m.r. (100MHz, CDCl$_3$) D.E.P.T. spectrum of *UV-dendr-(CN)*$_4$.



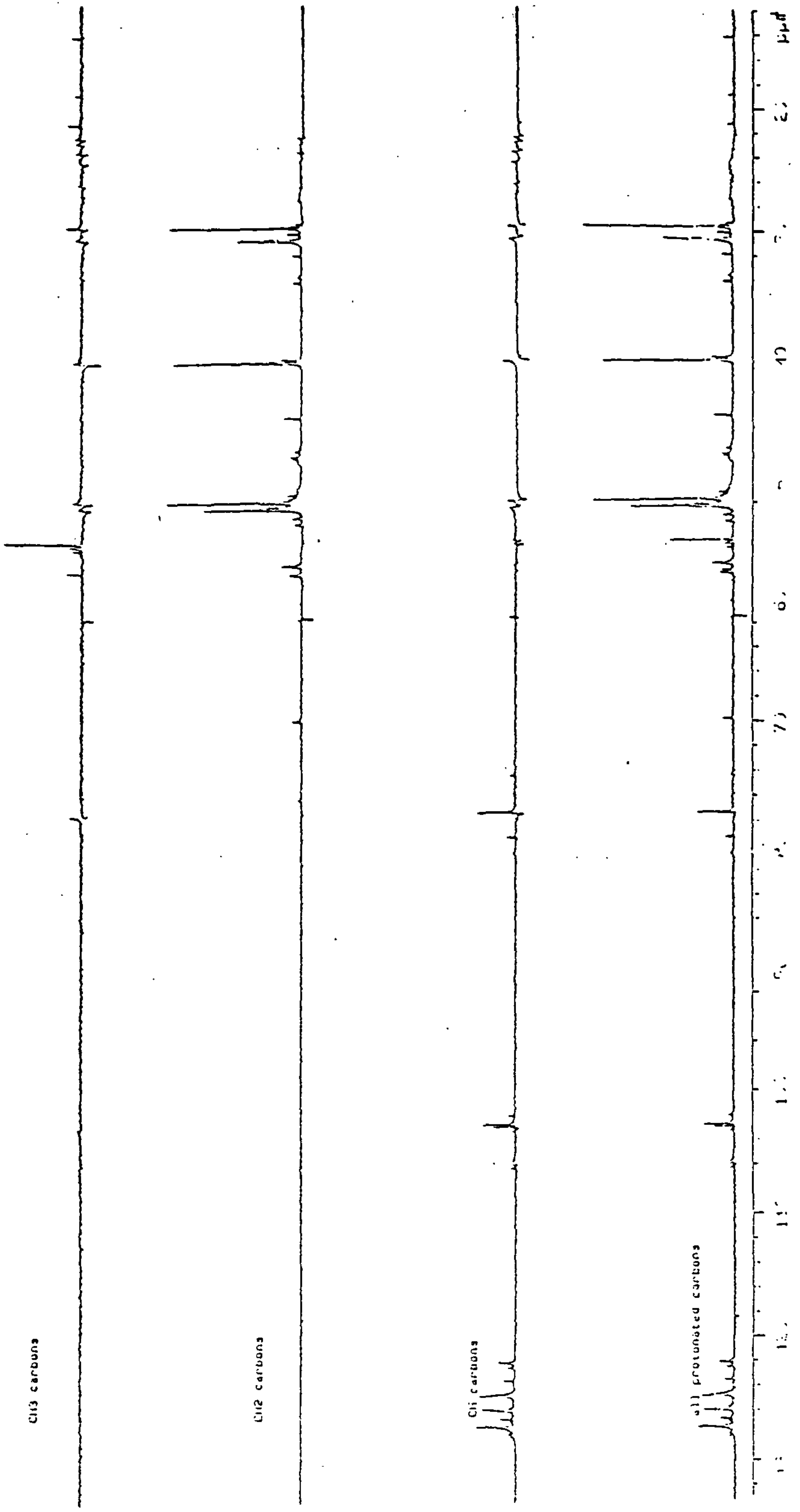
Appendix 1.37 ^{1}H n.m.r. (400MHz, $CDCl_3$) spectrum of *UV-dendr-(CN)$_4$*.



Appendix 1.38 FTIR spectrum of *UV-dendr-(CN)$_4$*.

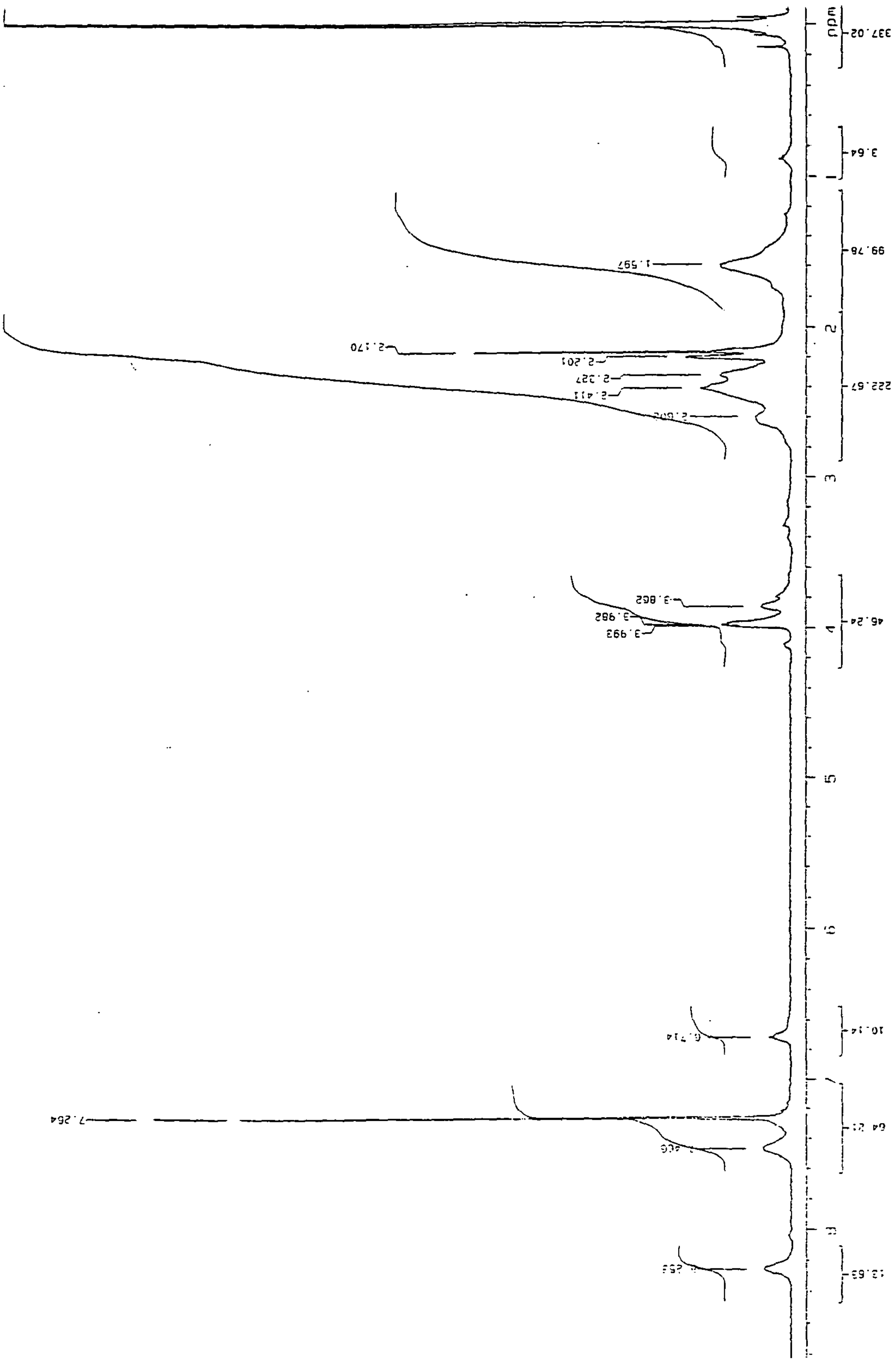


Appendix 1.39 ^{13}C n.m.r. (100MHz, CDCl$_3$) spectrum of *UV-dendr-(NH$_2$)$_4$*.

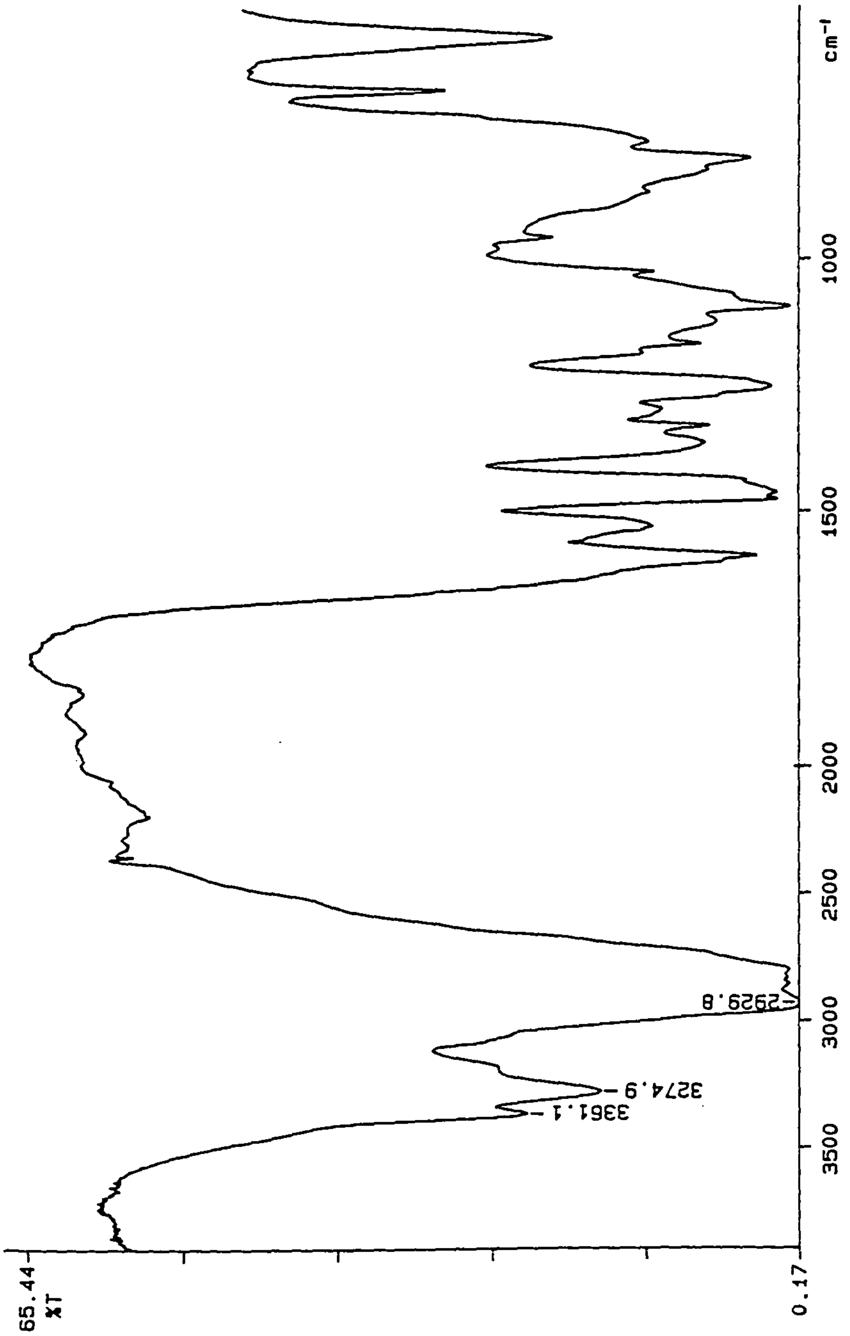


Appendix 1.40 ^{13}C n.m.r. (100MHz, CDCl$_3$) D.E.P.T. spectrum of *UV-dendr-*

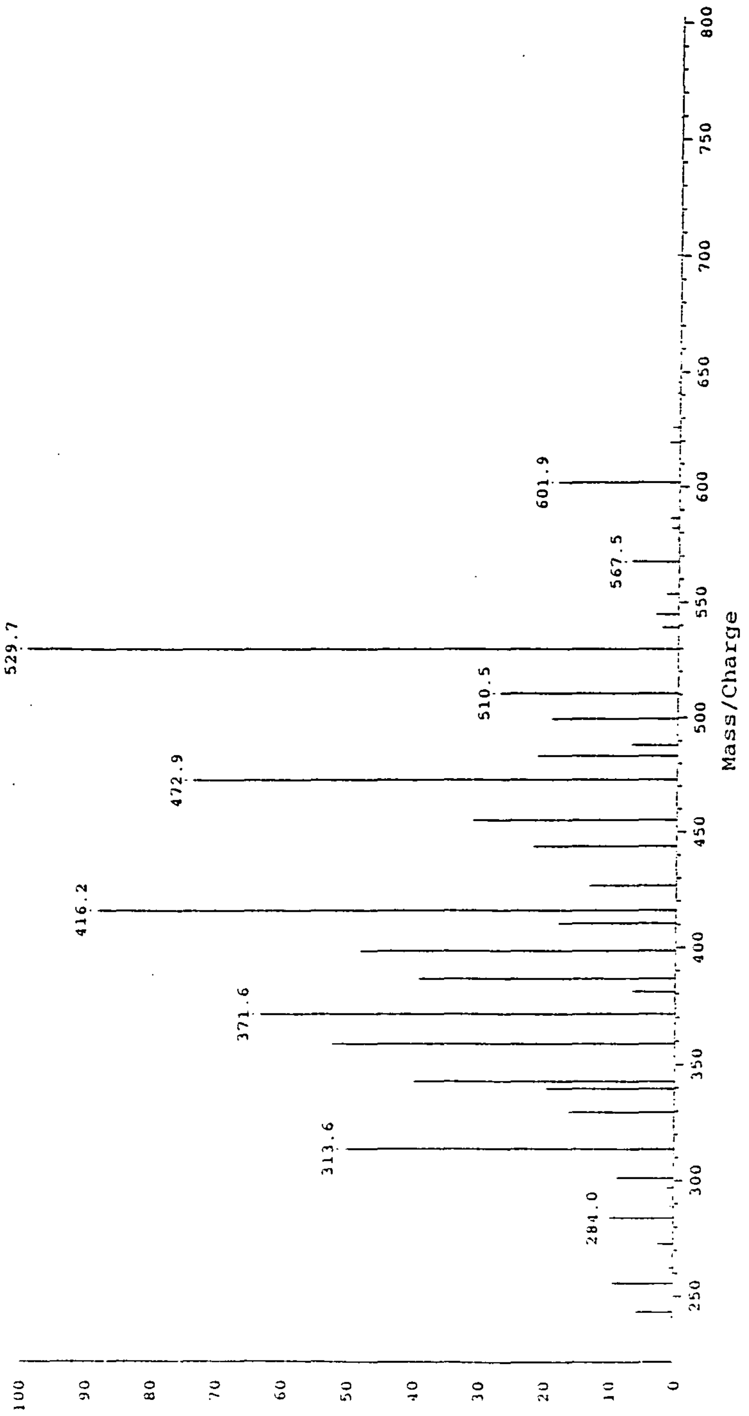
(NH$_2$)$_4$.



Appendix 1.41 ^{1}H n.m.r. (400MHz, $CDCl_3$) spectrum of *UV-dendr-(NH$_2$)$_4$*.



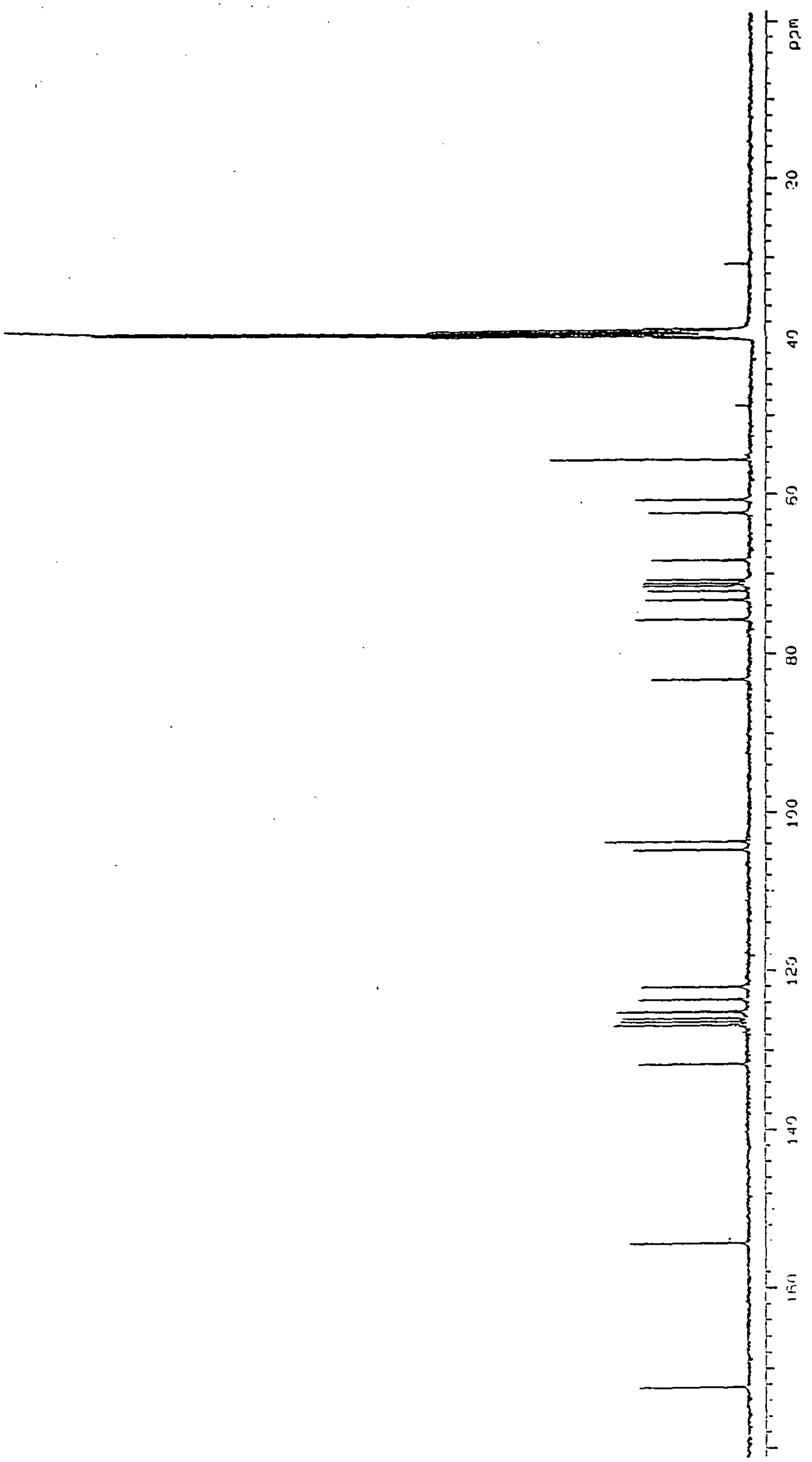
Appendix 1.42 FTIR spectrum of *UV-dendr-*$(NH_2)_4$.



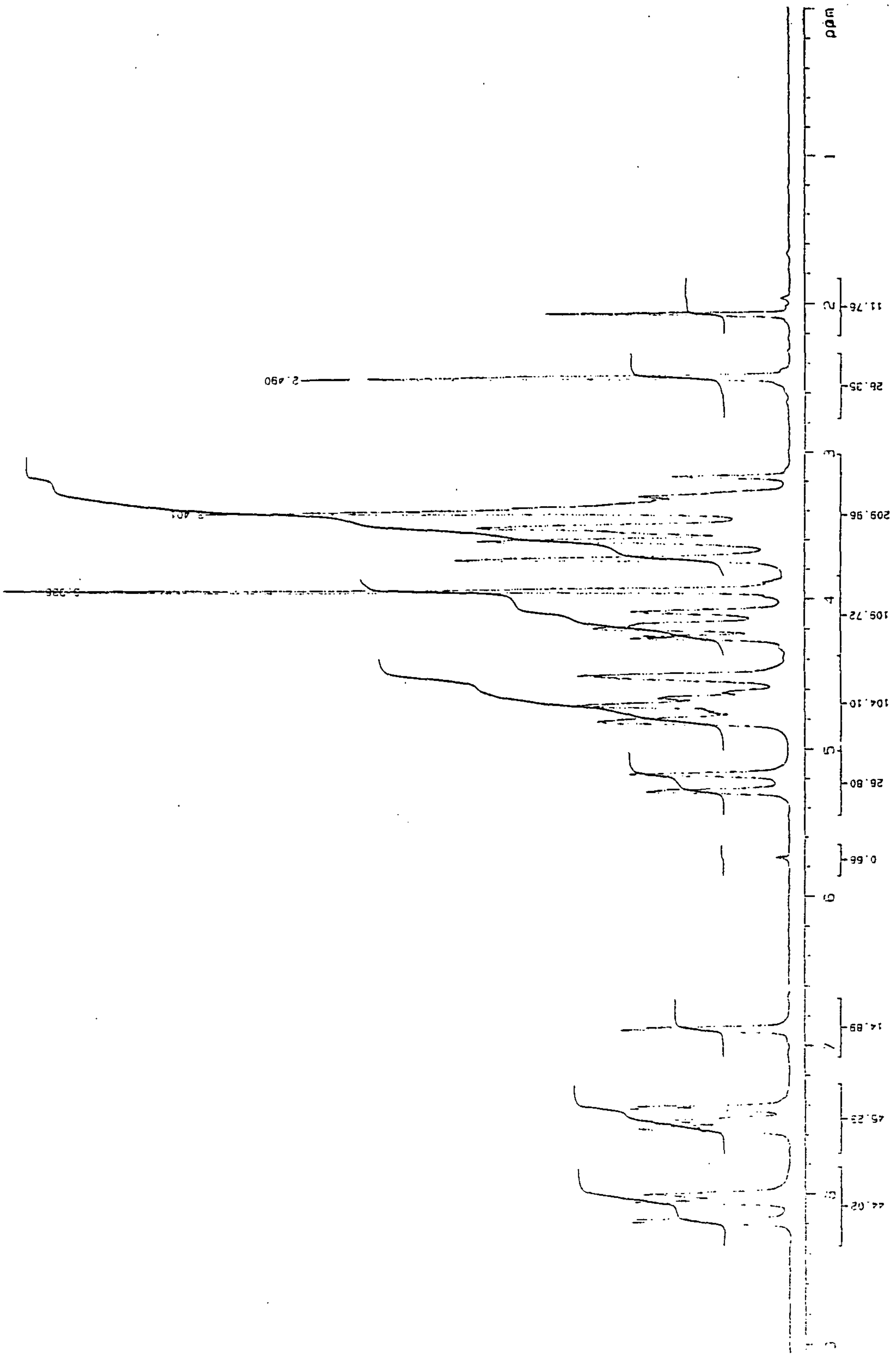
Appendix 1.43 MALDI-TOF Mass spectrum of *UV-dendr-(NH$_2$)$_4$*.

APPENDIX 2

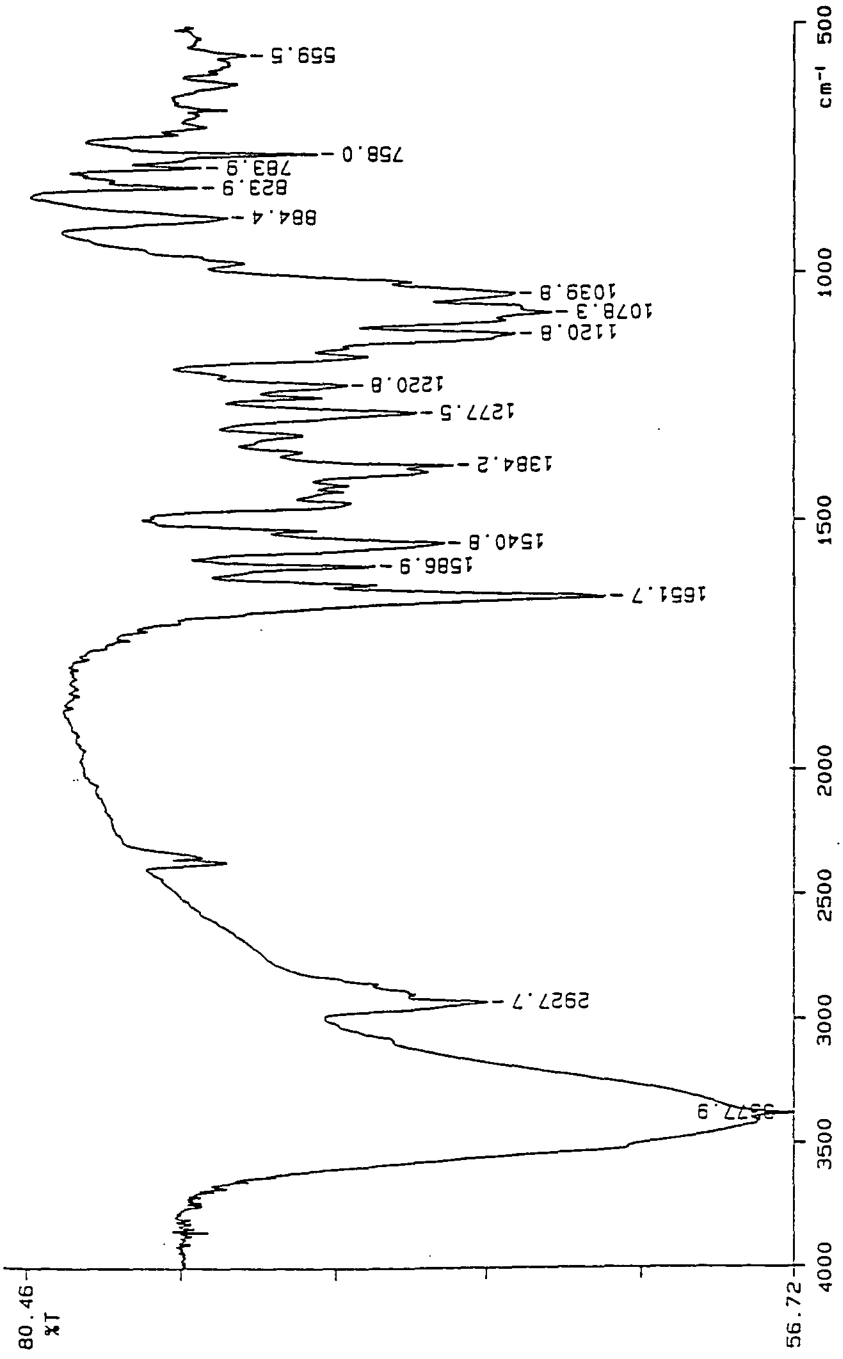
Characterisation Data for Chapter 3



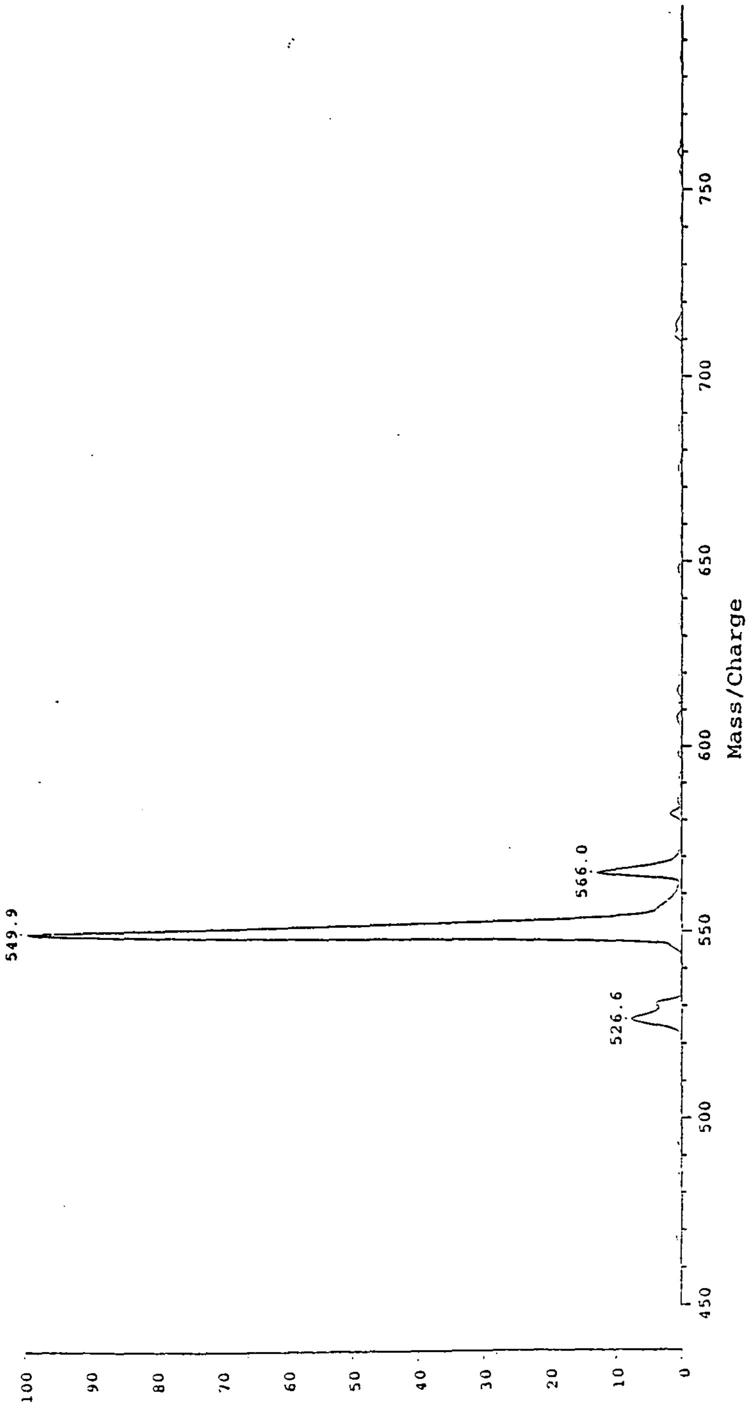
Appendix 2.1 ^{13}C n.m.r. (100MHz, d_6-dimethyl sulfoxide) spectrum of *UV-dendr-(carb)$_1$*.



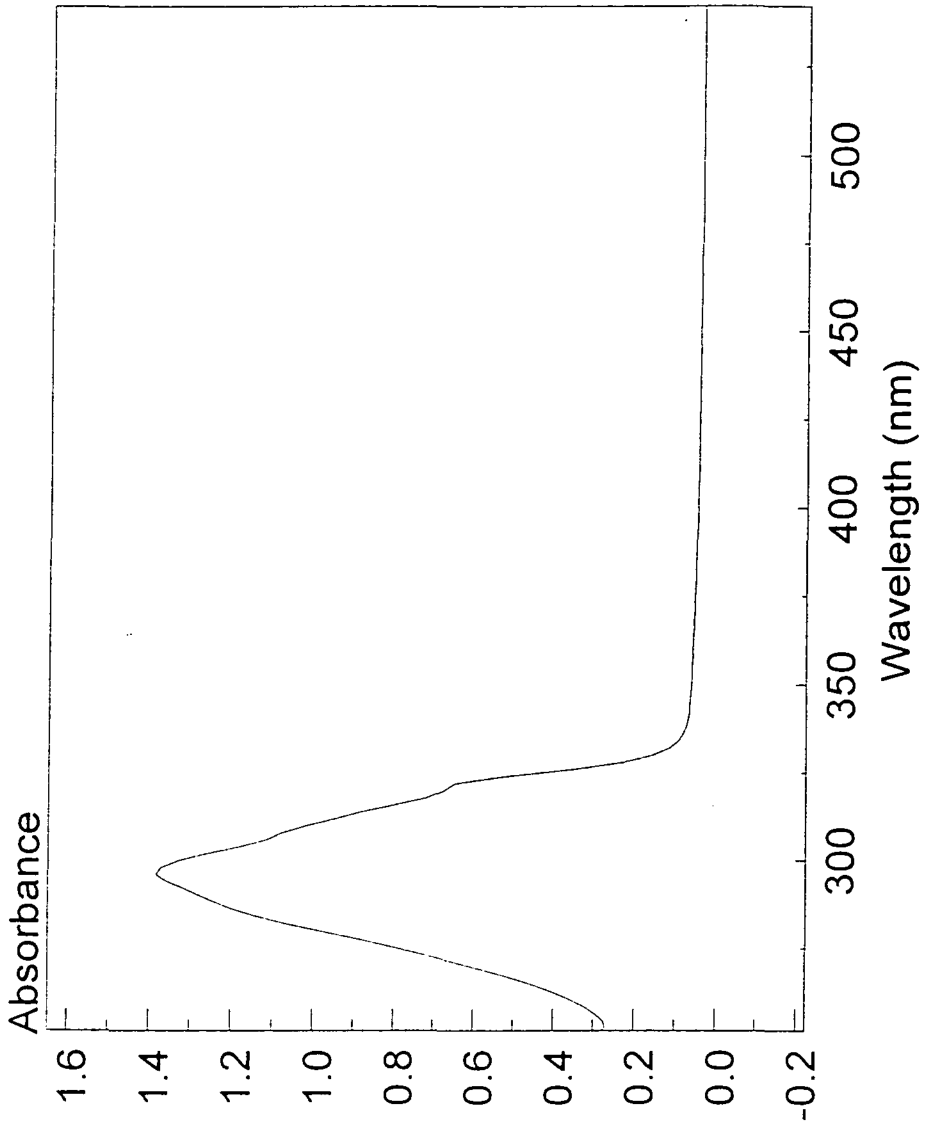
Appendix 2.2 ^{1}H n.m.r. (400MHz, d_6-dimethyl sulfoxide) spectrum of *UV-dendr-(carb)$_1$*.



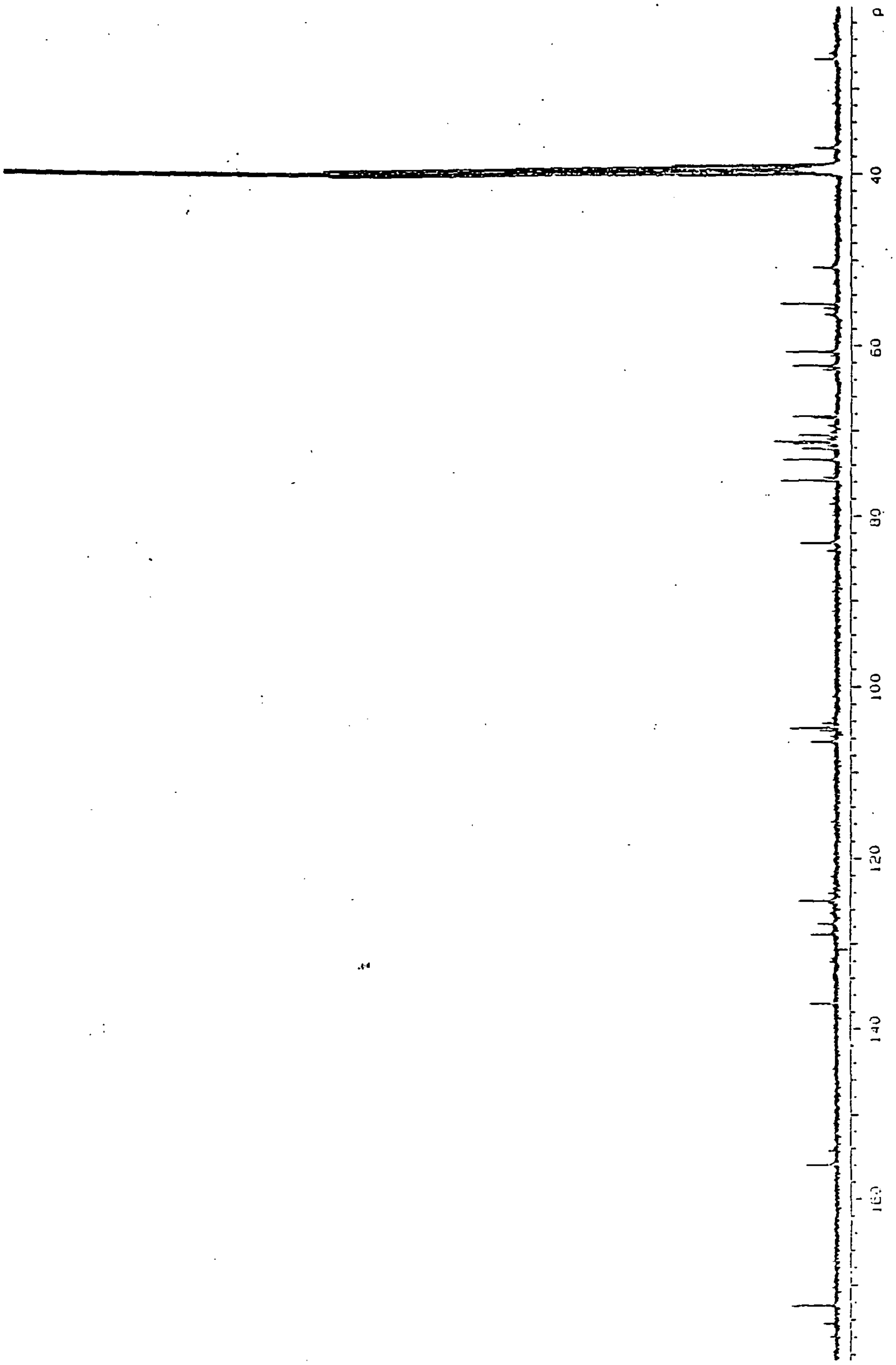
Appendix 2.3 FTIR spectrum of *UV-dendr-(carb)*$_1$.



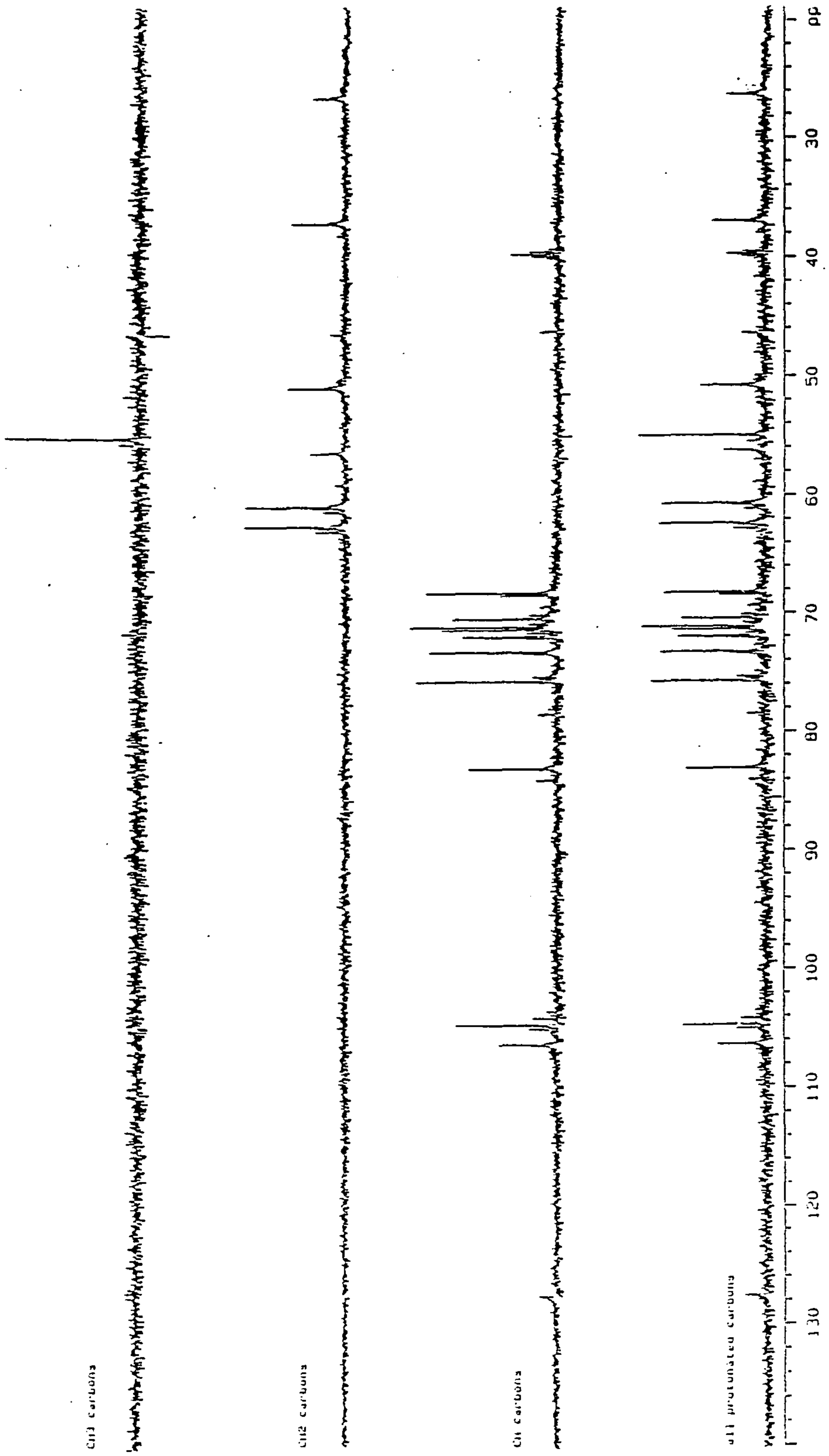
Appendix 2.4 MALDI-TOF Mass spectrum of *UV-dendr-(carb)$_I$*.



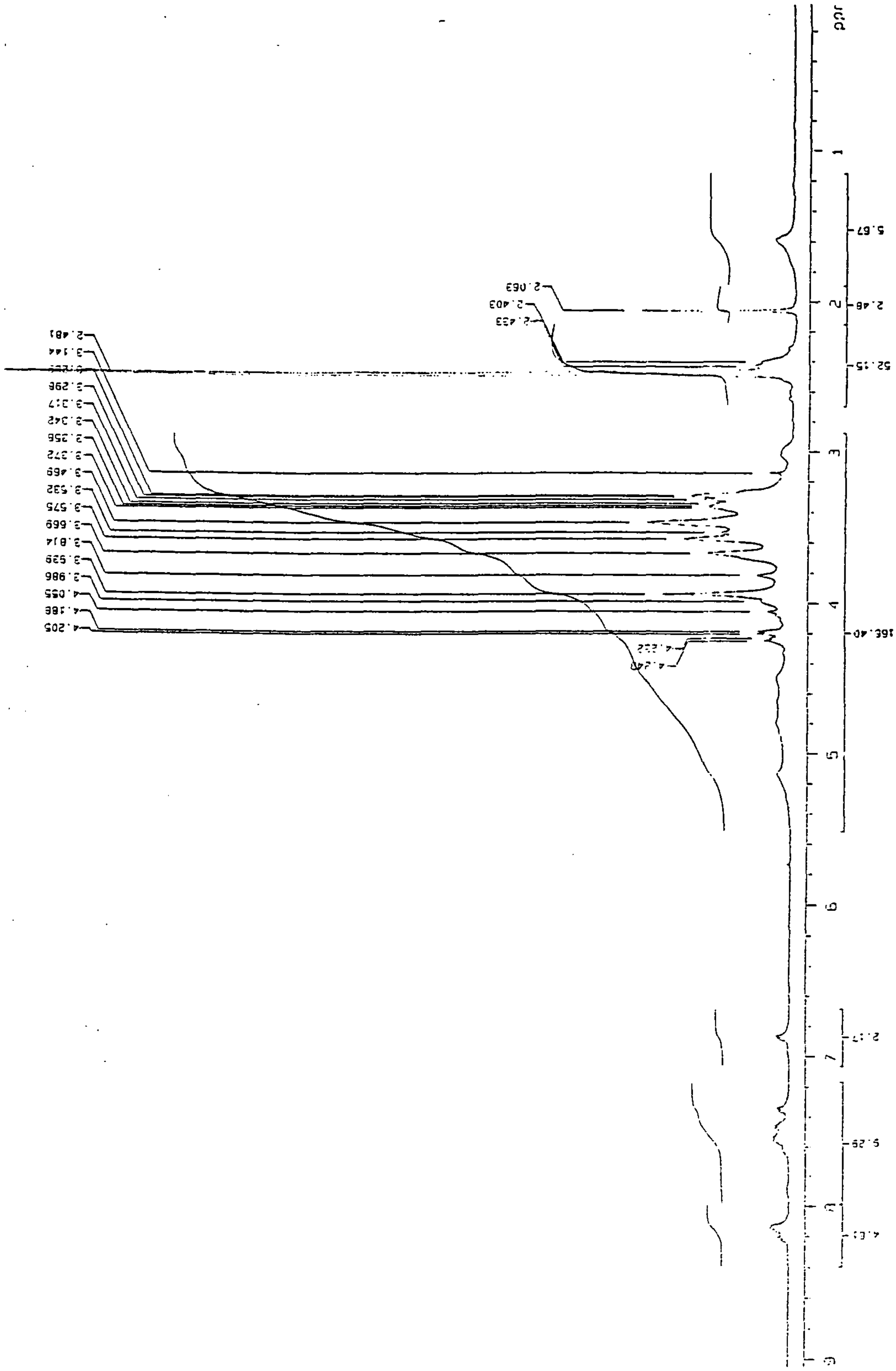
Appendix 2.5 UV spectrum of *UV-dendr-(carb)*$_1$.



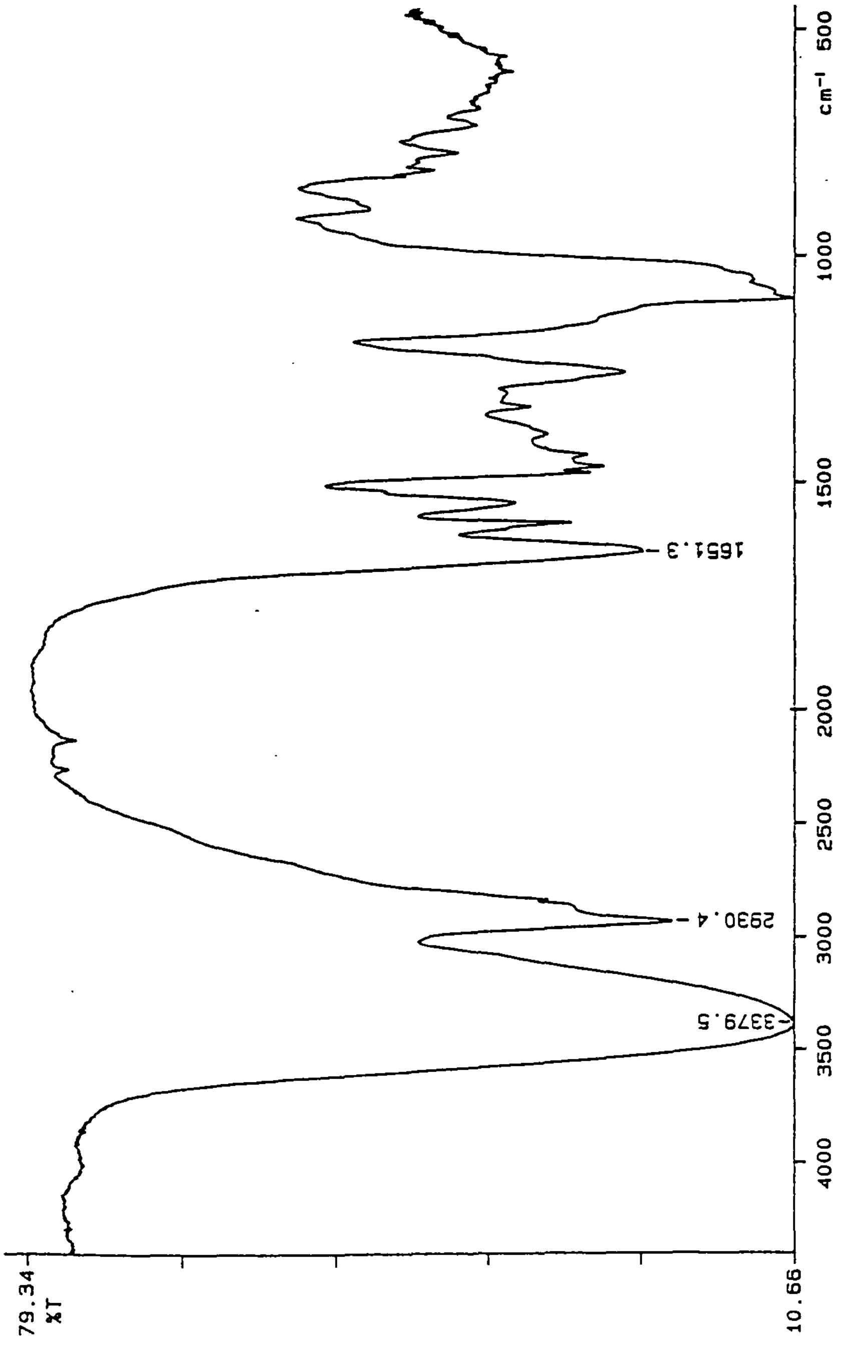
Appendix 2.6 ^{13}C n.m.r. (100MHz, d_6-dimethyl sulfoxide) spectrum of *UV-dendr-(carb)*$_2$.



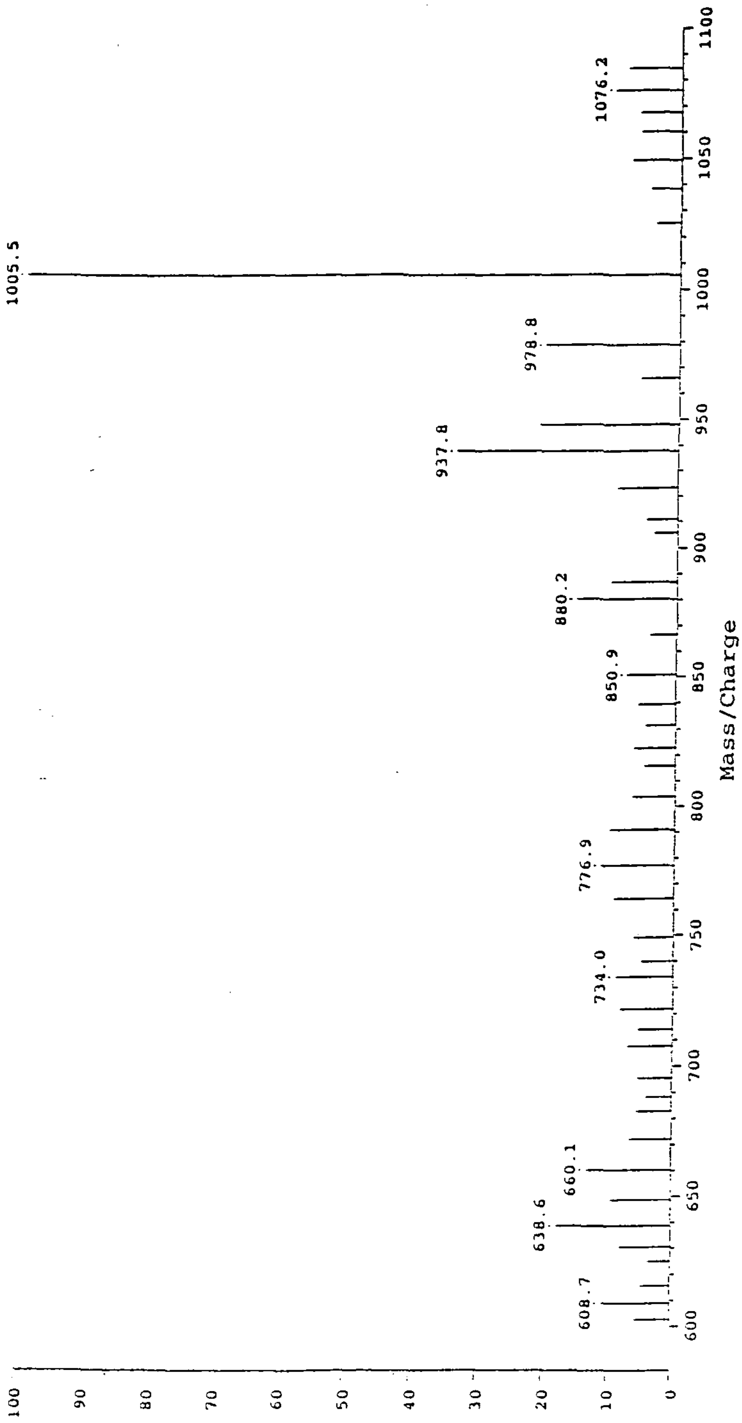
Appendix 2.7 ^{13}C n.m.r. (100MHz, d_6-dimethyl sulfoxide) D.E.P.T. spectrum of *UV-dendr-(carb)$_2$*.



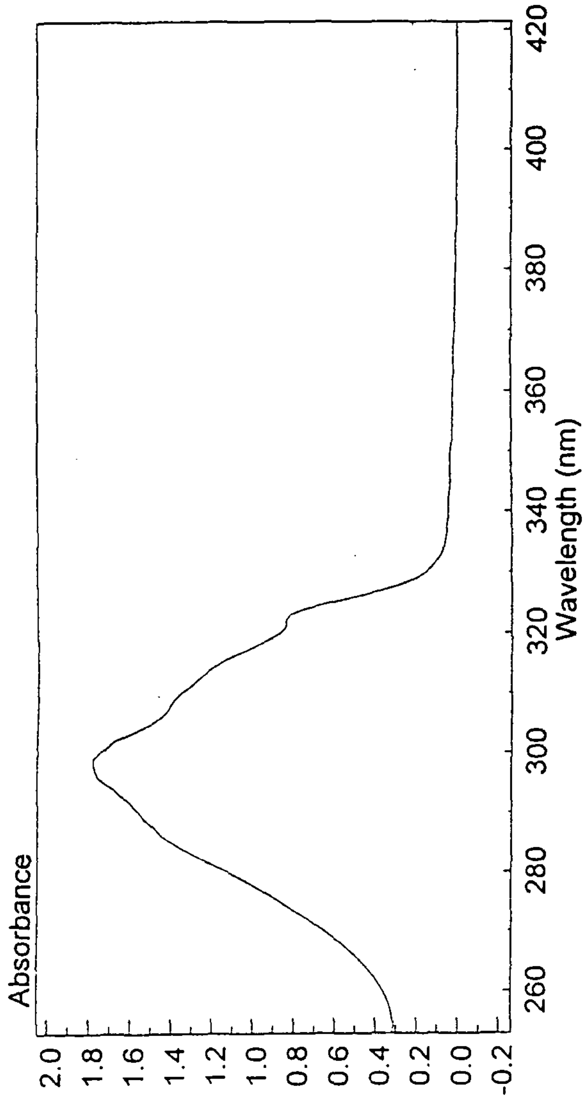
Appendix 2.8 ^{1}H n.m.r. (400MHz, d_6-dimethyl sulfoxide) spectrum of *UV-dendr-(carb)$_2$*.



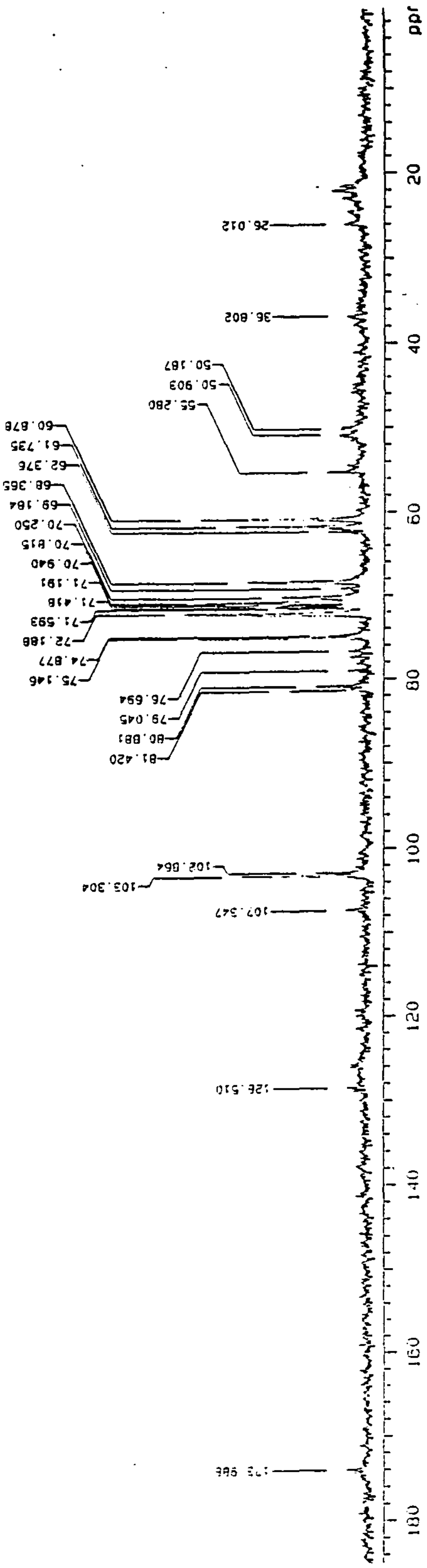
Appendix 2.9 FTIR spectrum of *UV-dendr-(carb)*$_2$.



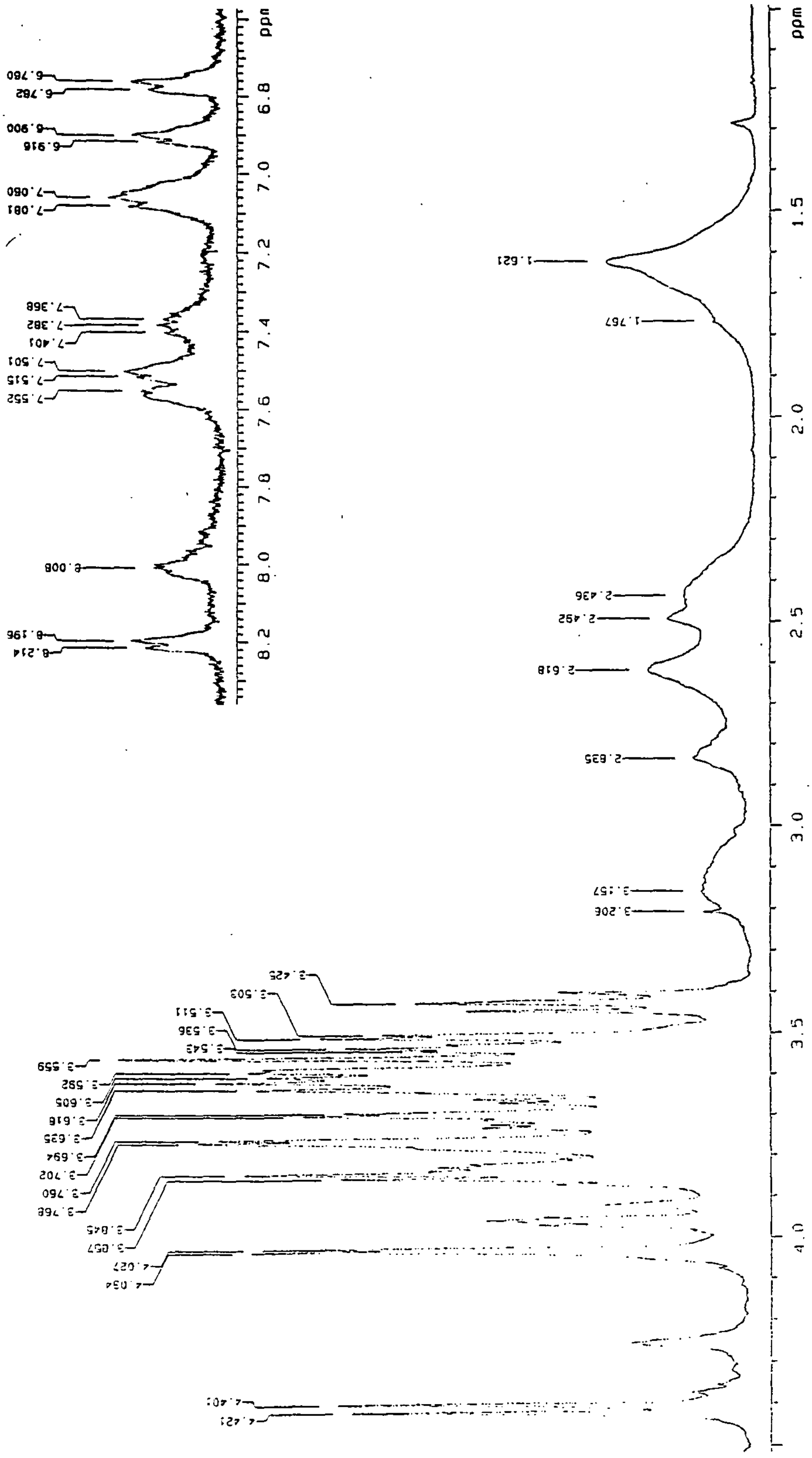
Appendix 2.10 MALDI-TOF Mass spectrum of *UV-dendr-(carb)*$_2$.



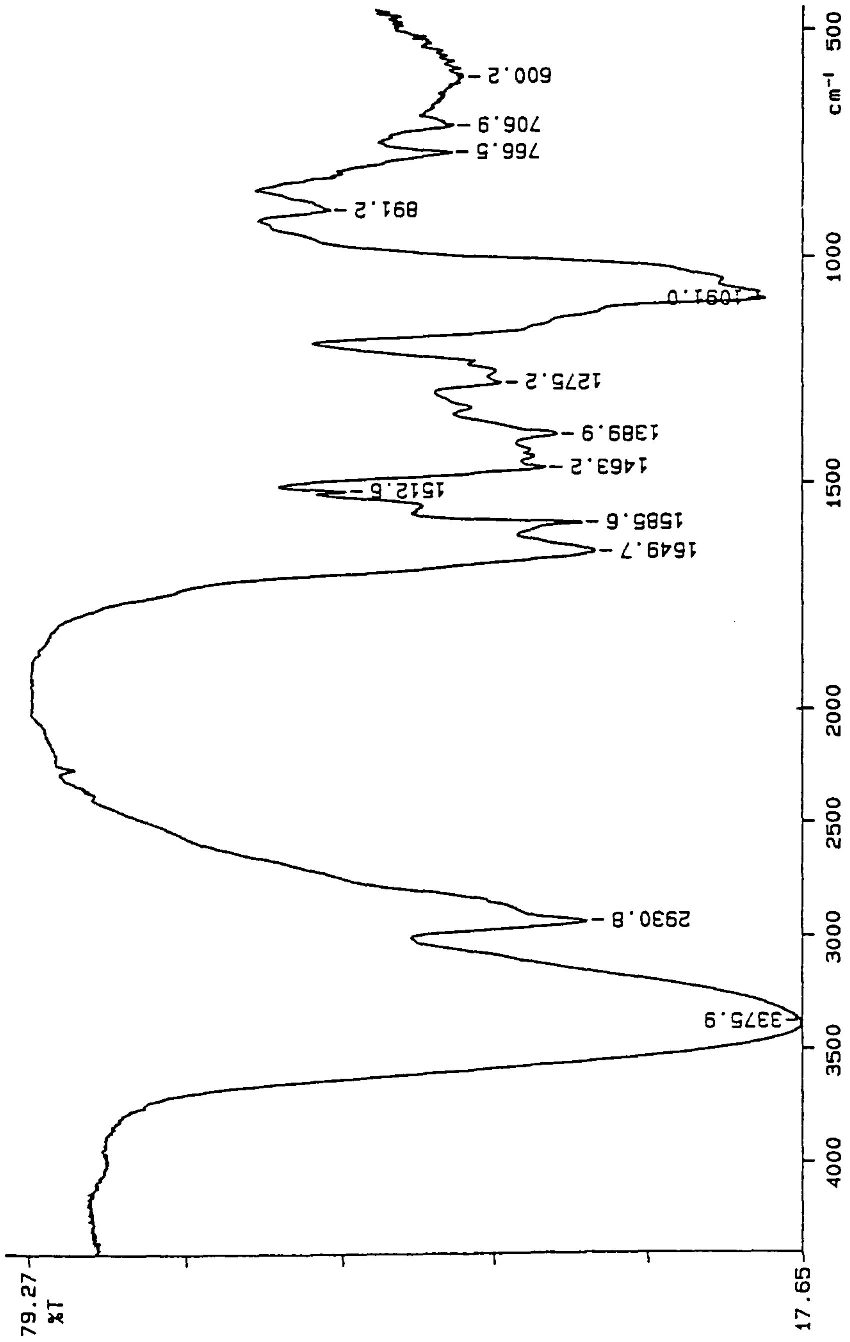
Appendix 2.11 UV spectrum of *UV-dendr-(carb)*$_2$.



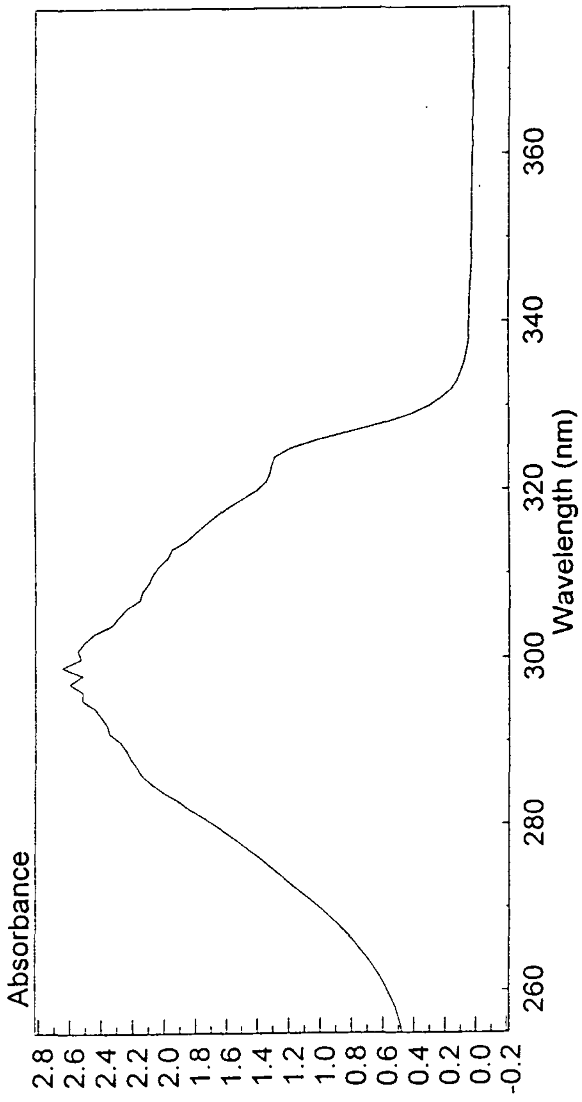
Appendix 2.12 ^{13}C n.m.r. (100MHz, d_6-dimethyl sulfoxide) spectrum of *UV-dendr-(carb)*$_4$.



Appendix 2.13 ^{1}H n.m.r. (400MHz, D_2O) spectrum of *UV-dendr-(carb)$_4$*.



Appendix 2.14 FTIR spectrum of *UV-dendr-(carb)*$_4$.



Appendix 2.15 UV spectrum of *UV-dendr-(carb)$_4$*.

APPENDIX 3

Instrumentation

Appendix 3 Instrumentation

^{13}C and ^{1}H n.m.r. spectra were recorded using a Varian VXR 400 spectrometer at 100 and 400MHz respectively.

FTIR spectra were recorded using a Perkin Elmer 1600 Series FTIR spectrometer.

UV spectra were recorded using a UNICAM UV/VIS spectrometer UV2.

MALDI-TOF mass spectra were recorded using a Kratos Kompact MALDI IV time of flight mass spectrometer.

Chemical and Electron impact ionisation mass spectra were recorded using a VG Analytical Model 7070E mass spectrometer.

Elemental analyses were performed using a Carlo-Elba-466 elemental analyser produced by Exeter Analytical Inc.

APPENDIX 4

Colloquia, Conferences and Courses Attended

Colloquia Attended

1994

October 5 Prof. N. L. Owen, Brigham Young University, Utah, USA
Determining Molecular Structure - the INADEQUATE NMR way

October 26 Dr. G. Rumbles, Imperial College
Real or Imaginary 3rd Order Non-Linear Optical Materials

November 2 Dr. P. G. Edwards, University of Wales, Cardiff
The Manipulation of Electronic and Structural Diversity in Metal Complexes - New Ligands

November 23 Dr. J. M. J. Williams, University of Loughborough
New Approaches to Asymmetric Catalysis

December 7 Prof. D. Briggs, ICI and University of Durham
Surface Mass Spectrometry

1995

January 25	Dr. D. A. Roberts, Zeneca Pharmaceuticals The Design and Synthesis of Inhibitors of the Renin-Angiotensin System
February 1	Dr. T. Cosgrove, Bristol University Polymers do it at Interfaces
March 1	Dr. M. Rosseinsky, Oxford University Fullerene Intercalation Chemistry
March 2	Prof. E. J. Meijer, Eindhoven University of Technology, Netherlands Dendrimers and Supramolecular Polymer Chemistry
April 26	Dr. M. Schroder, University of Edinburgh Redox-active Macrocyclic Complexes: Rings, Stacks and Liquid Crystals
April 27	Prof. D. J. Cole-Hamilton, University of St. Andrews Chemistry on the Nano Scale

May 3	Prof. E. W. Randall, Queen Mary and Westfield College New Perspectives in NMR Imaging
May 5	The Ingold Lecture - Prof. A. J. Kresge, University of Toronto, Canada Reactive Intermediates
May 9	Prof. R. Townsend, Unilever Exploratory Research Council Polymers for the Year 2000 – The Challenge Ahead
May 30	Prof. P. Calvert, University of Arizona, USA Freeforming: Chemical Methods for the Processing of Polymers, Ceramics and Composites
October 25	Dr. D. M. Davies, University of Northumbria Chemical Reactions in Organised Systems
November 17	Prof. D. Bergbreiter, Texas A&M, USA Design of Smart Catalysts, Substrates and Surfaces from Simple Polymers

November 22	Prof. I Soutar, Lancaster University A Water of Glass? Luminescence Studies of Water-Soluble Polymers

1996

January 10	Dr. W. Henderson, Waikato University, NZ Electrospray Mass Spectrometry - a New Sporting Technique
January 17	Prof. J. W. Emsley, Southampton University Liquid Crystals: More than Meets the Eye
January 31	Dr. J. Penfold, Rutherford Appleton Laboratory, Soft Soap and Surfaces
March 12	RSC Endowed Lecture - Prof. V. Balzani, Univ of Bologna Supramolecular Photochemistry
August 15	Prof. K. B. Wagener, University of Florida, USA Catalyst Selection and Kinetics in ADMET Polymerisation

October 22	Prof. B. J. Tighe, University of Aston Synthetic Polymers for Biomedical Application: Can we Meet Nature's Challenge?
October 23	Prof. H. Ringsdorf (Perkin Centenary Lecture), Johannes Gutenberg-Universitat, Mainz, Germany Function Based on Organisation
November 12	Prof. R. J. Young, Manchester Materials Centre, UMIST New Materials – Fact or Fantasy?
November 13	Dr. G. Resnati, Milan Perfluorinated Oxaziridines: Mild Yet Powerful Oxidising Agents
November 20	Prof. J. Earnshaw, Deptartment of Physics, Belfast Surface Light Scattering: Ripples and Relaxation
December 11	Dr. C. Richards, Cardiff University Sterochemical Games with Metallocenes

1997

January 16	Dr. S. Brooker, University of Otago, NZ	Macrocycles: Exciting yet Controlled Thiolate Coordination Chemistry
January 22	Dr. N. Cooley, BP Chemicals, Sunbury	Synthesis and Properties of Alternating Polyketones
January 29	Dr. J. Clarke, UMIST	What can we learn about polymers and biopolymers from computer-generated nanosecond movie-clips?
February 12	Dr. G. Boons, University of Birmingham	New Developments in Carbohydrate Chemistry
February 26	Dr. A. Ryan, UMIST	Making Hairpins from Rings and Chains
May 7	Prof. M. Harrington, Caltech, Pasadena, USA	Polymers both Enable and Limit the Discovery of Protein Alterations in Studies Ranging from Gene Regulation to Mad Cow Disease

May 20	Prof. J. Jin, President, Korean Chemical Society Poly PPV and its Derivatives – Synthesis, Structure and Properties
June 13	Prof. Dr. S. Kobayashi, Kyoto University, Japan Synthesis of Polyesters via Enzymatic Polymerisation

Conferences and Courses Attended

1995

January 10	IRC Polymer Physics Introduction Course, University of Leeds
January 12	IRC Polymer Engineering Introduction Course, University of Bradford
July 10-14	International Symposium on Olefin Metathesis (ISOM 11), Durham
Sept. 27-28	IRC Industrial Club Seminar, Durham

1996

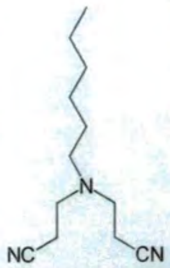
April 10-12	Aspects of Contemporary Polymer Science, MACRO Group UK Family Meeting, Manchester
June 3	The Melville Lectureship, Department of Chemistry, University of Cambridge

1997

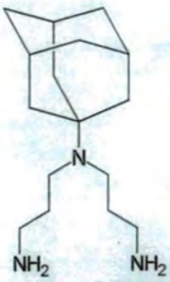
April 2-4	MACRO Group UK Spring Meeting for Younger Researchers, Leeds

Synthesis and Properties of some Carbohydrate-Terminated Dendrimer Wedges

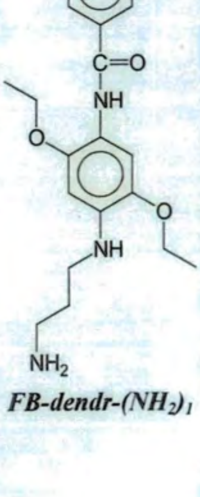
Richard L. Ainsworth



Hex-dendr-$(CN)_2$



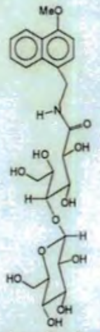
Ad-dendr-$(NH_2)_2$



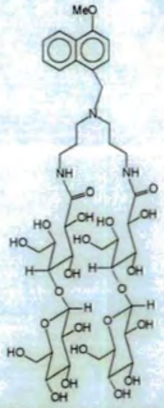
FB-dendr-$(NH_2)_1$

Synthesis and Properties of some Carbohydrate-Terminated Dendrimer Wedges

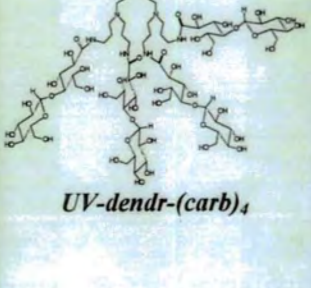
Richard L. Ainsworth



UV-dendr-(carb)$_1$



UV-dendr-(carb)$_2$



UV-dendr-(carb)$_4$