

AD-A231 256

NEW AND IMPROVED METHODS OF PRODUCTION

OF

ENERGY RICH MATERIALS

FIRST YEAR REPORT

J. CHRISTCEI

ROAL HOLLOWAY AND BEDFORD NEW COLLEGE

EXHIBITION STATEMENT

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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE NOV 90	3. REPORT TYPE AND DATES COVERED 1ST YEAR REPORT	
4. TITLE AND SUBTITLE NEW AND IMPROVED METHODS OF PRODUCTION OF ENERGY RICH MATERIALS 1ST YEAR REPORT			5. FUNDING NUMBERS	
6. AUTHOR(S) MR. J. CHRISTOFI				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) ROYAL HOLLOWAY AND BEDFORD NEW COLLEGE			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) COMMANDING OFFICER NAVAL WEAPONS SUPPORT CENTER ORDNANCE ENGINEERING DEPT. (CODE 50C) CRANE, IN 47522-5050			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES BEST AVAILABLE COPY. SOME INFORMATION IS ILLEGIBLE. I0112/02A				
12a. DISTRIBUTION/AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) This report deals with the synthesis of organic nitro compounds. Some examples are: Synthesis of 3- and 1-nitrocarbazole; 1,6- and 3,6-dinitrocarbazole; 1,3,6,8-tetranitrocarbazole; 2-nitrodibenzothiophene; 2,8-dinitrodibenzothiophene; 3-nitrodibenzothiophene; 3,7-dinitrodibenzothiophene; dibenzothiophene-5-oxide; 3-nitrodibenzothiophene-5-oxide; 3,7-dinitro-dibenzothiophene-5-oxide; dibenzothiophene-5,5-dioxide; 3-nitrodibenzothiophene-5,5-dioxide; 3,7-dinitrodibenzothiophene-5,5-dioxide; and 2-nitrodibenzothiophene-5,5-dioxide. Nitrations of some of the above are also described.				
14. SUBJECT TERMS (25) PROPELLANTS, SYNTHESIS (CHEMISTRY)			15. NUMBER OF PAGES	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED			16. PRICE CODE	
18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED		19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED		20. LIMITATION OF ABSTRACT UNLIMITED

NSN 7540-01-280-5500

91 1 29 014

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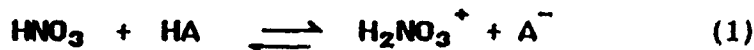
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1. INTRODUCTION

1.1 Electrophilic Aromatic Nitration by the Nitronium Ion¹

The nitration of aromatic compounds can be achieved in a variety of media. Mixed acid nitration is the most common type used in this work; however, nitric acid may also be used neat, in organic solutions or in aqueous media. Nitration through the nitronium ion, NO_2^+ , was first proposed by Euler² in 1903, but the existence of the ion was not conclusively demonstrated until 1946³. The kinetics of many different nitrations in various media have been studied extensively. Ingold showed that the rate expression for nitration took different forms under different reaction conditions, and yet all of the cases studied proceeded through the intermediate nitronium ion. The Ingold and Hughes mechanism^{3,4,5} of electrophilic aromatic nitration consists of four steps:-



The first two steps involve the acid catalysed formation of the nitronium ion, the reactive electrophile, from nitric acid. The nitronium ion then reacts with the aromatic to give the Wheland intermediate⁶ (later called the sigma-complex by Brown⁷).

Deprotonation of the Wheland intermediate completes the nitration by regenerating the aromaticity of the system. The acid catalyst is also regenerated in the last step.

It is important to remember when considering the reaction of nitronium ion with aromatics, that the nitronium ion is a polarisable electrophile. Hence, whereas linear nitronium ion does not contain an empty bonding molecular orbital, a gradual

displacement of a pi-electron pair to the more electronegative oxygen atom takes place when the nitronium ion approaches the aromatic substrate (facilitated by attraction of the cation by the nucleophilic nature of the aromatic).

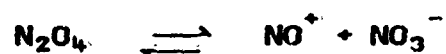
The Ingold mechanism can account well for observed substituent effects as long as step 3 (above) is the product determining stage. Electron-donating substituents on a benzene nucleus increase its reactivity and electron-withdrawing ones decrease it. Also, electron-donating groups direct the incoming nitro group to the ortho(o-) and para(p-) positions in relation to the substituent, while electron-withdrawing groups, with the exception of the halogens, lead to meta(m-) nitration. This is explained by the fact that electron-donating groups increase the electron density at o- and p- positions (as well as the ipso-position), and electron-withdrawing substituents decrease electron density at the o- and p- positions whereas the m- position is not much affected. The anomalous behaviour of the halogens arises from their combination of inductive electron withdrawal and mesomeric electron release.

1.2 Effect of Nitrous Acid

An important process which must be considered in any discussion of mixed acid nitration is that of nitrous acid catalysed nitration. Nitrous acid species present in nitric acid can produce both anticatalytic and catalytic effects on nitration, depending on the reaction conditions and the compound being nitrated. Thus, in general, the less reactive aromatics suffer an anti-catalytic effect, whereas phenols, amines and the polynuclear aromatics such as naphthalene undergo a marked acceleration in nitration. Clearly this catalytic effect will be important in the nitration of

carbazole and dibenzothiophene.

In aqueous sulphuric or perchloric acid solutions of less than 50% concentration, nitrous acid is present in its molecular form (with some N_2O_3 also present). In acid solutions above 60-65% concentration it is present as nitrosonium ions. In an excess of nitric acid, nitrous acid exists essentially as dinitrogen tetroxide which is nearly completely ionised,



with some NO_2^+ and NO_2^- also present. However, in organic solvent-nitric acid systems N_2O_4 is little ionised.

The retarding effect of nitrous acid on nitronium ion nitrations was interpreted by Ingold^{5,8} by consideration of its behaviour in the involved systems. In strong aqueous nitric acid systems added nitrous acid, ionised to NO^+ and NO_3^- , increases the NO_3^- ion concentration at the expense of molecular HNO_3 . Hence, during nitration the nitrate ions formed can deprotonate the nitracidium ion, H_2NO_3^+ , the precursor of the nitronium ion, thus leading to retardation of the reaction. At higher concentrations of nitrous acid, and some water present, stronger anticatalysis can be explained by nitrous acid also forming N_2O_3 ,



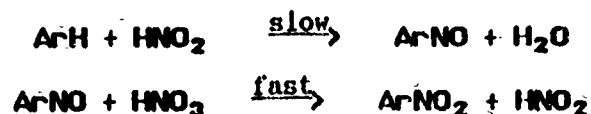
which then ionises to give nitrite ions,



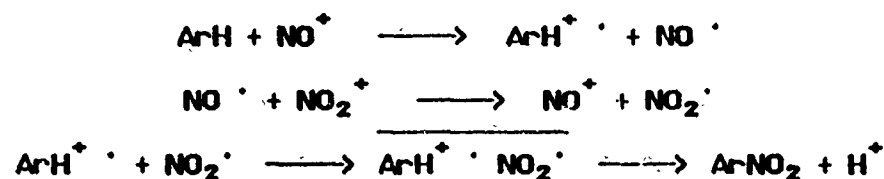
The nitrite ion, being a stronger base than the nitrate ion, deprotonates the nitracidium ion more efficiently and thus retards nitronium ion nitration.

Although nitration of most aromatic hydrocarbons with nitric acid are retarded by nitrous acid, nitration of phenols and anilines has been found to be strongly catalysed by it. Ingold suggested⁹

that the kinetics of the catalysed process indicate initial C-nitrosation followed by rapid oxidation of the nitroso compound by the nitric acid, reforming the nitrous acid:



The reactive nitrosating agent, NO^+ , can be formed from HNO_2 through H_2NO_2^+ or by ionisation of N_2O_4 or N_2O_3 . Later work by Clemens, Ridd and Sandall¹⁰ showed that this explanation was incorrect. These workers nitrated mesitylene in the presence and absence of nitrous acid catalysis and showed that the catalysed process involved the oxidation of the organic substrate by NO^+ followed by formation of the radical pair $\text{ArH}^+ \cdot \text{NO}_2 \cdot$ by diffusion together of the components:-



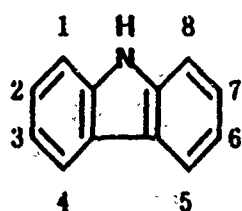
A very similar process was also shown¹¹ to occur with aromatic amines such as N,N - dimethyl aniline.

Reactive aromatics such as phenols and anilines show catalysis of their nitration by nitrous acid because firstly they are highly reactive towards electrophilic reagents in general. Thus to carry out mononitrations relatively free of dinitration it is often useful to choose conditions which render the nitronium ion not easily available, allowing the less reactive, but more plentiful carriers of the nitrosonium ion to react with the aromatics. This nitrous acid catalysis can be eliminated by removing the nitrous acid (with urea or other traps) and increasing the nitric acid concentration sufficiently to make nitronium ion freely available. If the aromatic material is very easily reduced, the possibility of

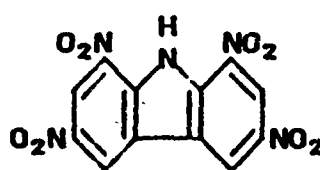
permanent nitrous acid removal is doubtful.

1.3 Nitration of carbazole

Carbazole is a reactive polycyclic aromatic and can be nitrated to tetranitrocarbazole using mixed $\text{H}_2\text{SO}_4/\text{HNO}_3$ acids nitration. Carbazole is first sulphonated by addition to sulphuric acid, and then nitrodesulphonated by the addition of nitric acid. The major product from this reaction is 1,3,6,8-TNC. Previous workers have shown^{12,13,14} that the major impurities formed in this reaction are penta-, and possibly hexa-, nitrocarbazole stemming from overnitration of carbazole, and also sulphonic acid derivatives of carbazole from the initial sulphonation. 1,3,6,8-TNC is currently used in pyrotechnic compositions, but traces of these impurities produce erratic results. This project is concerned primarily with the production of 1,3,6,8-TNC in a high state of purity and in high yield. This result can either be achieved using improved purification techniques on the crude product from this sulphonation/nitrodesulphonation, or by finding a new and cleaner route of synthesis.



CARBAZOLE

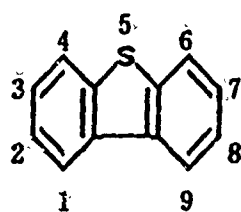


1,3,6,8-TETRANITROCARBAZOLE

As a first step, the various isomeric mono- and dinitrocarbazoles which are possible impurities were synthesised and also the nature of the sulphonic acid impurities was investigated. The literature¹³ purification process was quite lengthy and a new synthetic approach was attempted.

1.4 Nitration of Dibenzothiophene

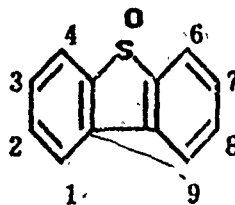
Dibenzothiophene, like carbazole, is a reactive polycyclic aromatic. Dibenzothiophene and carbazole are iso- π -electronic, i.e. their molecules have the same number of π -electrons, with approximately the same geometrical arrangement and bound about equally tightly, in a planar conjugated system. Dibenzothiophene is commonly numbered:



The sulphur atom in dibenzothiophene has one lone pair available for delocalisation into the aromatic system; the other lone pair being sp^2 hybridised and hence in the same plane as the ring. Consequently, like the amine group in carbazole which has one lone pair available for delocalisation, the sulphur atom acts as an electron donating group and directs electrophilic substituents to positions 'ortho' and 'para' to itself. Hence, nitration of dibenzothiophene leads mainly to 2-nitro²⁰, and 2,8-dinitro-dibenzothiophene²⁰.

The aim of this project is to further nitrate dibenzothiophene to 2,4,8-trinitro and/or 2,4,6,8-tetranitrodibenzothiophene. This task is complicated by the fact that the sulphur atom of the dibenzothiophene molecule is prone to oxidation, and the acids used in mixed acid nitrations are usually highly oxidative. Carefully controlled conditions are required to achieve further nitration without oxidation.

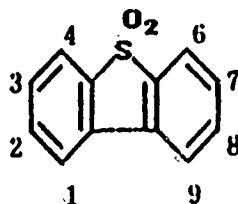
1.5 Nitration of Dibenzothiophene-5-oxide



In dibenzothiophene-5-oxide the two lone pairs on sulphur are no longer available for delocalisation into the aromatic system. The electron withdrawing effect of the sulfoxide group is felt most strongly at positions ortho and para to it. Hence, the sulfoxide group has the overall effect of directing electrophilic substituents to positions meta to itself, whilst making dibenzothiophene-5-oxide less reactive than dibenzothiophene.

Nitration of dibenzothiophene-5-oxide leads to 3-nitro²², and 3,7-dinitrodibenzothiophene-5-oxide²¹. The aim of this project is to further nitrate dibenzothiophene-5-oxide to 1,3,7-trinitro- and/or 1,3,7,9-tetranitrodibenzothiophene-5-oxide. However, this task is also complicated by the fact that the sulfoxide group is prone to oxidation, giving dibenzothiophene-5,5-dioxide.

1.6 Nitration of Dibenzothiophene-5,5-dioxide



Dibenzothiophene-5,5-dioxide nitrates in the same way as dibenzothiophene-5-oxide. The electron withdrawing effect of the sulphone group is greater than that of the sulphoxide group because of the extra oxygen atom. The overall effect of this is stronger directing of electrophilic substituents to positions meta to the sulphone group, but a less reactive compound. Nitration of dibenzothiophene-5,5-dioxide leads to 3-nitro-²³, and 3,7-dinitro-dibenzothiophene-5,5-dioxide²⁴. References to 1,3,7-trinitro-dibenzothiophene-5,5-dioxide^{26,27} have also been found, but a synthesis for it has not been given in any of the references obtained.

The aim of this project is to further nitrate dibenzothiophene-5,5-dioxide to 1,3,7-trinitro-, and 1,3,7,9-tetranitrodibenzothiophene-5,5-dioxide. There are no problems of oxidation of the sulphone group, however, its stronger electron withdrawing effect makes nitration more difficult.

2. EXPERIMENTAL TECHNIQUES

Thin Layer Chromatography

Thin layer chromatography of samples was performed using pre-coated plastic sheets of silica gel (layer thickness 0.25mm).

Column Chromatography

Column chromatography of samples was performed using a glass column (50cm*2cm) containing either aluminium oxide (activated neutral, 95%) or silica gel 70-230 mesh, 60A⁰.

NMR Spectroscopy

NMR spectra were recorded on a Jeol 270MHz high resolution NMR spectrometer.

IR Spectroscopy

IR spectra of samples were recorded using KBr discs of the samples on either a Perkin Elmer Infrared Spectrometer 197 or a Perkin Elmer 1600 Series FTIR.

UV Spectroscopy

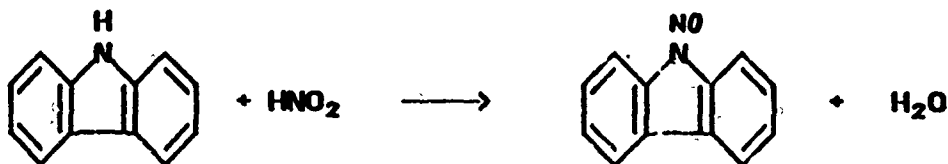
UV spectra were recorded on a Perkin Elmer Double Beam Spectrometer 124(2).

Analytical HPLC

Analytical HPLC was performed on a 25cm*4.6mm stainless steel column packed with 5µm C18 packing material (Spherisorb 50DS, Chrompack Ltd), using an eluent mixture of 70% HPLC grade methanol in demineralised water with a flow rate of 1cm³min⁻¹, and a UV detector of variable wavelength. Samples were dissolved (0.1mg/ml) in HPLC grade methanol for injection.

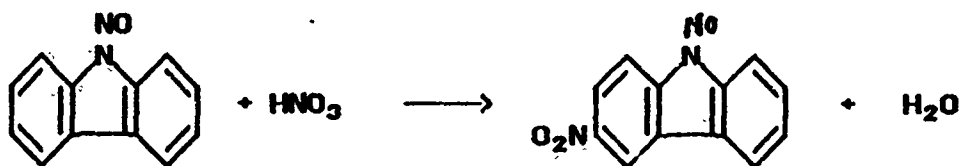
3. EXPERIMENTAL

3.1.1 Synthesis of 3-Nitrocarbazole¹⁵

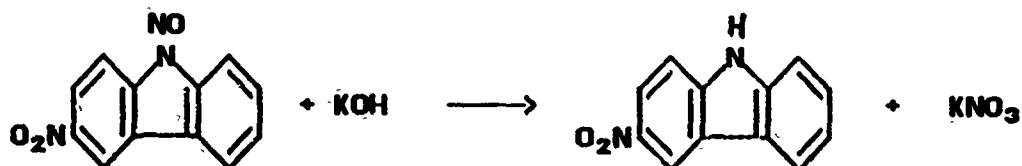


CARBAZOLE

N-NITROSOCARBAZOLE



3-NITRO-9-NITROSOCARBAZOLE



3-NITROCARBAZOLE

A mixture of carbazole (5g;0.03mole) and glacial acetic acid (40ml) was heated to boiling and then cooled somewhat. Sodium nitrite (2.1g;0.033mole) was then added slowly to the stirred mixture, gradually turning the white slurry brown. A mixture of equal portions of glacial acetic acid and nitric acid (sp.gr.1.4, 8.3ml), was then added slowly to the stirred mixture keeping the temperature below the boiling point as before. This turned the mixture dark brown/red in colour. The precipitated crystalline material (3-Nitro-9-Nitrosocarbazole) was filtered off and washed

with ethanol. It was pale green in appearance.

The crude 3-Nitro-9-Nitrosocarbazole was then heated over reflux for 30 minutes with a mixture of ethanol (500ml) and aqueous 40% potassium hydroxide solution (20ml). The deep red mixture that was formed was then filtered, and the filtrate poured into excess distilled water with stirring, producing a deep yellow precipitate. The precipitated crude 3-Nitrocarbazole was recrystallised from glacial acetic acid (75ml), in which operation not all the material went into solution. The insoluble portion was rejected.

Recrystallisation of the crude orange product of this reaction produced a yellow fine powdered solid.

Weight of yellow solid = 1.8477g

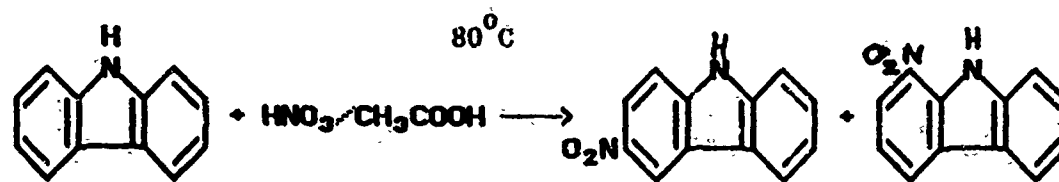
Yield = 30%

Expected melting point = 214°C

Actual melting point = $205-210^{\circ}\text{C}$

The N.M.R. spectrum of the solid could not be fully assigned. H.P.L.C. chromatographs suggested that the solid was in fact a mixture of two compounds, one of which was 3-nitrocarbazole.

3.1.2 Synthesis of 1-Nitrocarbazole¹⁶



CARBAZOLE

3-NITROCARBAZOLE

1-NITROCARBAZOLE

Nitric acid (sp. gr. 1.5; 4.4ml) in glacial acetic acid (10ml) was added drop wise over 15 minutes to a stirred mixture of carbazole (10g; 0.06mole) and glacial acetic acid (80ml) maintained at 80°C . The colour immediately changed from a white slurry to yellow,

and then brown. The mixture was then poured onto ice, forming a yellow/brown precipitate. This precipitate was recrystallised three times from xylene. The solid (3-Nitrocarbazole) was filtered off, and the filtrate was rotary evaporated down, removing more 3-Nitrocarbazole as it precipitated, until only a residue remained. This residue was dissolved in 1ml of toluene and column chromatographed to obtain the 1-Nitrocarbazole.

The product from this reaction was a brown powder.

Weight of 1-nitrocarbazole = 0.1866g

Yield = 1.5%

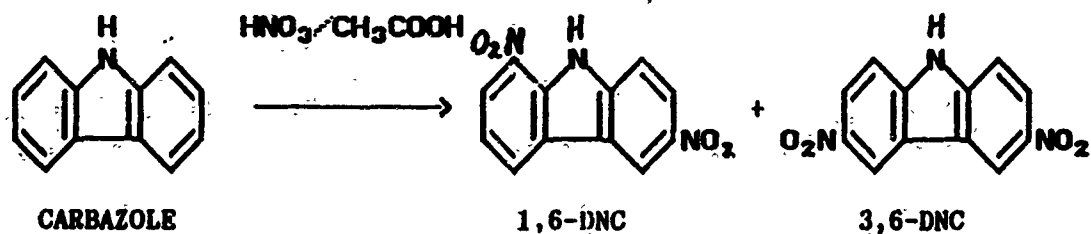
Weight of 3-nitrocarbazole = 8.2792g

Yield = 65%

Melting point of brown powder (1-nitrocarbazole) = 80-120°C

The N.M.R. spectrum of this compound was very complex and has not been fully assigned.

3.1.3. Synthesis of 1,6- and 3,6-Dinitrocarbazole¹⁷



(i) Synthesis of mixture

A slurry of carbazole (16.7g; 0.1mole) in glacial acetic acid (128g), stirred at 30-40°C, was treated during 1.5hr with sodium nitrite (7.1g; 0.1mole). The sodium nitrite turned the white slurry first yellow, then brown. After 2hr of agitation, most of the solid had dissolved (as 9-nitrosocarbazole), but the addition of an extra 1g of sodium nitrite failed to achieve complete solution. The yellow precipitate in brown solution had to be left overnight due to lack

of time.

During 1.3hr, nitric acid (sp. gr. 1.5; 49.3g; 33ml) diluted with an equal weight of glacial acetic acid was added with intermittent cooling at 30-40°C, and the slurry was stirred at that temperature for an additional 3.5hr. The yellow precipitate had dissolved to give a thick brown mixture. The mixture was then held at 55°C for 1.5hr, at 65°C for 1.5hr, and at 95°C for 2hr, cooled to 65°C and filtered. The pale green solid was washed with cold glacial acetic acid (70ml), with distilled water, and was dried in an oven at 120°C overnight.

The mixture of dinitrocarbazoles produced was a pale green powder.

Weight of crude mixture = 22.8g

Yield = 90%

Expected melting point = 312-354°C

Actual melting point = 307-336°C (charring above 280°C)

(ii) Separation of isomers

A sample of crude dinitrocarbazole (9.1g) was divided into two portions and each was stirred at 50°C with alcoholic potassium hydroxide (300cm³; 60g/l) and filtered. The insoluble red solid residues were combined, digested on a steam bath with dilute hydrochloric acid (whereupon the colour changed to yellow), filtered, washed with water, and dried to give 1,6-dinitrocarbazole which was recrystallised from nitrobenzene as glistening golden leaflets.

The red alkaline alcoholic solutions were acidified with concentrated hydrochloric acid, and the solid yellow precipitates thus formed were combined and washed thoroughly with warm distilled

water to remove potassium chloride. The residue was recrystallised from boiling nitrobenzene to give 3,6-dinitrocarbazole as fine yellow needles.

The crude isomeric mixture (9.1g) separated into the following ratio of isomers.

Weight of 3,6-DNC = 4.2881g

Yield = 50%

Expected melting point = $386-387^{\circ}\text{C}$

There was no apparatus available to check this, but the solid had not melted at 355°C .

Weight of 1,6-DNC = 2.2624g

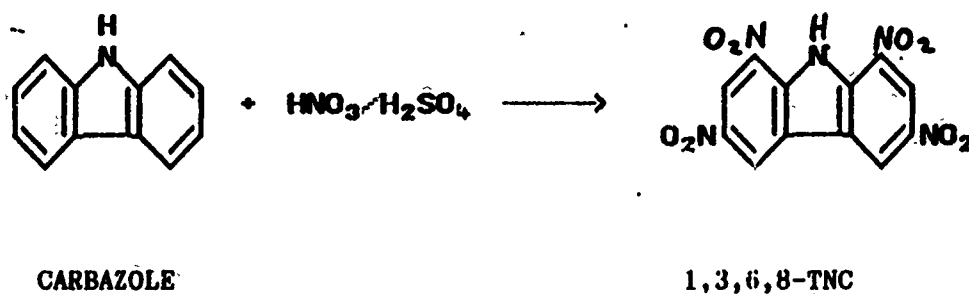
Yield = 22.5%

Expected melting point = $344-346^{\circ}\text{C}$

Actual melting point = $344-351^{\circ}\text{C}$ (charring above 280°C)

Both compounds were confirmed by ^1H N.M.R. (and ^{13}C N.M.R. for 1,6). For 3,6-DNC the ^1H N.M.R. spectrum (section 7) was very clear. It has peaks at 6.9δ (2 H, doublet, $J = 9.2\text{ Hz}$), 7.6δ (2H, doublet of doublets, $J = 2.6\text{ Hz}$ and $J = 9.2\text{ Hz}$), 8.6δ (2H, doublet, $J = 2.6\text{ Hz}$), 10.3δ (1H, doublet, $J = 0.7\text{ Hz}$). These peaks and splittings are as expected for this compound. For 1,6-DNC the ^1H N.M.R. spectrum (section 7) and the ^{13}C N.M.R. spectrum were also as expected. The ^1H N.M.R. spectrum has peaks at 6.6δ (1H, triplet, $J = 8.0\text{ Hz}$), 7.0δ (1H, doublet, $J = 9.5\text{ Hz}$), 7.5δ (2H, multiplet), 8.0δ (1H, doublet, $J = 7.7\text{ Hz}$), 8.4δ (1H, doublet, $J = 1.8\text{ Hz}$), 10.3δ (1H, singlet).

3.1.4 Synthesis of 1,3,6,8-Tetranitrocarbazole^{18, 13}



(i) Synthesis of 1,3,6,8-TNC via reference 18

Carbazole (13.4g; 0.08mole) was added slowly with vigorous stirring to 98% sulphuric acid (42ml), keeping the temperature between 30-50°C. The carbazole turned the acid first yellow, then green, and finally a brown mixture was formed. The temperature was then raised to 70-80°C and held there until a drop of the solution did not form a precipitate when added to a few drops of water. The solution was then cooled and added drop wise with stirring to fuming nitric acid (40.2g; 0.6mole) kept at 30-40°C. The temperature was then raised to 78°C and kept there for two hours to complete nitration. On cooling the solution was added to approximately two volumes of ice. The yellow precipitate formed was filtered, boiled several times with water until the water was neutral to litmus, and finally dried in an oven at 110°C for five hours. The impure 1,3,6,8-TNC was analysed by TLC and column chromatography.

Crude 1,3,6,8-TNC produced in this way was a fine pale yellow powder.

Weight of crude TNC = 16.3178g

Yield = 62.5%

Expected melting point = 296-298°C

Actual melting point = 250-276°C (charring above 230°C)

H.P.L.C. of this product revealed three peaks due to impurities (approximate purity 80%). However, T.L.C. could only separate it into three spots. Column chromatography (eluent-hexane/ethyl acetate in the ratio 3:1) was used to separate a small sample of this compound into its three components (pure ethyl acetate had to be used to flush out the third component). The first component eluted was a yellow solid and was confirmed to be 1,3,6,8-TNC by ^1H N.M.R. The second component eluted was a red/orange solid and was shown by ^1H N.M.R. to be a mixture of compounds, possibly containing penta- or hexa-nitrocarbazole. The third component eluted was a brown solid, and was a crude mixture that had proved difficult to remove from the column.

(ii) Synthesis of pure 1,3,6,8-TNC via reference 13

(Several changes were made to the purification process described in reference 13 on the advice of the authors).

Carbazole (16.7g; 0.1mole) was added slowly with stirring to 98% sulphuric acid (96g; 52.3cm³). The temperature was kept below 50°C, and when all the carbazole had been added the mixture was then heated (steam bath) to 90°C for 45 minutes. At this stage a drop of sulphonation mixture gave no precipitate when added to 5cm³ water.

One tenth (5cm³) of this solution was extracted from the reaction flask to study the products of sulphonation of carbazole. This cooled sample was poured onto ice (200g) and solid sodium chloride (45g) was added, warming on the steam bath to dissolve all salts. On cooling, a white voluminous solid was precipitated which on filtering became a fine white solid.

Having taken out one tenth for the above isolation, 98% sulphuric acid (130cm³) was added to the rest of the reaction mixture which had been cooled to 40°C. Fuming nitric acid (95%; 0.4mole; 18cm³)

was then added in small amounts, allowing the temperature to fall after each addition. The temperature range was 40-55°C, but never over 60°C. When all the nitric acid had been added, the mixture was heated to 70°C for one hour. On cooling the red brown mixture was poured onto ice (600g) and sodium chloride (1g per 5cm³ of ice) was added. The mixture was allowed to settle (overnight), filtered, the solid washed copiously with distilled water, and dried. The solid pale yellow 1,3,6,8 TNC was purified first by extraction with 90% aqueous acetone (20cm³ per gram of solid), and then by recrystallisation from toluene (40cm³ toluene per gram of solid). The residue filtered from hot toluene was repeatedly recrystallised to recover more 1,3,6,8-TNC. The pure 1,3,6,8-TNC was then washed with ether to remove toluene, and dried.

Crude 1,3,6,8-TNC produced in this way was a fine, pale yellow powder.

Weight of crude 1,3,6,8-TNC = 27.2848g

Crude yield = 78.6%

After purification by acetone extraction and toluene recrystallisation:

Weight of pure 1,3,6,8-TNC = 4.5141g, Overall yield = 12.5%

Expected melting point = 296-298°C

Actual melting point = 295-300°C

H.P.L.C. confirmed that this 1,3,6,8-TNC now had only a very small amount of one impurity (approximate purity = 99.8%).

¹H N.M.R. of this pure TNC had peaks at 9.3 δ (2H, doublet, J = 2.0 Hz), and at 10.0 δ (2H, doublet, J = 2.0 Hz).

The isolation of the product of sulphonation of carbazole during this reaction produced a fine, white crystalline solid.

Weight of sulphonation product = 1.3030g

This product had an elemental analysis of C 16.28 H 1.36 N 1.52 S 10.29. These values suggest that the compounds empirical formula is $C_{12}H_{12}NS_3O_9$. The closest compound to this is the tri-sodium salt of carbazole 1,3,6-trisulphonic acid ($C_{12}H_9NS_3O_9Na_3$).

The 1H -N.M.R. spectrum (section 7) of this product was exactly that expected for the tri-sodium salt of carbazole 1,3,6-trisulphonic acid. It had peaks at 7.7 δ (1H, doublet, $J = 8.5$ Hz), 8.0 δ (1H, doublet of doublets, $J = 8.5$ Hz and $J = 1.8$ Hz), 8.4 δ (1H, doublet, $J = 1.8$ Hz), 8.7 δ (1H, doublet, $J = 1.8$ Hz), 8.9 δ (1H, doublet, $J = 1.1$ Hz).

3.1.5 Synthesis of product from sulphonation of carbazole

Carbazole (5g) was added slowly, with stirring, to conc. sulphuric acid (29g; 16cm³; sp. gr. 1.835). As the white carbazole was added to the colourless sulphuric acid the mixture was first yellow, then gradually got darker until it was dark brown. The temperature was kept below 50°C, and when all the carbazole had been added the mixture was heated to 90°C for 45 minutes. At this stage, a drop of sulphonation mixture gave no precipitate when added to 5cm³ water. The cooled mixture was poured onto ice (100cm³) and then the solid sodium chloride (15g) was added, warming on the steam bath to dissolve all salts (with addition of an extra 25cm³ distilled water). On cooling, a white voluminous solid was precipitated from the brown solution. When filtered and dried, this solid was a grey powder. It was recrystallised from hot sodium chloride solution (15g sodium chloride in 100cm³ distilled water).

The product from this reaction was a fine, grey, crystalline powder.

Weight of crude product = 6.5083g

After recrystallisation from hot sodium chloride solution:

Weight of product = 2.9648g

The ^1H N.M.R. spectrum showed that this compound was exactly the same as that isolated as an intermediate in the previous reaction, i.e. the tri-sodium salt of carbazole 1,3,6-trisulphonic acid. Hence, yield = 46%.

3.1.6 Attempts to synthesise 1,3,6,8-TNC via nitration of carbazole with mixed acids other than $\text{H}_2\text{SO}_4/\text{HNO}_3$

(i) Mixed acid nitration of carbazole with $\text{HBF}_4/\text{HNO}_3$

Carbazole (5g; 0.03mole) was added slowly with vigorous stirring to HBF_4 (30cm³; 50%) at room temperature. This formed a slurry which became very thick and would not stir. More HBF_4 (20cm³) was added, and the slurry began to stir again. However, the pale blue slurry was still too viscous, so it was heated to 40°C. The slurry was added drop wise with stirring to HNO_3 (7.6g; 5.1cm³; sp. gr. 1.5) at room temperature, at which stage a brown solution was formed and heat was evolved. The mixture was stirred for two hours, then poured onto a large excess of ice and the brown precipitate formed was filtered, boiled in distilled water until neutral, and dried.

This mixed acid nitration was repeated on carbazole, and also on mixed dinitrocarbazole, at temperatures of 70-80°C (as in section 3.1.4.). Both of these nitrations also produced solid brown powder as the product.

The product of nitration of carbazole at room temperature was a brown powdered solid. It was shown by ^1H N.M.R. to be a mixture of dinitrocarbazoles.

Weight of product = 4.4802g

Yield = 58%

Melting point = melted in two stages as if more than one compound

was present. First stage 194-220°C, then remaining solid melted at 340-above 355°C.

The product from nitration of carbazole with heat (70°C) in this mixture, again resulted in a brown solid. A ¹H N.M.R. spectrum of this compound could not be obtained due to insolubility.

Weight of product = 6.3102g

Melting point = above 360°C

The product from nitration of dinitrocarbazole in this mixture, with heat (70-80°C), was a pale green solid exactly the same as the starting material, and was confirmed to be unchanged dinitrocarbazole by ¹H N.M.R.

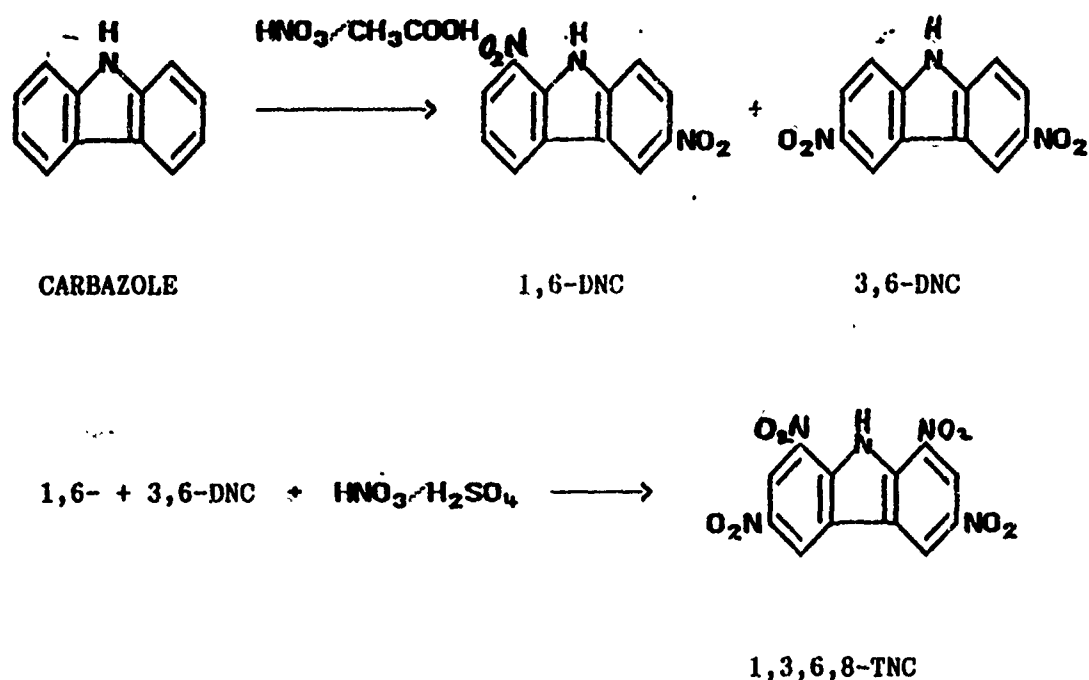
(ii) Mixed acid nitration of carbazole with (CF₃CO)₂O/HNO₃

Carbazole (2.5g; 0.015mole) was added in small portions with vigorous stirring to trifluoroacetic anhydride (20cm³) at room temperature. A mixture of HNO₃ (95%; 2.7cm³) and (CF₃CO)₂O (13g; 8.7cm³) was added drop wise over 15 minutes, turning the white slurry first yellow, then pale green, and then dark green. The temperature rose to 30°C during the addition, and some NO₂ fumes were given off. The mixture was then stirred for two hours to complete nitration, cooled, and poured onto ice. The dark green/brown precipitate was boiled with distilled water (three times in 250cm³ of distilled water) until the water was almost neutral to litmus paper, filtered, and dried in an oven at 110°C. It was dark brown when dry.

The product from this nitration was a green/brown solid. Its ¹H N.M.R. spectrum was difficult to obtain due to insolubility. It had many peaks in the aromatic region, but none of them corresponded to 1,3,6,8-TNC.

Weight of product = 2.86g ; Melting point = 260-above 355°C.

3.1.7 Synthesis of 1,3,6,8-TNC via a two step process



The mixture of dinitrocarbazoles was prepared as described in section 3.1.3. This crude mixture was then nitrated following a similar procedure to that described in section 3.1.4. The dark brown product formed was washed copiously with distilled water and recrystallised from toluene to produce an orange crystalline solid. When washed with ether to remove toluene, the orange solid became a powder. It was dried in an oven at 110°C for four hours. Samples of this compound were then purified in two different ways. Firstly, a 1g sample of the crude material was boiled in distilled water (3*200cm³) until almost neutral, dried, and weighed. It was then recrystallised from toluene, boiling the toluene for five minutes at 111°C and cooling to -10°C to achieve the best yield, dried, and reweighed. Next a 5g sample of the crude product was purified by Soxhlet extraction in toluene.

The crude mixture of dinitrocarbazoles was prepared as in section 2.3.

Weight of crude DNC mixture = 20.9713g

Crude yield = 81.7%

Expected melting point = 312-354°C

Actual melting point = 300-above 355°C

The crude product from the second step of this reaction was a dark brown solid. It was confirmed to be 1,3,6,8-TNC via ¹H N.M.R.

Weight of crude TNC = 23.4863g

Yield = 84.6%

Expected melting point = 296-298°C

Actual melting point = 280-287°C

H.P.L.C. of this crude TNC revealed two impurity peaks, one less than the crude TNC produced via reference 18 (approximate purity = 93%).

Overall crude yield = 69.1%

Results from the attempted purification of this product are given in the table below.

AMOUNT OF CRUDE PRODUCT (g)	PERCENTAGE REMAINING				
	BOILED IN	RECRYSTALLISED	SOXHLET	OVERALL	APPROX.
	WATER	FROM TOLUENE	EXTRACTION IN TOLUENE	YIELD (%)	PURITY (%)
1	63	47	--	32	99
5	--	--	58	40	97

3.1.8 Large scale synthesis of 1,3,6,8-TNC via a two step process

A large scale synthesis very similar to the previous one had to be performed to prepare 100g of TNC for testing in pyrotechnic compositions. The only change to the synthesis was in the first step, the nitration of carbazole to dinitrocarbazole. The previous synthesis of the dinitrocarbazole mixture (described in section 3.1.3) was fairly long. A simplified version is described below.

Carbazole (83.6g; 0.5mole) was added slowly with stirring to glacial acetic acid (640g; 609.5ml) over a period of one hour. During a second hour a 1:1 mixture of fuming HNO_3 (63ml) / CH_3COOH (63ml) was added, keeping the temperature between 30-40°C. The mixture was then heated (steam bath) to 75°C for four hours, cooled overnight, and poured onto ice (1.5 litres). The brown/green precipitate was filtered, washed with distilled water (2 litres) until the filtrate was no longer yellow (and was neutral to litmus), and dried in an oven at 140°C overnight.

This crude mixture of dinitrocarbazoles was then nitrated to TNC via a method similar to that described in section 3.1.4. The crude, dark brown product (crude 1,3,6,8-TNC) was washed with distilled water (3 litres) and dried in an oven at 140°C overnight.

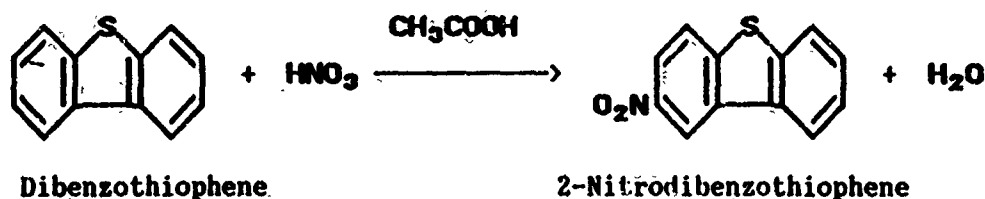
The crude 1,3,6,8-TNC was recrystallised by placing the whole amount in 2 litres of toluene, boiling at 111°C for 5 minutes, filtering hot, and cooling to -10°C in an ice slush bath. The residue filtered hot was continually recrystallised in the same toluene to increase the yield. All of the TNC recrystallised from the toluene was combined and recrystallised in the same way from another two litres of toluene. This whole synthesis was repeated a second time (results overleaf), the products being analysed by H.P.L.C. and N.M.R.

EXPT. No.	PERCENTAGE YIELDS				
	CARBAZOLE	DNC	OVERALL	1ST RECRYST	2ND RECRYST.
	TO DNC	TO TNC	CRUDE YIELD	FROM TOLUENE	FROM TOLUENE
1	96	84	80	78	90
2	95	94	89	74	89

OVERALL YIELD	APPROX. PURITY*	Mpt. (°C) EXPECTED
		296-298
59	97	295-298
59	97	290-295

* Approximate purities obtained from relative areas of H.P.L.C. peaks.

3.2.1 Synthesis of 2-Nitrodibenzothiophene²⁰



Dibenzothiophene (5g ;0.03mole) was dissolved in glacial acetic acid (40cm³) and kept at 30⁰C. Fuming nitric acid (5cm³,d,1.51) was added dropwise over a period of thirty minutes. When the addition was complete the reaction mixture was stirred at room temperature for one hour, poured onto ice (200cm³) , and filtered. The yellow solid was refluxed for several hours with ethanol (95%;50cm³) , and the insoluble 2-nitrodibenzothiophene removed by filtration. On dilution of the ethanol another yellow precipitate was obtained and was kept for analysis.

The crude product from this reaction was a dirty yellow solid.

Crude weight = 1.7616g

Yield = 28%

Expected melting point = 186-187⁰C

Actual melting point = 166-175⁰C

On recrystallisation from ethanol the product became a deep yellow solid.

Weight = 0.3351g

Yield = 12%

Expected melting point = 186-187⁰C

Actual melting point = 173-180⁰C

H.P.L.C. :- Retention time = 10.3mins; purity = 96.8%

¹H N.M.R. :-

The ¹H N.M.R. spectrum has peaks at 7.70 δ (2H, multiplet), 8.20 δ (1H, doublet, J = 8 Hz), 8.40 δ (2H, singlet), 8.70δ (1H, doublet, J

= 8 Hz), 9.30 δ (1H, singlet).

The residue obtained from dilution of ethanol filtrate was a yellow solid.

Crude weight = 2.7695g

Melting point = 175-187 $^{\circ}$ C

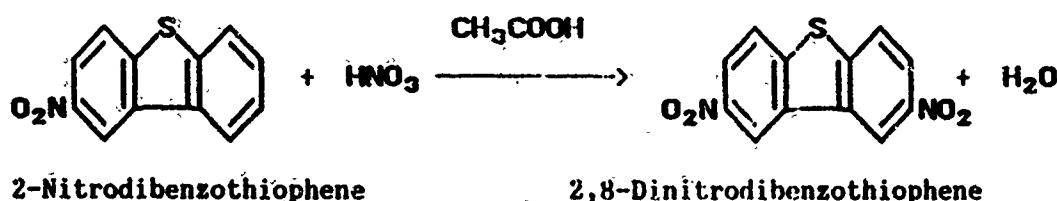
H.P.L.C. :- Retention time = 4.7mins; purity = 64.8%

^1H N.M.R. :-

The ^1H N.M.R. spectrum of this residue has peaks at 7.60 δ (2H, triplet of doublets, $J = 1\text{Hz}$ and $J = 7\text{Hz}$), 7.70 δ (2H, triplet of doublets, $J = 1\text{Hz}$ and $J = 7\text{Hz}$), 8.08 δ (2H, doublet of doublets, $J = 1\text{Hz}$ and $J = 8\text{Hz}$), 8.12 δ (2H, doublet of doublets, $J = 1\text{Hz}$ and $J = 8\text{Hz}$).

By comparison of H.P.L.C. and ^1H N.M.R. spectra this residue was identified as dibenzothiophene-5-oxide.

3.2.2 Synthesis of 2,8-Dinitrodibenzothiophene²⁰



2-Nitrodibenzothiophene (1g; 0.004mole) was added in small portions to a mixture of fuming nitric acid (2.5cm³; d.1.51) in glacial acetic acid (10cm³). When the addition was complete more fuming nitric acid (15cm³) was added dropwise. The reaction mixture was heated to 50 $^{\circ}$ C, then allowed to cool whilst stirring for a period of one hour. The mixture was then poured onto ice water (100cm³), and the resulting yellow precipitate was recrystallised from glacial acetic acid and then from dioxane.

The crude product from this reaction was a light brown solid.

Crude weight = 0.8689g

Yield = 79%

Expected melting point = 320-330⁰C

Actual melting point = 260-310⁰C

After recrystallisation from acetic acid, and then from dioxane.

Weight = 0.0900g

Yield = 9%

Expected melting point = 339-340⁰C

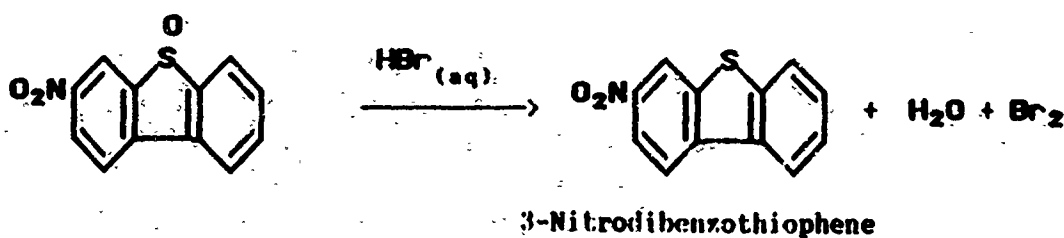
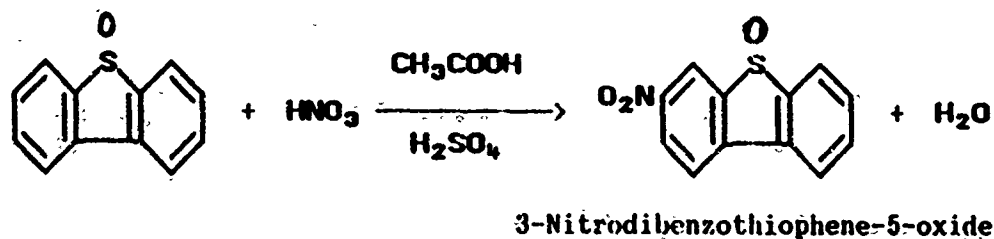
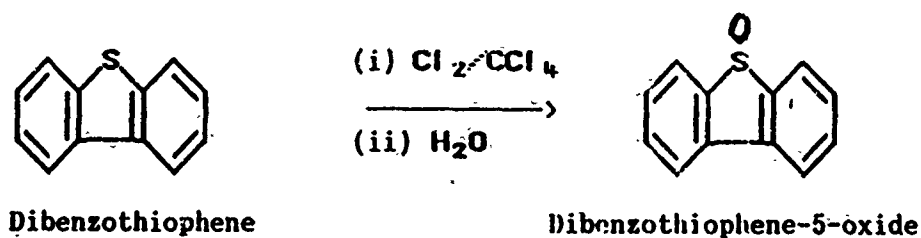
Actual melting point = 324-334⁰C

H.P.L.C. :- Retention time = 8.9mins; purity = 71.6%

¹H N.M.R. :-

The ¹H N.M.R. spectrum has peaks at 8.40 δ (2H, doublet, J = 8Hz), 9.15 δ (2H, doublet of doublets, J = 1Hz and J = 8Hz), 9.65 δ (2H, singlet).

3.2.3 Synthesis of 3-Nitrodibenzothiophene²¹



To a warm solution of 3-nitrodibenzothiophene-5-oxide²² (0.6g; 0.002mole) in glacial acetic acid (5ml) was added concentrated hydrobromic acid (1.5ml; sp.gr. 1.38). The reduction, accompanied by the liberation of bromine, was allowed to proceed for 30 minutes at 40°C whereupon the yellow precipitate was removed by pouring onto ice water (50cm³), filtered, and dried. The crude material was recrystallised from ethanol (95% aqueous).

The crude product from this reaction was a yellow/beige solid.

Crude weight = 0.4523g

Yield = 90%

Expected melting point = 149-151°C

Actual melting point = 123-129°C

After recrystallisation from 95% aqueous ethanol the product remained the same colour.

Weight = 0.2300g

Yield = 46%

Expected melting point = 153-154°C

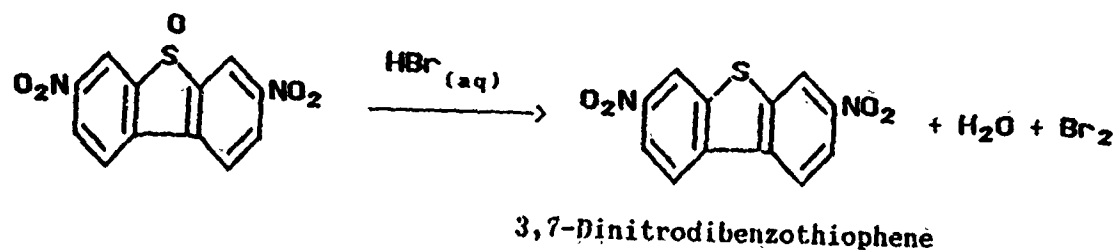
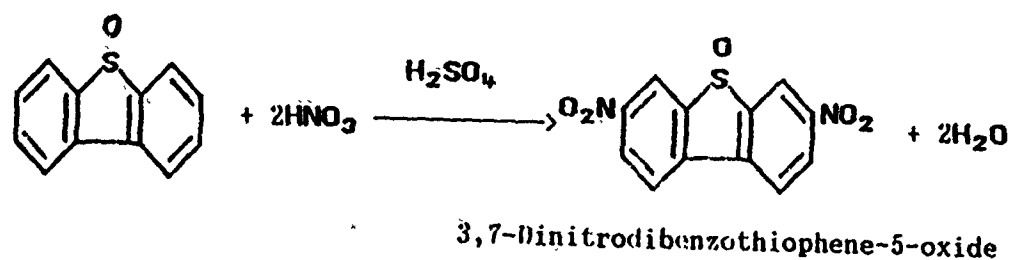
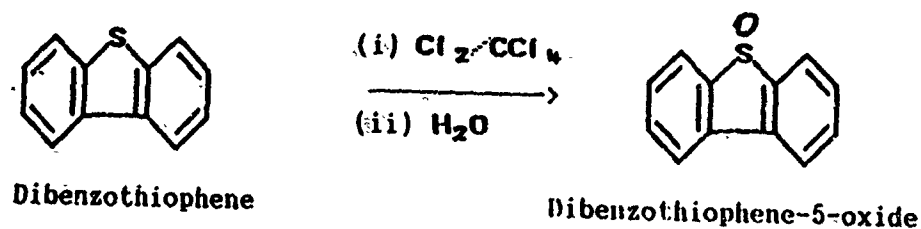
Actual melting point = 140-146°C

H.P.L.C. :- Retention time = 11.46mins; purity = 97.3%

¹H N.M.R. :-

The ¹H N.M.R. spectrum has peaks at 7.65 δ (2H, multiplet of two overlapping triplet of doublets, J = 1Hz and J = 7Hz), 8.20 δ (1H, doublet of doublets, J = 1Hz and J = 8Hz), 8.35 δ (1H, doublet of doublets, J = 3Hz and J = 9Hz), 8.55 δ (1H, doublet of doublets, J = 1Hz and J = 7Hz), 8.65 δ (1H, doublet, J = 9Hz), 9.1 δ (1H, doublet, J = 2Hz).

3.2.4 Synthesis of 3,7-Dinitrodibenzothiophene²¹



To a solution of 3,7-dinitrodibenzothiophene-5-oxide (1.3g; 0.005mole) in glacial acetic acid (35ml) at 80°C was added concentrated hydrobromic acid (2.5ml; sp.gr.1.38). The vessel was placed in a water bath to moderate the temperature of the reaction which was allowed to proceed for 30 minutes. The reaction mixture was poured onto ice water (100cm³), and the yellow precipitate filtered, washed with water, and dried. The product was recrystallised from toluene.

The crude product from this reaction was a yellow solid.

Crude weight = 1.1300g

Yield = 92%

Expected melting point = 338-341°C

Actual melting point = 354-360°C

On recrystallisation from toluene the product became a bright yellow

solid.

Weight = 0.3400g

Yield = 28%

Expected melting point = $342-344^{\circ}\text{C}$

Actual melting point = $360 \pm^{\circ}\text{C}$

H.P.L.C. :- Retention time = 8.70mins; purity = 94.0%

^1H N.M.R. :-

The ^1H N.M.R. spectrum has peaks at 8.40 δ (2H, doublet of doublets, $J = 2\text{Hz}$ and $J = 9\text{Hz}$), 8.8 δ (2H, doublet, $J = 9\text{Hz}$), 9.2 δ (2H, doublet, $J = 2\text{Hz}$).

3.2.5 Nitration of Dibenzothiophene with forcing conditions

(An attempt to make tetranitrodibenzothiophene)

Dibenzothiophene (1g; 0.005mole) was added in small portions to a stirred mixture of fuming nitric acid (4cm^3 ; sp.gr.1.5) in conc. sulphuric acid (10cm^3) kept at 50°C , giving a deep red/brown mixture. The reaction mixture was heated at 90°C for two hours, cooled, and poured onto ice water. The product was filtered, washed with water, dried, and recrystallised from acetone.

The crude product from this reaction was a pale yellow solid.

Crude weight = 1.7956g

Yield (if tetranitrodibenzothiophene) = 90%

Melting point = $120-135^{\circ}\text{C}$

After recrystallisation twice from acetone the product was orange/brown in colour.

Weight = 1.1494g

Yield (if tetranitro) = 57%

Melting point = $183-200^{\circ}\text{C}$

H.P.L.C. results :-

PEAK	RETN. TIME (MINS)	AREA (%)
1	2.11	2.4
2	4.21	39.7
3	4.54	27.0
4	8.97	29.6
5	10.21	1.3

The ^1H N.M.R. spectrum of this crude mixture was a complex mixture of peaks. The three major components of this mixture must be separated before identification can be accomplished.

3.2.6 Nitrations of 2,8-Dinitrodibenzothiophene

(i) Nitration 1 of 2,8-Dinitrodibenzothiophene

Crude 2,8-dinitrodibenzothiophene (0.5g; 0.002mole) was added slowly to a mixture of fuming nitric acid (5cm^3) in conc. sulphuric acid (5cm^3) that had been cooled to 0°C . The dark brown mixture was kept at 0°C for about 4 hours, poured onto ice water and the yellow precipitate formed was filtered, washed copiously with water, and dried in an oven at 70°C overnight.

The crude product from this reaction was a yellow solid.

Crude weight = 0.4189g

Yield (if tetranitro) = 60%

Melting point = $298-302^\circ\text{C}$

H.P.L.C. results for crude product:-

PEAK	RETN. TIME (MINS)	AREA (%)
1	1.90	9.0
2	4.10	15.0
3	4.43	39.0
4	6.94	1.0
5	10.82	36.0

Because of the difference in solubility between dibenzothiophenes and dibenzothiophene oxides, or dioxides, an attempt was made to separate them by washing the product with acetone (5cm³). The soluble and insoluble fractions were analysed by H.P.L.C. and ¹H N.M.R.

Soluble fraction :-

; Insoluble fraction :-

Weight = 0.0600g

Weight = 0.2200g

Mpt. = 358⁰C

Mpt. = 314-318⁰C

H.P.L.C. results

PEAK	RETN. TIME (MINS)	AREA (%)	PEAK	RETN. TIME (MINS)	AREA (%)
1	2.08	27.4	1	1.91	19.0
2	4.19	6.7	2	4.19	17.0
3	4.42	10.0	3	4.43	48.0
4	6.73	0.7	4	10.05	16.0
5	10.18	53.3	5		

¹H N.M.R.

The ¹H N.M.R. spectra of these products have not been fully assigned.

(ii) Nitration 2 of 2,8-Dinitrodibenzothiophene

A similar method was adopted to that of nitration 1 except that the reaction mixture was kept at -10°C for 4 hours, and then at -5°C in the freezer overnight.

The crude product from this reaction was a yellow solid.

Crude weight = 0.3161g

Yield (if tetranitro) = 48%

Melting point = $296-304^{\circ}\text{C}$

H.P.L.C. results for crude product:-

PEAK	RETN. TIME (MINS)	AREA (%)
1	1.94	19.0
2	4.16	12.5
3	4.39	40.8
4	9.68	27.7

This product was extracted with acetone, as in nitration 1, to try to separate the dibenzothiophenes from their oxides. The soluble and insoluble fractions were analysed by H.P.L.C. and ^1H N.M.R.

Soluble fraction :-

; Insoluble fraction :-

Weight = 0.0160g

Weight = 0.2106g

H.P.L.C. results

(due to a drop in pressure the retention times are longer)

PEAK	RETN. TIME (MINS)	AREA (%)	PEAK	RETN. TIME (MINS)	AREA (%)
1	2.05	27.6	1	1.88	19.6
2	4.40	7.5	2	4.51	63.4
3	4.66	8.8	3	10.16	2.6
4	11.41	56.1	4	10.93	14.4

¹H N.M.R.

The ¹H N.M.R. spectrum of the soluble fraction was very complex. Purification is needed.

The insoluble fraction was not sufficiently soluble to obtain a solution ¹H N.M.R..

(iii) Nitration 3 of 2,8-Dinitrodibenzothiophene

Crude 2,8-dinitrodibenzothiophene (1g; 0.004mole) was added in small portions to a mixture of fuming nitric acid (3.5cm³) in conc. sulphuric acid (3.5cm³). When the addition was complete extra fuming nitric acid (1cm³) was added dropwise. The reaction mixture was stirred for one hour at room temperature and then poured into ice water. The crude yellow precipitate was filtered, washed with water, and dried.

The crude product from this reaction was a yellow solid.

Crude weight = 0.9675g

Yield (if tetranitro) = 74%

Melting point = 264-290°C (charring above 200°C)

H.P.L.C. results for the crude product :-

PEAK	RETN. TIME (MINS)	AREA (%)
1	1.90	23.0
2	4.12	36.7
3	4.32	33.0
4	8.59	7.3

This product was extracted with acetone, as in nitration 1, to try to separate the dibenzothiophenes from their oxides. The soluble and insoluble fractions were analysed by H.P.L.C. and ¹H N.M.R.

Soluble fraction :-

; Insoluble fraction :-

Weight = 0.1532g

Weight = 0.5963g

H.P.L.C. results

PEAK	RETN. TIME (MINS)	AREA (%)	PEAK	RETN. TIME (MINS)	AREA (%)
1	1.87	20.6	1	1.82	32.2
2	4.18	43.6	2	4.17	27.3
3	7.12	1.5	3	4.41	35.9
4	11.52	34.4	4	10.05	2.2
			5	11.06	2.4

¹H N.M.R.

The ¹H N.M.R. spectrum of the soluble fraction was very complex. Purification is needed.

The ¹H N.M.R. spectrum of the insoluble fraction was also complex. The major peaks occur at 8.46 δ (2H, doublet; J = 1Hz), 9.38 δ (1H, triplet, J = 1Hz).

(iv) Nitration 4 of 2,8-Dinitrodibenzothiophene

A similar method to nitration 3 was adopted. This time the reaction mixture was stirred for 2 hours at room temperature, and trifluoromethanesulphonic (triflic) acid was used instead of conc. sulphuric.

The crude product from this reaction was a yellow solid.

Crude weight = 0.9460g

Yield (if tetranitro) = 73%

Melting point = 268-282⁰C (charring above 210⁰C)

H.P.L.C. results for crude product:-

PEAK	RETN. TIME (MINS)	AREA (%)
1	1.86	23.6
2	4.15	34.7
3	4.38	32.1
4	9.01	1.9
5	9.68	6.1

¹H N.M.R.

The ¹H N.M.R. spectrum of this crude product had major peaks at 8.42 δ (4H, triplet, J = 9Hz), 9.34 δ (1H, singlet). This spectrum has not been fully assigned.

(v) Nitration 5 of 2,8-Dinitrodibenzothiophene

A similar method to nitration 3 was adopted except that the reaction mixture was stirred at room temperature for 24 hours instead of 1 hour.

The crude product from this reaction was a yellow solid.

Crude weight = 1.0200g

Yield (if tetranitro) = 78%

Melting point = 240-256⁰C (charring above 200⁰C)

H.P.L.C. results of crude product :-

PEAK	RETN. TIME (MINS)	AREA (%)
1	1.92	26.0
2	4.16	44.7
3	4.39	28.1
4	9.90	1.2

¹H N.M.R.

This spectrum has not been fully assigned.

(vi) Nitration 6 of 2,8-Dinitrodibenzothiophene

A similar method to nitration 3 was adopted. The reaction mixture was stirred at 70°C for 2 hours. A yellow precipitate formed after about 1 hour and increased in mass until eventually the reaction mixture was a thick sludge.

The crude product from this reaction was a yellow solid.

Crude weight = 1.1486g

Yield (if tetranitro) = 88%

Melting point = 235-240°C (charring above 200°C)

H.P.L.C. results for crude product:-

PEAK	RETN. TIME (MINS)	AREA (%)
1	1.92	18.9
2	2.67	1.5
3	4.31	78.9
4	7.18	0.4

¹H N.M.R.

The ¹H N.M.R. spectrum of this crude product had major peaks at 8.30 δ (doublet, J = 8Hz), 8.40 δ (doublet J = 8Hz), 8.60 δ (doublet, J = 9Hz), 8.70 δ (doublet of doublets, J = 2Hz and J = 9Hz), 8.96 δ (singlet), 9.30 δ (doublet, J = 3Hz). This spectrum has not been fully assigned.

(vii) Nitration 7 of 2,8-Dinitrodibenzothiophene

An identical method to nitration 6 was adopted, with heating at 70°C for 6 hours instead of only 2.

The crude product from this reaction was a yellow solid.

Crude weight = 1.0981g

Yield (if tetranitro) = 84%

Melting point = 212-238°C (charring above 190°C)

H.P.L.C. results for crude product:-

PEAK	RETN. TIME (MINS)	AREA (%)
1	1.90	14.2
2	2.31	0.9
3	4.26	81.9
4	8.29	1.1

(+ other small peaks <1%)

An attempt was made to purify this product by recrystallisation from acetone but this had no significant effect. The next solvent tried was toluene. The recrystallisation produced three fractions; an insoluble fraction, a soluble fraction, and a residue recovered from the toluene when it was rotary evaporated down.

Soluble fraction :-

; Insoluble fraction :-

Weight = 0.0627g

Weight = 0.0160g

PEAK	RETN. TIME (MINS)	AREA (%)	PEAK	RETN. TIME (MINS)	AREA (%)
1	1.95	13.3	1	1.99	51.8
2	4.23	86.7	2	4.29	45.0
			3	9.27	1.1
			4	10.25	0.2
			5	11.27	1.9

Residue Weight = 0.1144g

PEAK	RETN. TIME (MINS)	AREA (%)
1	1.96	51.8
2	2.21	45.0
3	4.23	1.1
4	4.66	0.2

¹H N.M.R.

The ¹H N.M.R. spectrum of the soluble fraction has peaks at 8.40 δ (doublet, J = 8Hz), 8.71 δ (doublet of doublets, J = 2Hz and J = 9Hz), 8.89 δ (singlet), 8.95 δ (singlet), 9.30 δ (singlet), 9.31 δ doublet, J = 2Hz).

The ¹H N.M.R. spectrum of the insoluble fraction has peaks at 8.39 δ (doublet, J = 8Hz), 8.70 δ (doublet of doublets, J = 2Hz and J = 8Hz), 8.94 δ (singlet), 9.16 δ (doublet, J = 2Hz), 9.29 δ (singlet), 9.30 δ (doublet, J = 2Hz), 9.78 δ (doublet, J = 2Hz).

The ¹H N.M.R. spectrum of the residue has peaks at 8.30 δ (1H, doublet, J = 8Hz), 8.40 δ (1H, doublet, J = 8Hz), 8.60 δ (1H, doublet of doublets, J = 2Hz and J = 9Hz), 8.70 δ (1H, doublet of doublets, J = 2Hz and J = 8Hz), 8.72 δ (1H, singlet), 8.59 δ (singlet), 9.30 δ (3H, doublet of doublets, J = 2Hz and J = 3Hz).

All three spectra are quite complex and have not been fully assigned.

(viii) Nitration 8 of 2,8-Dinitrodibenzothiophene

Crude 2,8-dinitrodibenzothiophene (1g; 0.004 mole) was added slowly with stirring to a mixture of fuming nitric acid (3cm³) in triflic acid (5cm³). The yellow/brown starting material gave a dark brown solution. The mixture was stirred at room temperature overnight, poured into ice water, and the yellow precipitate formed was filtered, washed with water, and dried.

The crude product from this reaction was a yellow solid.

Crude weight = 1.0101g

Yield (if tetranitro) = 78%

Melting point = 260-276°C (charring above 185°C)

H.P.L.C. results for crude product:-

PEAK	RETN. TIME (MINS)	AREA (%)
1	1.92	17.1
2	2.20	3.6
3	4.20	45.0
4	4.43	30.4
5	10.34	1.4

¹H N.M.R.

The ¹H N.M.R. spectrum of this crude product is complex. It's major peaks occur at 8.40 δ (doublet, J = 1Hz), 8.44 δ (doublet of doublets, J = 1Hz and J = 3Hz), 8.47 δ (doublet, J = 1Hz), 9.35 δ (triplet, J = 1Hz).

This spectrum has not been fully assigned. Purification is necessary.

(ix) Nitration 9 of 2,8-Dinitrodibenzothiophene

A similar method to nitration 8 was used except that the reaction mixture was heated at 70⁰C for 3 hours.

The crude product from this reaction was a yellow solid.

Crude weight = 1.0784g ; Yield (if tetranitro) = 83%

Melting point = 222-258⁰C (charring above 190⁰C)

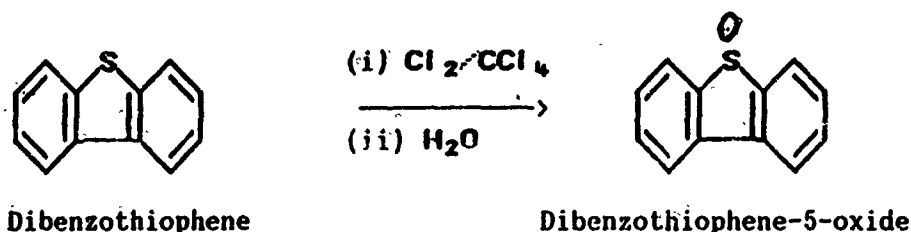
H.P.L.C. results of crude product

PEAK	RETN. TIME (MINS)	AREA (%)
1	1.87	18.7
2	4.30	75.9

¹H N.M.R.

The ¹H N.M.R. spectrum of this crude product is complex. Purification is necessary.

3.3.1 Synthesis of Dibenzothiophene-5-oxide²²



A solution of dibenzothiophene (15g) in carbontetrachloride (150cm³) was treated at 0-5°C with chlorine until 6g had been added. The solution turned red, and the addition compound produced was hydrolysed by vigorously shaking the reaction mixture with ice and water. The beige precipitate was filtered, washed with water, and dried. The crude product was recrystallised from toluene.

The crude product from this reaction was a beige solid.

Crude weight = 13.4712g

Yield = 84%

Expected melting point = 174-180°C

Actual melting point = 177-186°C

On recrystallisation from toluene the product was off white in colour.

Weight = 9.0925g

Yield = 57%

Expected melting point = 185-187°C

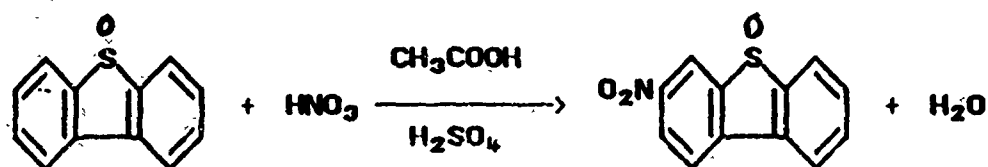
Actual melting point = 184-188°C

H.P.L.C. :- Retention time = 4.70mins; purity = 99.0%

¹H N.M.R. :-

The ¹H N.M.R. spectrum has peaks at 7.60 δ (2H, triplet of doublets, J = 1Hz and J = 8Hz), 7.75 δ (2H, triplet of doublets, J = 1Hz and J = 7Hz), 8.1 δ (2H, doublet of doublets, J = 1Hz and J = 7Hz), 8.15 δ (2H, doublet of doublets, J = 1Hz and J = 7Hz).

3.3.2 Synthesis of 3-Nitrodibenzothiophene-5-oxide²²



Dibenzothiophene-5-oxide

3-Nitrodibenzothiophene-5-oxide

To an ice cold mixture of dibenzothiophene-5-oxide (3g; 0.02mole), glacial acetic acid (10cm³), and conc. sulphuric acid (10cm³), was added with stirring fuming nitric acid (7.5cm³; sp.gr.1.5) over a period of 15 minutes. After the resulting clear solution had stood at 0-5°C for 30 minutes, it was poured into 40g of cracked ice. The gummy orange solid which was formed soon solidified and was filtered off and washed with water. It was recrystallised from ethanol.

The crude product from this reaction was a pink/orange solid.

Crude weight = 3.5800g

Yield = 97%

Expected melting point = 201-205°C

Actual melting point = 180-200°C

After recrystallisation from ethanol the product was an orange solid.

Weight = 1.7088g

Yield = 46%

Expected melting point = 209.5-210.5°C

Actual melting point = 198-204°C

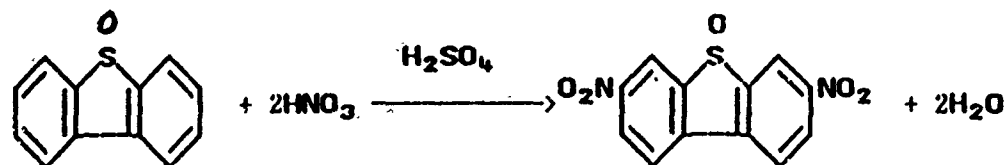
H.P.L.C. :- Retention time = 4.70mins; purity = 87.6%

¹H N.M.R. :-

The ¹H N.M.R. spectrum has peaks at 7.70 δ (1H, triplet of doublets, J = 1Hz and J = 7Hz), 7.80 δ (1H, triplet of doublets, J = 1Hz and J = 7Hz), 8.2 δ (1H, doublet, J = 7Hz), 8.30 δ (1H, doublet, J

= 8Hz), 8.40 δ (1H, doublet, $J = 4\text{Hz}$), 8.60 δ (1H, doublet of doublets, $J = 2\text{Hz}$ and $J = 8\text{Hz}$), 9.00 δ (1H, doublet, $J = 3\text{Hz}$).

3.3.3 Synthesis of 3,7-Dinitrodibenzothiophene-5-oxide²¹



Dibenzothiophene-5-oxide

3,7-Dinitrodibenzothiophene-5-oxide

A solution of dibenzothiophene-5-oxide (1g; 0.005mole) in conc. sulphuric acid (5cm³) was cooled to 12°C and fuming nitric acid (2cm³) was added slowly so that the reaction temperature remained at 10-15°C. The mixture was kept at this temperature for 30 minutes and then allowed to come to room temperature over a 30 minute period. The orange precipitate obtained by pouring the reaction mixture onto ice water was filtered, washed with water and dried. It was recrystallised from acetone.

The crude product from this reaction was a cream coloured solid.

Crude weight = 1.3943g

Yield = 96%

Expected melting point = 257-258°C

Actual melting point = 242-254°C

After recrystallisation from acetone the product was a pink/orange solid.

Weight = 0.5388g

Yield = 37%

Expected melting point = 257-258°C

Actual melting point = 257-260°C

H.P.L.C. : Retention time = 4.10mins; purity = 97.5%

¹H N.M.R. :-

The ¹H N.M.R. spectrum has peaks at 8.55 δ (2H, doublet, J = 8Hz, 8.60 δ (2H, doublet of doublets, J = 2Hz and J = 9Hz), 9.00 δ (2H, doublet, J = 2Hz).

3.3.4 Nitrations of 3,7-Dinitrodibenzothiophene-5-oxide

(i) Nitration 1 of 3,7-Dinitrodibenzothiophene-5-oxide

Crude 3,7-dinitrodibenzothiophene-5-oxide (0.5g;0.002mole) was added in small portions to a mixture of fuming nitric acid (2cm³) in triflic acid (2.5cm³). The reaction mixture was stirred at room temperature for 3 hours, poured into ice water, and the precipitate formed was filtered, washed with water, and dried in an oven at 70⁰C overnight.

The crude product from this reaction was a yellow solid.

Crude weight = 0.4800g.

Yield (if tetranitro) = 74%

Melting point = 234-250⁰C (charring above 180⁰C)

H.P.L.C. results for crude product:-

PEAK	RETN. TIME (MINS)	AREA (%)
1	4.11	90.9
2	4.51	5.1
3	8.98	4.0

¹H N.M.R.

The ¹H N.M.R. spectrum has peaks at 8.47 δ (2H, doublet, J = 8Hz), 8.55 δ (2H, doublet of doublets, J = 2Hz and J = 8Hz), 9.02 δ (2H, doublet, J = 2Hz). Both the H.P.L.C. retention time and the ¹H N.M.R. spectrum confirm that the major component from this reaction is unreacted 3,7-dinitrodibenzothiophene-5-oxide.

(ii) Nitration 2 of 3,7-dinitrodibenzothiophene-5-oxide

Crude 3,7-dinitrodibenzothiophene-5-oxide (1g; 0.003mole) was added in small portions with stirring to a mixture of fuming nitric acid (3cm³) in conc. sulphuric acid (5cm³). The reaction mixture was heated at 70°C for 2 hours with stirring, cooled, and poured into ice water. The precipitate formed was filtered, washed with water and dried. The crude product from this reaction was a pale yellow solid.

Crude weight = 0.8336g ; Yield (if tetranitro) = 64%

Melting point = 258-266°C (charring above 240°C)

H.P.L.C. results for crude product:-

PEAK	RETN. TIME (MINS)	AREA (%)
1	4.09	1.6
2	4.40	15.3
3	4.72	76.9
4	6.11	1.8
5	10.08	3.5

¹H N.M.R.

The ¹H N.M.R. spectrum of this crude product has peaks at 8.10 δ (1H, doublet, J = 9Hz), 8.61 δ (2H, doublet, J = 9Hz), 8.67 δ (1H, doublet, J = 9Hz), 8.68 δ (2H, doublet of doublets, J = 2Hz and J = 9Hz), 8.90 δ (2H, doublet, J = 2Hz), 9.08 δ (1H, doublet, J = 2Hz), 9.16 δ (1H, doublet, J = 2Hz), 9.36 δ (1H, doublet, J = 2Hz).

The major component corresponds to peaks at 8.61 δ, 8.68 δ, and 8.90 δ. These peaks correspond to the component with H.P.L.C. retention time 4.72 mins., and can be assigned to 3,7-dinitrodibenzothiophene-5,5-dioxide. The remaining peaks

correspond to the component with H.P.L.C. retention time 4.40 mins., and can be assigned to 1,3,7-trinitrodibenzothiophene-5,5-dioxide.

-(iii) Nitration 3 of 3,7-Dinitrodibenzothiophene-5-oxide

A similar method as for nitration 2 was used, except that triflic acid was used instead of conc. sulphuric acid.

The crude product from this reaction was a pale yellow solid.

Crude weight = 0.8820g

Yield (if tetranitro) = 68%

Melting point = 266-312⁰C (charring above 240⁰C)

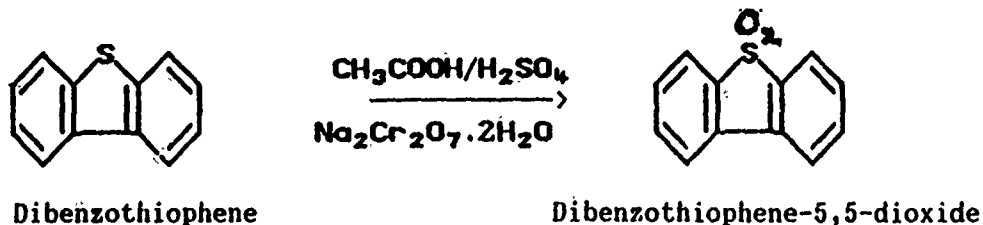
H.P.L.C. results for crude product:-

PEAK	RETN. TIME (MINS)	AREA (%)
1	4.07	0.7
2	4.44	9.9
3	4.71	83.8
4	6.08	1.7
5	10.10	3.2

¹H N.M.R.

The ¹H N.M.R. of this product was almost identical to that of nitration 2 and hence, due to the similarity in H.P.L.C. retention times, peak 3 can be assigned to 1,3,7-trinitrodibenzothiophene-5,5-dioxide and peak 4 to 3,7-dinitrodibenzothiophene-5,5-dioxide.

3.4.1 Synthesis of Dibenzothiophene-5,5-dioxide²³



To a cold mixture of glacial acetic acid (110cm³), 50% sulphuric acid (40cm³), and sodium dichromate (18g) was added dibenzothiophene (11g; 0.06mole). The mixture was kept at 60°C and shaken for half an hour, after which the temperature started to drop. The reaction mixture was poured into ice water and the yellowish heavy precipitate was filtered off, washed with water, and dried. the crude product was recrystallised from toluene.

The crude product from this reaction was a cream coloured solid.

Crude weight = 10.7400g

Yield = 83%

Expected melting point = 232°C

Actual melting point = 229-234°C

After recrystallisation from toluene the product was an off white solid.

Weight = 3.0713g

Yield = 24%

Expected melting point = 232°C

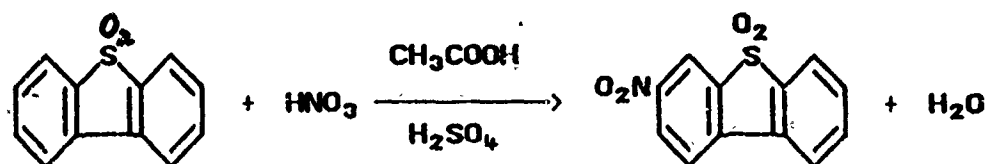
Actual melting point = 229-234°C

H.P.L.C. :- Retention time = 4.14mins; purity = 99.0%

¹H N.M.R. :-

The ¹H N.M.R. spectrum has peaks at 7.70 δ (2H, triplet, J = 7Hz), 7.80 δ (2H, triplet, J = 7Hz), 8.00 δ (2H, doublet, J = 7Hz) , 8.20 δ (2H, doublet, J = 8Hz).

3.4.2 Synthesis of 3-Nitrodibenzothiophene-5,5-dioxide²³



Dibenzothiophene-5,5-dioxide 3-Nitrodibenzothiophene-5,5-dioxide

To a mixture of glacial acetic acid (5cm³) and conc. sulphuric acid (5cm³) in a three necked flask equipped with stirrer, thermometer, and dropping funnel was added dibenzothiophene-5,5-dioxide (1g; 0.005mole). A yellow paste formed and this was kept at a temperature of 4°C while fuming nitric acid (3.5g; sp.gr.1.5) was added over a five minute period. After stirring for one-half hour, the reaction mixture was poured into ice water (100cm³) and the yellow precipitate formed was filtered, washed with water, and dried. The crude product was recrystallised from acetone.

The crude product from this reaction was an orange/yellow solid.

Crude weight = 1.1530g

Yield = 89%

Expected melting point = 265-266°C

Actual melting point = 246-262°C

After recrystallisation twice from acetone and twice from dioxane the product was a pink solid.

Weight = 0.0948g

Yield = 7%

Expected melting point = 265-266°C

Actual melting point = 253-266°C

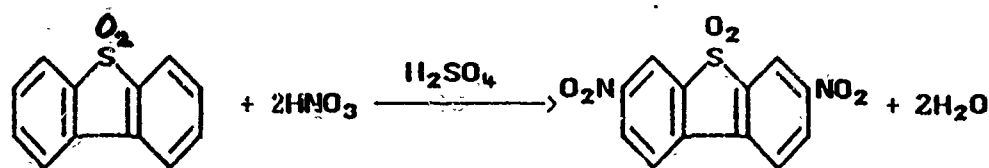
H.P.L.C. :- Retention time = 4.60mins; purity = 98.9%

¹H N.M.R. :-

The ¹H N.M.R. spectrum has peaks at 7.80 δ (1H, triplet, J = 7Hz), 7.90 δ (1H, triplet, J = 7Hz), 8.15 δ (1H, doublet, J = 7Hz), 8.40

δ (1H, doublet, $J = 8\text{Hz}$), 8.50 δ (1H, doublet, $J = 9\text{Hz}$), 8.70 δ (1H, doublet of doublets, $J = 2\text{Hz}$ and $J = 8\text{Hz}$), 8.89 δ (1H, doublet, $J = 2\text{Hz}$).

3.4.3 Synthesis of 3,7-Dinitrodibenzothiophene-5,5-dioxide²⁴



Dibenzothiophene-5,5-dioxide 3,7-Dinitrodibenzothiophene-5,5-dioxide

To a cold solution of dibenzothiophene-5,5-dioxide (1g; 0.005 mole) in conc. sulphuric acid (5cm³), fuming nitric acid (3cm³; sp.gr. 1.5) was added dropwise with shaking; the temperature rose to 60-70°C. The product was heated on a boiling water bath for 40 minutes, cooled, and poured into ice water. The white precipitate formed was filtered, washed with water, and dried. The crude product was recrystallised from acetone.

The crude product from this reaction was a yellow solid.

Crude weight = 1.2610g

Yield = 82%

Expected melting point = 290°C

Actual melting point = 262-278°C

After recrystallisation twice from acetone the product was a bright yellow crystalline solid.

Weight = 0.1340g

Yield = 31%

Expected melting point = 290°C

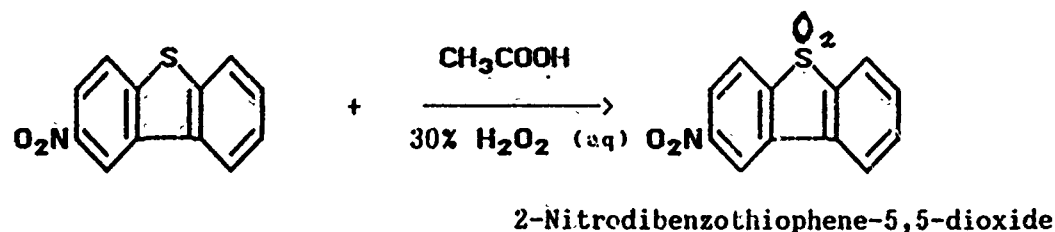
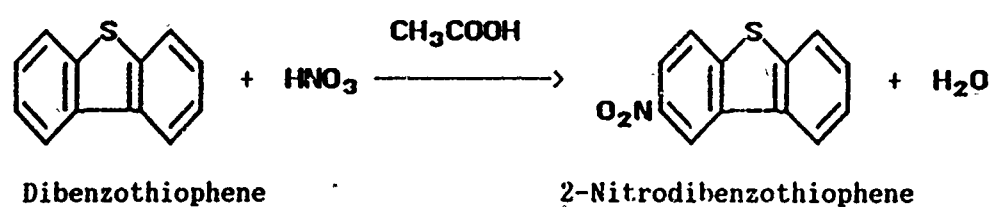
Actual melting point = 282-287°C

H.P.L.C. :- Retention time = 4.60mins; purity = 72.5%

¹H N.M.R. :-

The ¹H N.M.R. spectrum has peaks at 8.65 δ (2H, doublet, J = 8Hz), 8.70 δ (2H, doublet of doublets, J = 2Hz and J = 8Hz), 9.00 δ (2H, doublet, J = 2Hz).

3.4.4 Synthesis of 2-Nitrodibenzothiophene-5,5-dioxide²¹



A solution of 2-nitrodibenzothiophene²⁰ (2.2g; 0.01mole) in glacial acetic acid (60cm³) was refluxed with 30% hydrogen peroxide (11cm³) following the directions of Gilman and Nobis⁶. The solution was heated at 90°C for one hour and then refluxed for thirty minutes. A second quantity of hydrogen peroxide (7cm³) was then added and refluxing continued for an additional 20 minutes. The solid was removed from the cooled mixture and washed with a small amount of cold acetic acid. The crude product was recrystallised from acetone.

The crude product from this reaction was a pale yellow solid.

Crude weight = 1.2678g

Yield = 51%

Expected melting point = 249-250°C

Actual melting point = 190-200°C

After recrystallisation from acetone the product was still a pale yellow solid.

Weight = 1.1648g

Yield = 47%

Expected melting point = $249-250^{\circ}\text{C}$

Actual melting point = $195-216^{\circ}\text{C}$

H.P.L.C. :- Retention time = 4.10mins; purity = 54.3%

^1H N.M.R. :-

The ^1H N.M.R. spectrum has peaks at 7.70 δ (1H, triplet, $J = 7\text{Hz}$), 7.90 δ (1H, triplet of doublets, $J = 1\text{Hz}$ and $J = 7\text{Hz}$), 8.00 δ (1H, doublet, $J = 8\text{Hz}$), 8.10 δ (1H, doublet, $J = 8\text{Hz}$), 8.20 δ (1H, doublet, $J = 8\text{Hz}$), 8.44 δ (1H, doublet of doublets, $J = 2\text{Hz}$ and $J = 7\text{Hz}$), 9.00 δ (1H, doublet, $J = 2\text{Hz}$).

3.4.5 Nitration of Dibenzothiophene-5,5-dioxide with forcing conditions

Dibenzothiophene-5,5-dioxide (1g; 0.005mole) was added slowly with stirring to a mixture of fuming nitric acid (2.5cm^3 ; sp.gr. 1.5) in conc. sulphuric acid (5cm^3) kept at 50°C . The mixture was heated at 90°C for 2 hours, cooled and poured into ice water. The yellow precipitate was filtered, washed with water, and dried. The crude product was recrystallised from acetone.

The crude product from this reaction was a pale yellow solid.

Crude weight = 1.0500g

Yield (if tetranitro) = 53%

Melting point = $226-266^{\circ}\text{C}$

After recrystallisation twice from acetone the product was still a pale yellow solid.

Weight = 0.3911g

Yield (if tetranitro) = 20%

Melting point = 236-270°C

H.P.L.C. results :-

PEAK	RETN. TIME (MINS)	AREA (%)
1	2.05	0.1
2	4.21	32.4
3	4.52	65.5
4	5.60	2.0

¹H N.M.R.

The ¹H N.M.R. spectrum of this product has peaks at 8.10 δ (1H, doublet, J = 9Hz), 8.63 δ (2H, doublet, J = 8Hz), 8.67 δ (1H, doublet, J = 9Hz), 8.69 δ (2H, doublet of doublets, J = 2Hz and J = 8Hz), 8.93 δ (2H, doublet, J = 2Hz), 9.10 δ (1H, doublet, J = 2Hz), 9.20 δ (1H, doublet, J = 2Hz), 9.34 δ (1H, doublet, J = 2Hz).

If the ¹H N.M.R. spectrum of 3,7-dinitrodibenzothiophene-5,5-dioxide is extracted from these peaks, the remaining peaks can be assigned to 1,3,7-trinitrodibenzothiophene-5,5-dioxide. The ¹H N.M.R. shows that the major component is 3,7-dinitro-, hence from the H.P.L.C. 3,7-dinitro- is the peak with retention time 4.52 mins. and 1,3,7-trinitro- is the peak with retention time 4.21 mins..

3.4.6 Nitration of 3,7-Dinitrodibenzothiophene-5,5-dioxide

(i) Nitration 1 of 3,7-Dinitrodibenzothiophene-5,5-dioxide

A mixture of fuming nitric acid (2cm³) and conc. sulphuric acid (2cm³) was held at room temperature and 3,7-dinitrodibenzothiophene-5,5-dioxide (0.5g;0.002mole) was added slowly with stirring. When the addition was complete the mixture was heated under reflux for 4 hours, cooled, and poured into ice water.

The pale yellow precipitate was filtered, washed copiously with water, and dried.

The crude product from this reaction was a yellow solid.

Crude weight = 0.3520g

Yield (if tetranitro) = 54%

Melting point = 250-358⁰C (charring above 210⁰C)

H.P.L.C. results for crude product:-

PEAK	RETN. TIME (MINS)	AREA (%)
1	3.99	9.5
2	4.31	48.5
3	4.67	39.0
4	5.92	2.0
5	9.83	1.0

The crude product was washed with acetone (3cm³) to see if any of the peaks was more soluble than the others. The soluble and insoluble fractions were analysed by H.P.L.C. and ¹H N.M.R.

Soluble fraction :-

; Insoluble fraction :-

Weight = 0.0030g

Weight = 0.1170g

H.P.L.C. results

PEAK	RETN. TIME (MINS)	AREA (%)	PEAK	RETN. TIME (MINS)	AREA (%)
1	1.92	2.0	1	1.88	1.0
2	4.16	4.0	2	4.04	6.0
3	4.39	30.0	3	4.35	38.0
4	4.77	55.0	4	4.73	43.0
5	6.17	8.0	5	6.09	12.0

¹H N.M.R.

The ¹H N.M.R. spectrum of the insoluble fraction was identical to that of the nitration of dibenzothiophene-5,5-dioxide with forcing conditions. The only difference was that the ratio of 1,3,7-trinitro- to 3,7-dinitrodibenzothiophene-5,5-dioxide was greater. Hence, by comparison of H.P.L.C. retention times, 1,3,7-trinitro- can be assigned to the peak with retention time 4.3-4.4 minutes, and 3,7-dinitro- to the peak with retention time 4.7-4.8 minutes.

(ii) Nitration 2 of 3,7-Dinitrodibenzothiophene-5,5-dioxide

A similar method to nitration 1 was used, except that the reaction mixture was refluxed for 7 hours instead of 4.

The crude product from this reaction was a pale yellow solid.

Crude weight = 0.3937g

Yield (if tetranitro) = 61%

Melting point = 240-258⁰C (charring above 220⁰C)

H.P.L.C. results :-

PEAK	RETN. TIME (MINS)	AREA (%)
1	2.04	0.6
2	4.05	7.0
3	4.36	48.5
4	4.72	43.9

¹H N.M.R.

The ¹H N.M.R. spectrum was almost identical to that of nitration 1. The crude product is therefore a mixture of 1,3,7-trinitro- (retn. time 4.36 mins) and unreacted 3,7-dinitrodibenzothiophene-5,5-dioxide (retn. time 4.72 mins).

(iii) Nitration 3 of 3,7-Dinitrodibenzothiophene-5,5-dioxide

To a cold solution of 3,7-dinitrodibenzothiophene-5,5-dioxide (1g;0.03mole) in conc. sulphuric acid (5cm³), nitric acid (3cm³) was added dropwise with shaking. The reaction mixture was heated on a steam bath for 2 hours, cooled, and poured onto ice water. The white precipitate formed was filtered, washed with water, and dried.

The crude product from this reaction was a pale yellow solid.

Crude weight = 0.7667g

Yield (if tetranitro) = 59%

Melting point = 230-240⁰C (charring above 225⁰C)

H.P.L.C. results :-

PEAK	RETN. TIME (MINS)	AREA (%)
1	1.82	1.9
2	4.00	3.3
3	4.22	43.2
4	4.53	51.6

¹H N.M.R.

The ¹H N.M.R. spectrum was almost identical to that of nitration

1. The crude product is therefore a mixture of 1,3,7-trinitro- (retn. time 4.22 mins) and unreacted 3,7-dinitrodibenzothiophene-5,5-dioxide (retn. time 4.53 mins).

(iv) Nitration 4 of 3,7-Dinitrodibenzothiophene-5,5-dioxide

A similar method to nitration 3 was used except that triflic acid replaced conc. sulphuric acid, and the reaction mixture was heated for 5 hours on a steam bath instead of 2.

The crude product from this reaction was a pale yellow solid.

Crude weight = 0.8590g

Yield (if tetranitro) = 66%

Melting point = 238-340⁰C (charring above 230⁰C)

H.P.L.C. results :-

PEAK	RETN. TIME (MINS)	AREA (%)
1	1.82	0.6
2	3.97	1.7
3	4.20	28.6
4	4.52	69.1

¹H N.M.R.

The ¹H N.M.R. spectrum was almost identical to that of nitration

1. The crude product is therefore a mixture of 1,3,7-trinitro- (retn. time 4.20 mins) and unreacted 3,7-dinitrodibenzothiophene-5,5-dioxide (retn. time 4.52 mins).

(v) Nitration 5 of 3,7-Dinitrodibenzothiophene-5,5-dioxide

A similar method to nitration 1 was used except that the reaction mixture was heated at 90⁰C on a steam bath for 6 hours.

The crude product from this reaction was a pale yellow solid.

Crude weight = 0.8240g

Yield (if tetranitro) = 63%

Melting point = 230-240⁰C (charring above 210⁰C)

H.P.L.C. results :-

PEAK	RETN. TIME (MINS)	AREA (%)
1	1.91	1.7
2	3.97	7.5
3	4.29	46.0
4	4.65	44.1

¹H N.M.R.

The ¹H N.M.R. spectrum was almost identical to that of nitration

1. The crude product is therefore a mixture of 1,3,7-trinitro- (retn. time 4.29 mins) and unreacted 3,7-dinitrodibenzothiophene-5,5-dioxide (retn. time 4.65 mins).

(vi) Nitration 6 of 3,7-Dinitrodibenzothiophene-5,5-dioxide

A similar method to nitration 5 was used except that after 6 hours of heating on a steam bath the reaction mixture was left standing at room temperature overnight, then heated for a second 6 hours, then left standing over the weekend before being heated for a final 6 hours.

The crude product from this reaction was a pale yellow solid.

Crude weight = 0.7768g

Yield (if tetranitro) = 60%

Melting point = 255-260°C (charring above 240°C)

H.P.L.C. results :-

PEAK	RETN. TIME (MINS)	AREA (%)
1	1.90	1.8
2	4.01	9.5
3	4.33	53.0
4	4.74	27.2
5	6.19	8.5

¹H N.M.R.

The ¹H N.M.R. spectrum was almost identical to that of nitration

1. The crude product is therefore a mixture of 1,3,7-trinitro- (retn. time 4.33 mins) and unreacted 3,7-dinitrodibenzothiophene-5,5-dioxide (retn. time 4.74 mins).

(vii) Nitration 7 of 3,7-Dinitrodibenzothiophene-5,5-dioxide

A similar method to nitration 6 was used except that triflic

acid was used instead of conc. sulphuric acid.

The crude product from this reaction was a pale yellow solid.

Crude weight = 0.6920g

Yield (if tetranitro) = 53%

Melting point = 235-310°C (charring above 230°C)

H.P.L.C. results :-

PEAK	RETN. TIME (MINS)	AREA (%)
1	1.90	1.9
2	4.00	6.3
3	4.33	37.2
4	4.72	50.3
5	6.12	3.8

¹H N.M.R.

The ¹H N.M.R. spectrum was almost identical to that of nitration 1. The crude product is therefore a mixture of 1,3,7-trinitro- (retn. time 4.33 mins) and unreacted 3,7-dinitrodibenzothiophene-5,5-dioxide (retn. time 4.72 mins).

(viii) Nitration 8 of 3,7-Dinitrodibenzothiophene-5,5-dioxide

Crude 3,7-dinitrodibenzothiophene-5,5-dioxide (10g; 0.03mole) was added slowly with stirring to a mixture of fuming nitric acid (15cm³) in conc. sulphuric acid (30cm³) in a three necked round bottomed flask equipped with thermometer and reflux condenser. The mixture was refluxed at 110-115°C for 4 hours. After about 1 hour the solid began to precipitate out, so a further solution of fuming nitric acid (15cm³) in conc. sulphuric acid (30cm³) was added. This happened again after about 3 hours and again the same acid mixture was added. However, this time the precipitate would not redissolve.

After 4 hours of refluxing the mixture was cooled, poured onto ice water, and the precipitate formed was filtered, washed with water and dried. Recrystallisation was tried using methanol, acetone, ethyl acetate, carbontetrachloride, and toluene. Toluene was found to be the most suitable.

The crude product from this reaction was a pale yellow solid.

Crude weight = 7.5900g

Yield (if tetranitro) = 59%

Yield (if trinitro) = 72%

Melting point = 280-285°C

H.P.L.C. results for the crude product :-

PEAK	RETN. TIME (MINS)	AREA (%)
1	1.93	1.7
2	4.01	19.6
3	4.33	76.9
4	6.90	1.2

After recrystallisation from toluene (50 cm³/g, reduced to 20 cm³/g to obtain a precipitate) there was a soluble fraction, an insoluble fraction, and a residue recovered from the toluene filtrate. All three fractions were analysed by H.P.L.C. and ¹H N.M.R..

Soluble fraction :-

Weight = 2.7324g

Insoluble fraction :-

Weight = 2.2770g

Soluble fraction
H.P.L.C. results

; Insoluble fraction

PEAK	RETN. TIME (MINS)	AREA (%)	PEAK	RETN. TIME (MINS)	AREA (%)
1	1.93	0.7	1	1.91	1.1
2	4.33	94.3	2	4.31	86.7
3	6.18	5.0	3	6.10	12.2

Residue = 1.2144g

H.P.L.C. results

PEAK	RETN. TIME (MINS)	AREA (%)
1	1.96	2.0
2	2.53	0.3
3	4.26	97.5
4	5.57	0.1
5	9.61	0.1

The peak at retention time approx. 4.3 mins. corresponds to
1,3,7-trinitrodibenzothiophene-5,5-dioxide.

Melting point (purity 94%) = 282-290°C.

¹H N.M.R.

The ¹H N.M.R. spectrum of relatively pure 1,3,7-trinitrodibenzothiophene-5,5-dioxide has peaks at 8.10 δ (1H, doublet, J = 9Hz), 8.67 δ (1H, doublet of doublets, J = 2Hz and J = 9Hz), 9.07 δ (1H, doublet, J = 2Hz), 9.16 δ (1H, doublet, J = 2Hz), 9.35 δ (1H, doublet, J = 2Hz).

4. RESULTS AND DISCUSSION

4.1 Carbazole

Literature syntheses of the mononitrocarbazoles gave poor yields. These compounds were difficult to purify and consequently had complex ^1H N.M.R. spectra that were difficult to interpret. The dinitrocarbazoles were produced in better yields and their ^1H N.M.R. spectra were easy to interpret. TNC was synthesised and purified in a number of ways to try to find the best method. A summary of these syntheses is given in the table overleaf.

It can be seen from the table that a high degree of purity of 1,3,6,8-TNC has been achieved. However, it seems that there is a balance between purity and yield. High purity must be achieved for the material to be compatible for pyrotechnic use, but high yields must also be achieved for large scale synthesis to be viable.

ROUTE TO 1,3,6,8-TNC	CRUDE YIELD (%)	PURIFICATION TECHNIQUE	OVERALL YIELD (%)	APPROX. PURITY (%)	Mpt. (°C) EXPECTED 296-298
REF. 18	63	--	--	--	250-276
REF. 13	79	90% Aq. ACETONE WASH. RECRYST. FROM TOLUENE	13	99.8	295-300
TWO STEP NITRATION: 1) SMALL SCALE	69	a) WASHED IN BOILING WATER. RECRYST. FROM TOLUENE. b) SOXHLET EXTRACTION FROM TOLUENE.	32	99.0	294-298
2) LARGE SCALE	i) 80	TWO REPEATED	59	97.0	295-300
	ii) 89	RECRYSTS. OF CRUDE TNC EACH USING 2 LITRES OF TOLUENE.	59	97.0	290-295

4.1.1 Comparative T.L.C.

All compounds of carbazole that had been made were spotted on one T.L.C. plate together, and eluted in hexane/ethyl acetate (50:50) to see how they would compare.

SAMPLE No.	NAME/ORIG	Rf VALUES
JC 0	Carbazole	0.67;0.58;0.46
JC 1	3-Nitro-	0.65;0.51;0.36
JC 2	3,6-DNC	0.25
JC 3	1,6-DNC	0.63
JC 4	1,6 + 3,6-	0.63;0.26
JC 5	1-Nitro-	0.59;0.45;0.00
JC 6	1,3,6,8-TNC (4.4.2)	0.66;0.60;0.56
JC 8	DNC + Acids (4.6.1)	0.63;0.26
JC 9	Carbazole+Acids(4.6.1)	0.70;0.64;0.60;0.50;0.29;0.22
JC 10	Carbazole+Acids+Δ(4.6.1)	0.61;0.50;0.30;0.00
JC 11	Carbazole+Acids(4.6.2)	0.63;0.49;0.41;0.30;0.00

A rough indication of the components of the crude compounds can be drawn from the table above.

4.2 Dibenzothiophene

The literature syntheses of mono- and dinitrodibenzothiophenes gave lower yields than reported. The products were difficult to purify due to insolubility, and a large percentage of the yield was lost on purification. Impurity and insolubility caused problems in obtaining a clear ^1H N.M.R. spectrum, especially for 2-nitro- and 2,8-dinitrodibenzothiophene. However, the ^1H N.M.R. spectrum of dibenzothiophene itself is slightly complex and not quite what is expected.

The fact that dibenzothiophene-5-oxide was the major product in the synthesis of 2-nitrodibenzothiophene gives an indication of how easily dibenzothiophene is oxidised. Ease of oxidation is one reason why the nitration of dibenzothiophene and 2,8-dinitrodibenzothiophene produced mixtures of products.

4.3 Dibenzothiophene-5-oxide

Literature syntheses of mono- and dinitro- compounds were cleaner than those of dibenzothiophene, but purification still gave problems due to insolubility. Impurities in these products are likely to come from oxidation to the dioxide. The ^1H N.M.R. spectra were clear and easily interpreted.

4.4 Dibenzothiophene-5,5-dioxide

Literature syntheses of the mono- and dinitro- compounds were cleaner than both of the previous groups, but again purification was a problem. Unlike carbazole, this compound is difficult to tetra-nitrate but can be tri-nitrated. ^1H N.M.R. spectra of these compounds were clear and easily interpreted.

5. CONCLUSIONS

5.1 Carbazole

Nitrocarbazole samples synthesised include 3- and 1-nitrocarbazoles, 3,6- and 1,6-dinitrocarbazoles, and 1,3,6,8-tetranitrocarbazole. The 3- and 1-nitrocarbazoles have not been fully characterised due to the complexity of their ^1H N.M.R. spectra.

1,3,6,8-TNC has been synthesised and purified in a variety of ways. At present 100g of 1,3,6,8-TNC, purity approximately 97%, has been sent for testing, as it is not yet certain whether it is the amount of impurity or the type of impurities that cause erratic behaviour of pyrotechnic compositions. Paul and Honey¹³ have also produced pure 1,3,6,8-TNC, suitable for pyrotechnic use, with yields of 40-50%. However, their purification procedures involve a methanol wash and a sulphite wash before toluene recrystallisation.

5.2 Dibenzothiophene

Nitrodibenzothiophene samples synthesised include 2-nitro-, 2,8-dinitro-, 3-nitro-, and 3,7-dinitrodibenzothiophene. The products from nitration of dibenzothiophene with forcing conditions, and from the various nitrations of 2,8-dinitrodibenzothiophene have not been identified at this stage. ¹H N.M.R. spectra of crude products are often complex. The major components must be separated from the mixtures. This can be achieved by preparative H.P.L.C., if use of a column becomes available, or by flash column chromatography.

5.3 Dibenzothiophene-5-oxide

Nitrodibenzothiophene-5-oxide samples synthesised include 3-nitro-, and 3,7-dinitrodibenzothiophene-5-oxide. Nitration of 3,7-dinitrodibenzothiophene-5-oxide will not take place if conditions are not strongly nitrating (as seen in nitration 1), but if conditions are too powerfully oxidising the result is a mixture of 3,7-dinitro- and 1,3,7-trinitrodibenzothiophene-5,5-dioxide. Conditions will have to be carefully controlled if nitration is to be achieved without oxidation.

5.4 Dibenzothiophene-5,5-dioxide

Nitrodibenzothiophene-5,5-dioxide samples synthesised include 3-nitro-, 3,7-dinitro-, and 2-nitrodibenzothiophene-5,5-dioxide. Oxidation of 2,8-dinitrodibenzothiophene was not attempted as previous attempts²¹ have failed. The nitration of dibenzothiophene-5,5-dioxide with forcing conditions, and the various nitrations of 3,7-dinitrodibenzothiophene-5,5-dioxide have all produced mixtures of 1,3,7-trinitro-, and the unreacted 3,7-dinitro-. These reactions are summarised in the table overleaf.

REACTION	CONDITIONS	3,7-DINITRO-	1,3,7-TRINITRO-
Nit. of dibenz- -5,5-dioxide	90 ⁰ C/2Hrs./in H ₂ SO ₄	66%	33%
Nit.1 (3,7-Dinitro- 5,5-dioxide)	Reflux/4Hrs/in H ₂ SO ₄	39%	48%
Nit.2 ,,	Reflux/7Hrs/in H ₂ SO ₄	44%	49%
Nit.3 ,,	S. Bath/2Hrs/in H ₂ SO ₄	52%	43%
Nit.4 ,,	S. Bath/5Hrs/CF ₃ SO ₃ H	69%	29%
Nit.5 ,,	90 ⁰ C/6Hrs/H ₂ SO ₄	44%	46%
Nit.6 ,,	90 ⁰ C/6Hrs * 3 Days/ H ₂ SO ₄	27%	53%
Nit.7 ,,	90 ⁰ C/6Hrs * 3 Days/ CF ₃ SO ₃ H	50%	37%
Nit.8 ,,	110 ⁰ C/6Hrs/ H ₂ SO ₄	0%	77%

It can be seen from the table that nitration is influenced by temperature and, to a lesser extent, by time. As expected, higher temperatures and longer times both appear to increase the extent of reaction. The table also shows that reactions done in sulphuric acid have nitrated further than those done in triflic acid. This is an unexpected result as triflic acid is the stronger, less oxidative of the two acids. This behaviour could be due to the fact that triflic acid is very hygroscopic; in addition it was used in almost a 1:1 ratio with nitric acid and this could have reduced its acidity. In future reactions with triflic acid it must be used in large excess, or with potassium/sodium nitrite rather than HNO₃. Synthesis of 1,3,7,9-tetranitrodibenzothiophene-5,5-dioxide will probably only be achieved by nitration of 1,3,7-trinitrodibenzothiophene-5,5-dioxide under reflux in mixed fuming nitric and conc. sulphuric acids.

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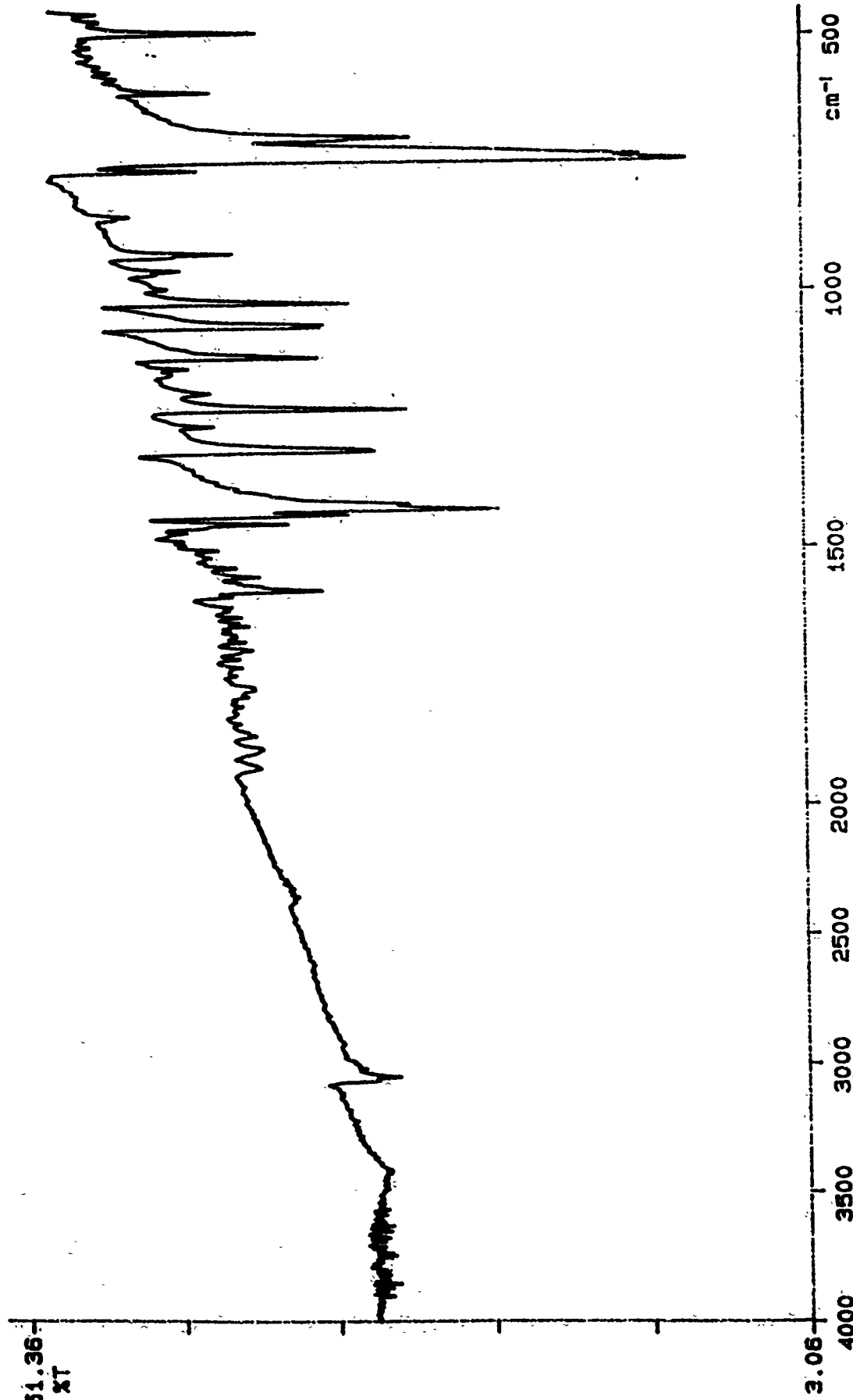
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7. SPECTRA

P.E

51.36
XT



90/08/10 15:29
X: 4 scans, 4.0cm-1. flat
Dibenzothiophene

FX

BIPHENYLTHIOPHENE



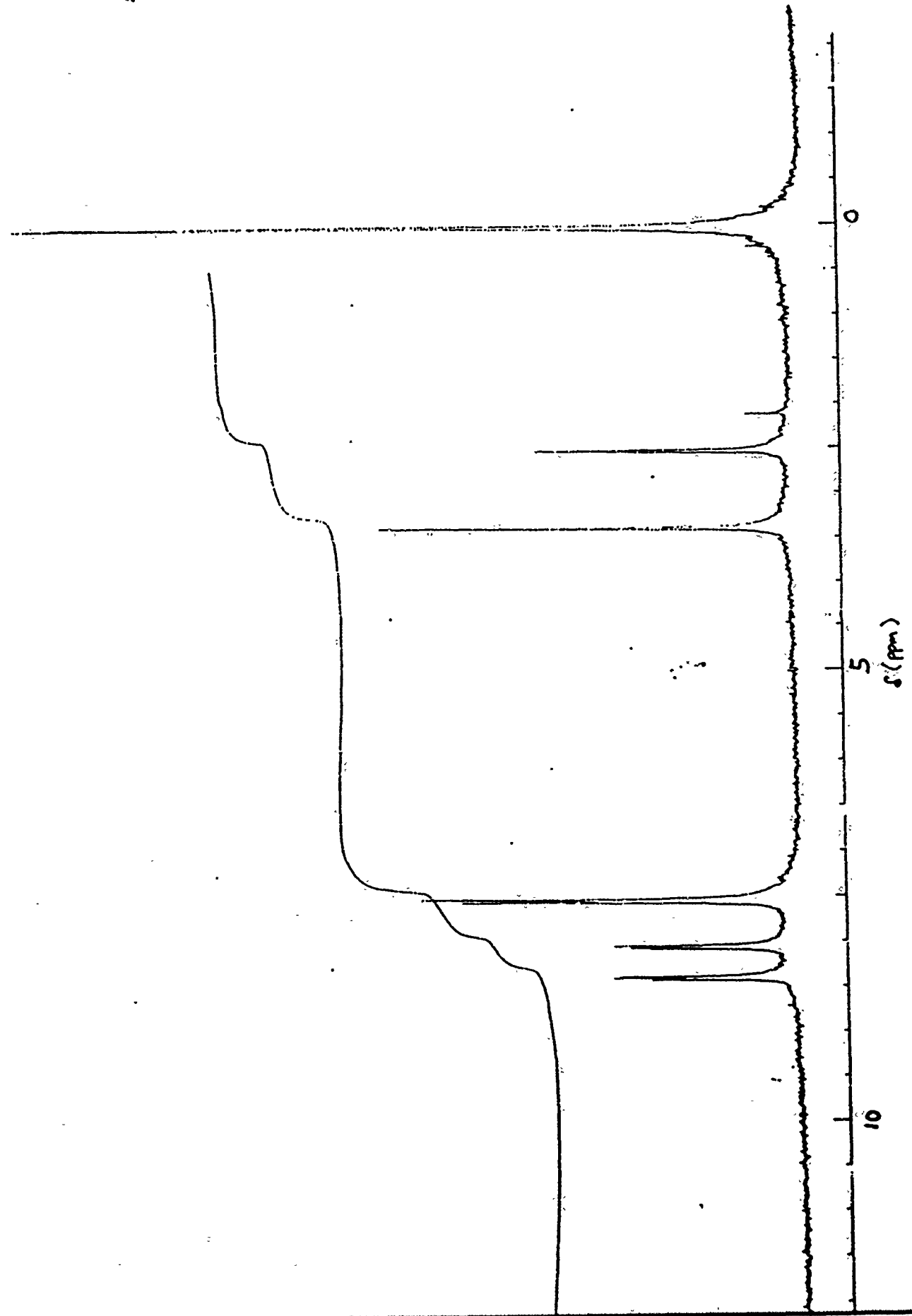
21.0
7M5
10mg/L
5

H

83.0

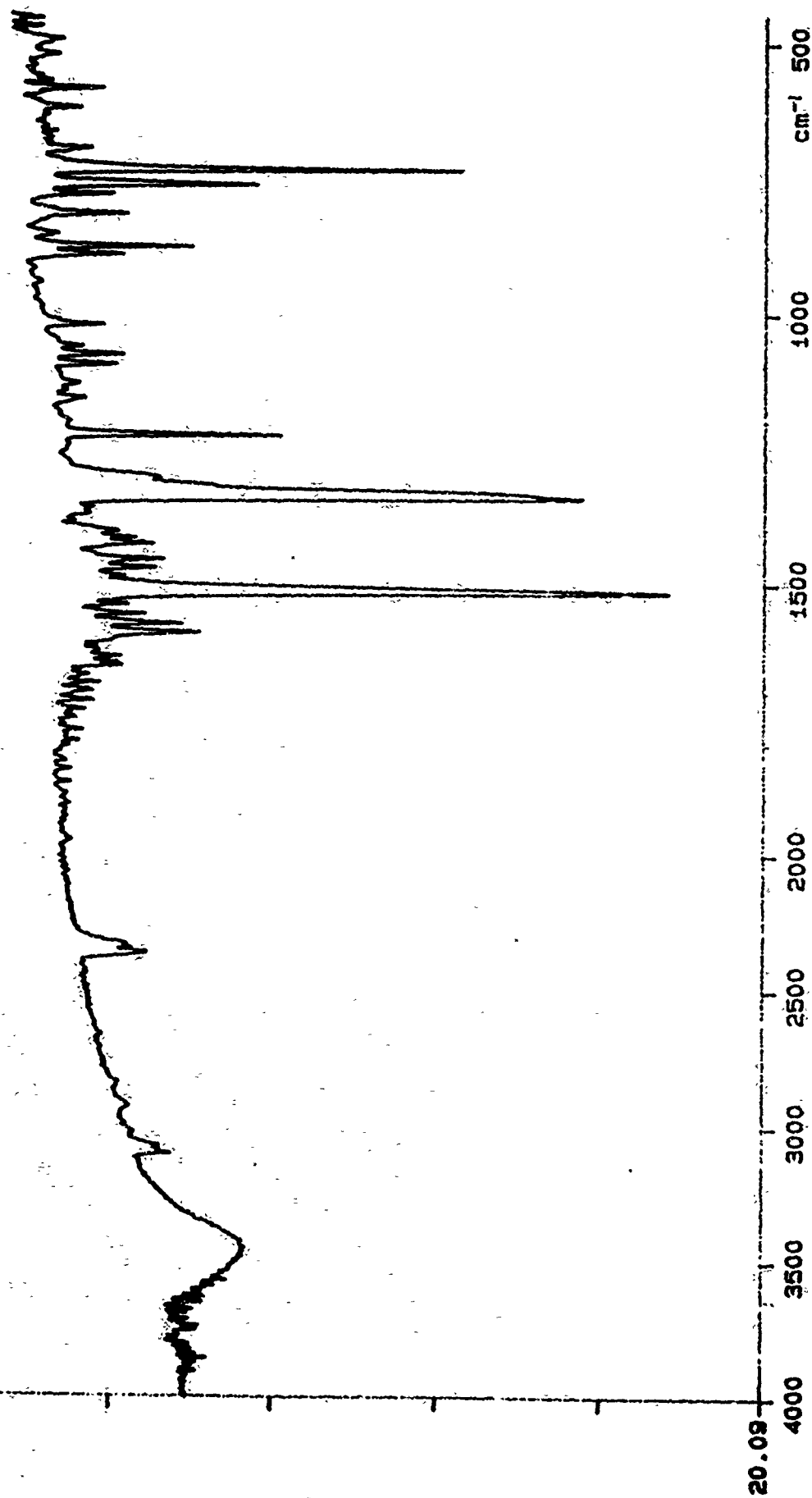
24
+000

12/6/90
J.C.



P-E

95.77
ST



90/08/10 15:53
X: 4 scans, 4.0cm-1
2 Nitrobenzothiothiophene

FX

2-NITROBENZOTHIOPHENE

FX

2-NITROBENZOTHIOPHENE



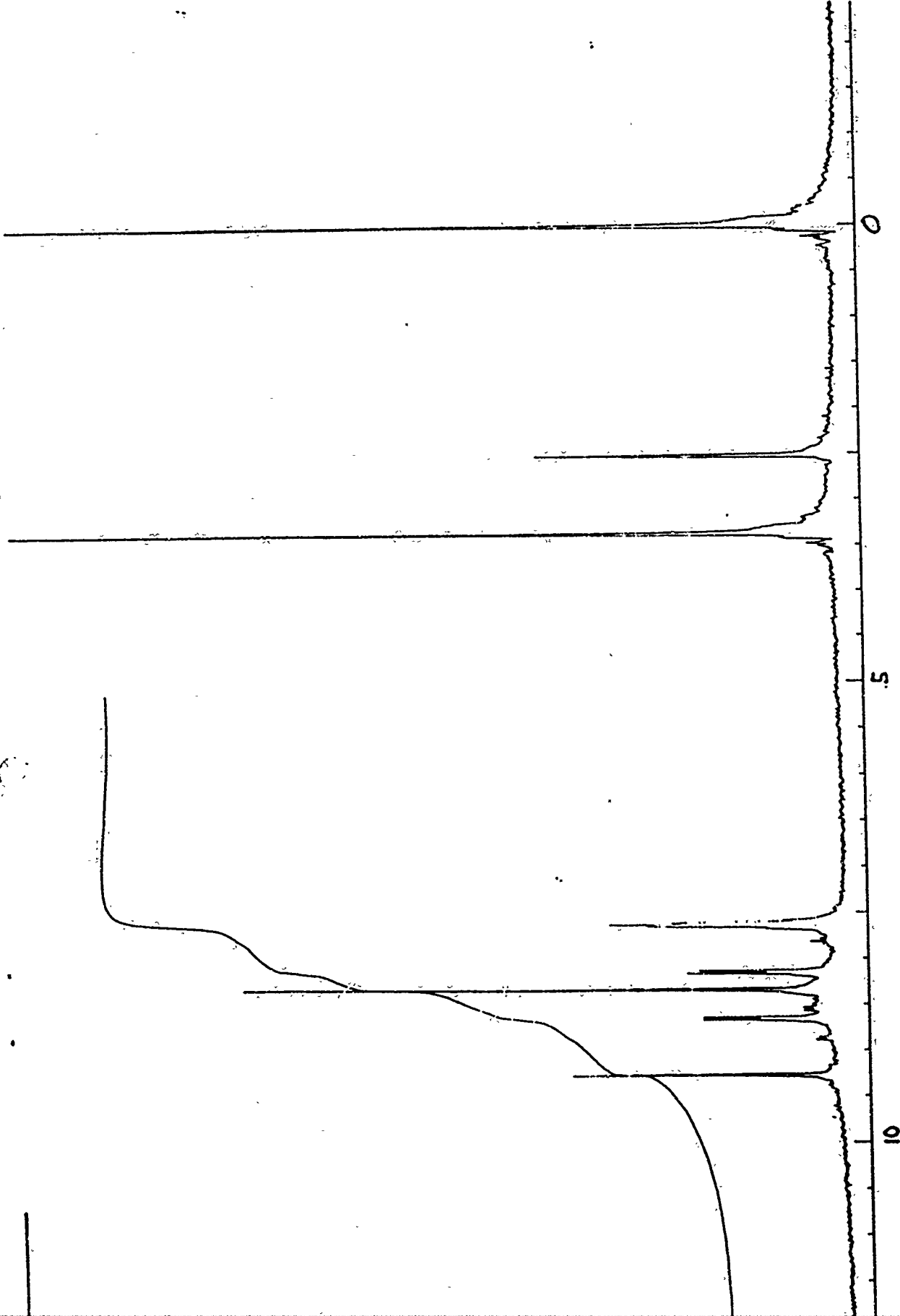
DMISO 5
100%
TMS
22.1 °C

¹H ✓

83.0 ✓

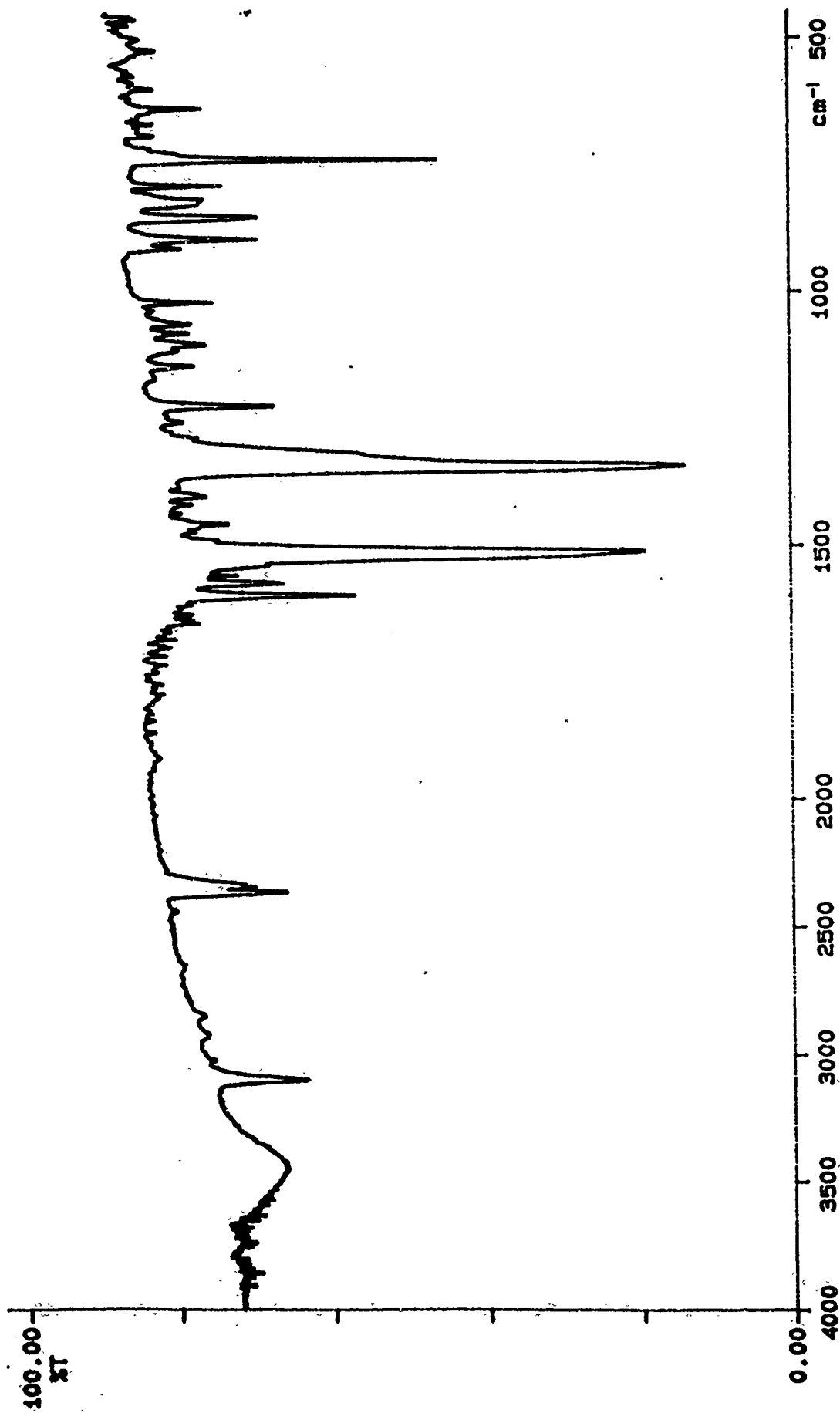
24
4000

18/6/90
J.C.



delta (ppm)

P-E



90/08/10 16:21
X: 4 scans, 4.0cm-1
2,8 Dinitrobenzothiophene

2,8-DINITRO-

2,8-DINITRO-
BENZOTHIOPHENE

d_6 DMSO 5
10mg/L
THS
21.7°C

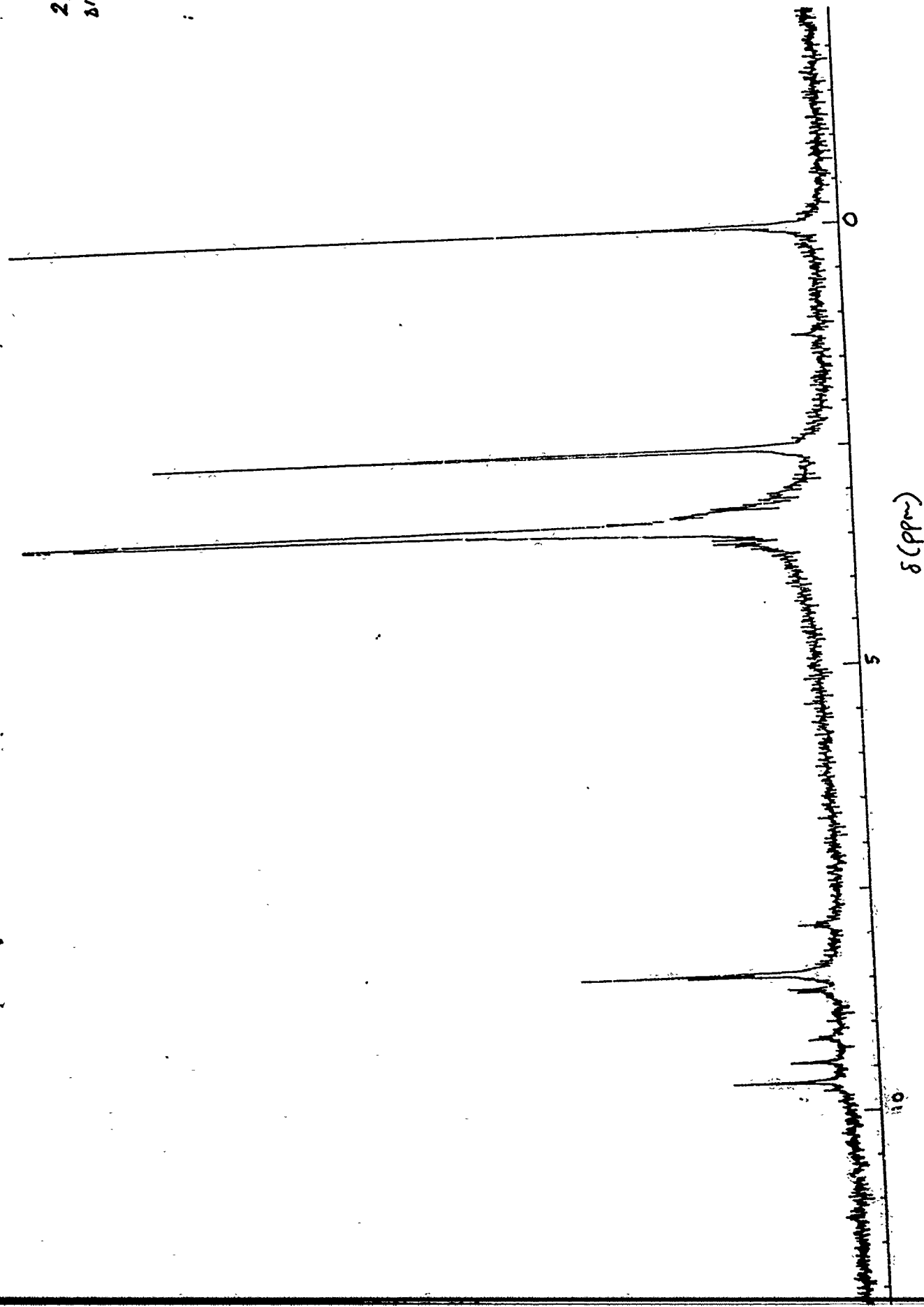
1H

83.0

24

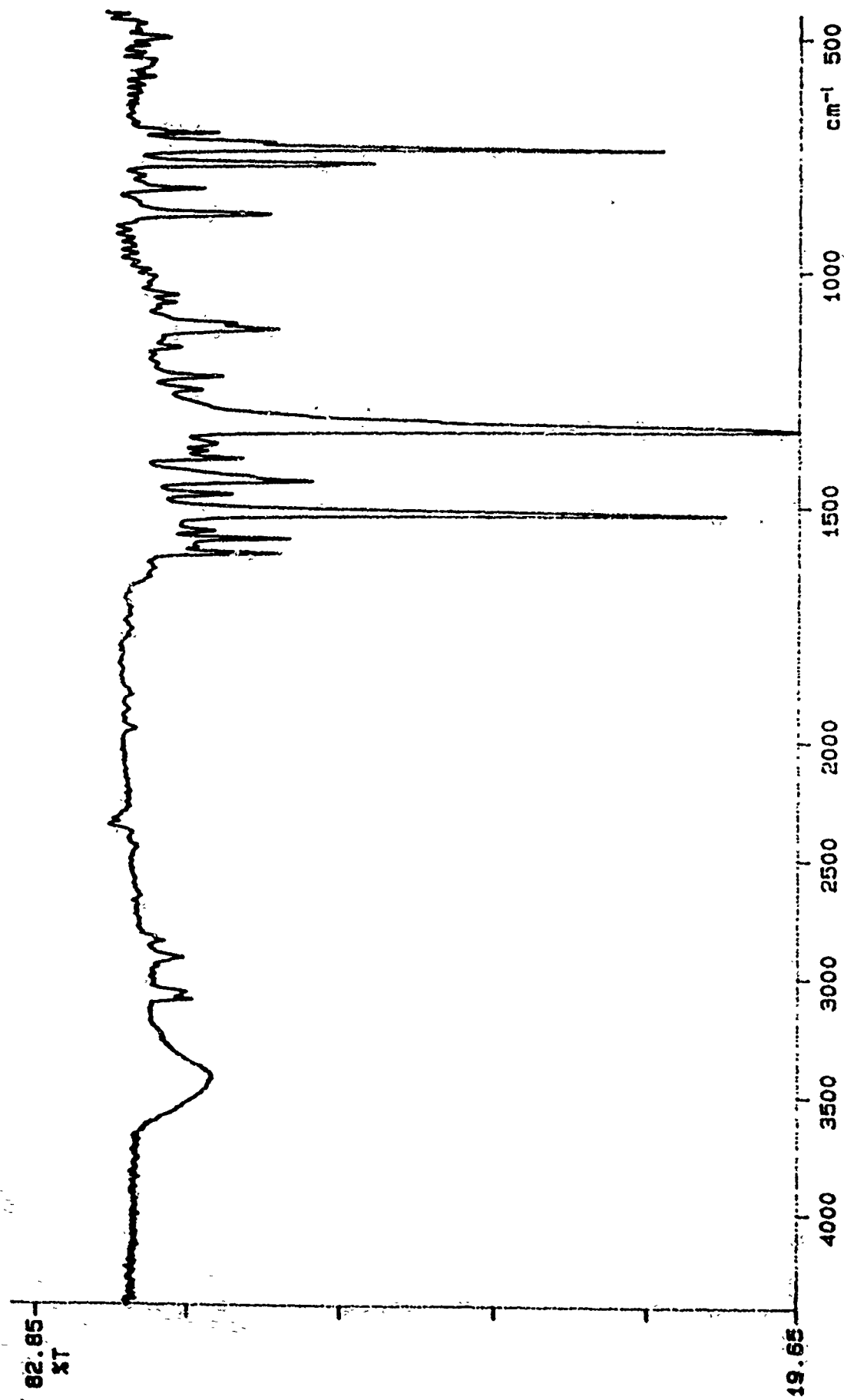
4000

28/6/90
J.C.



P-E

62.65
XT



90/08/13 12:08
X: 4 scans, 4.0cm-1, flat
3 Nitrobenzothioephene

3-NITRO-
DIBENZOTHIOPHENE



d^6 DMSO 5
10mg/ml
TMS
22.0°C

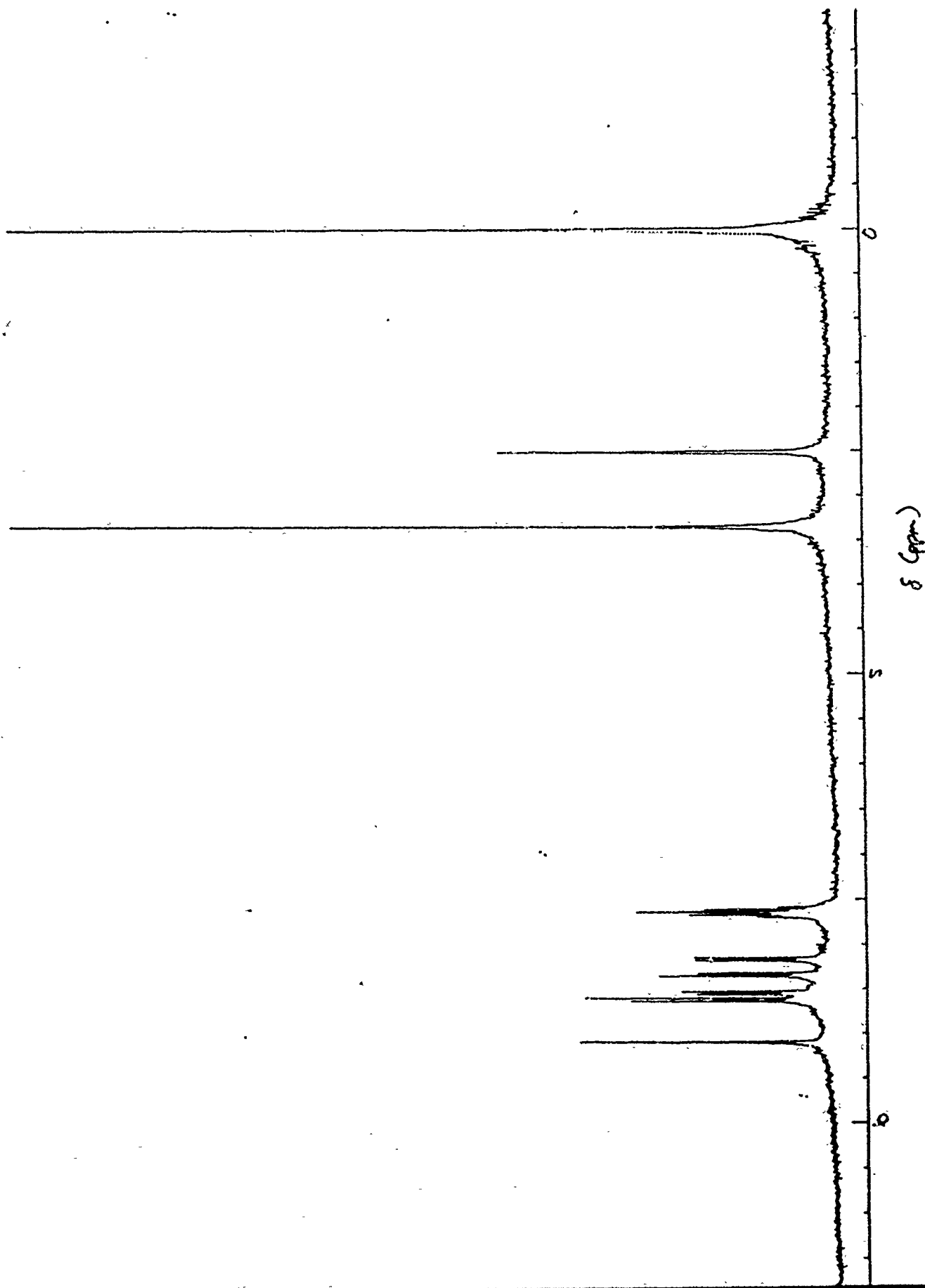
11

83.0

24

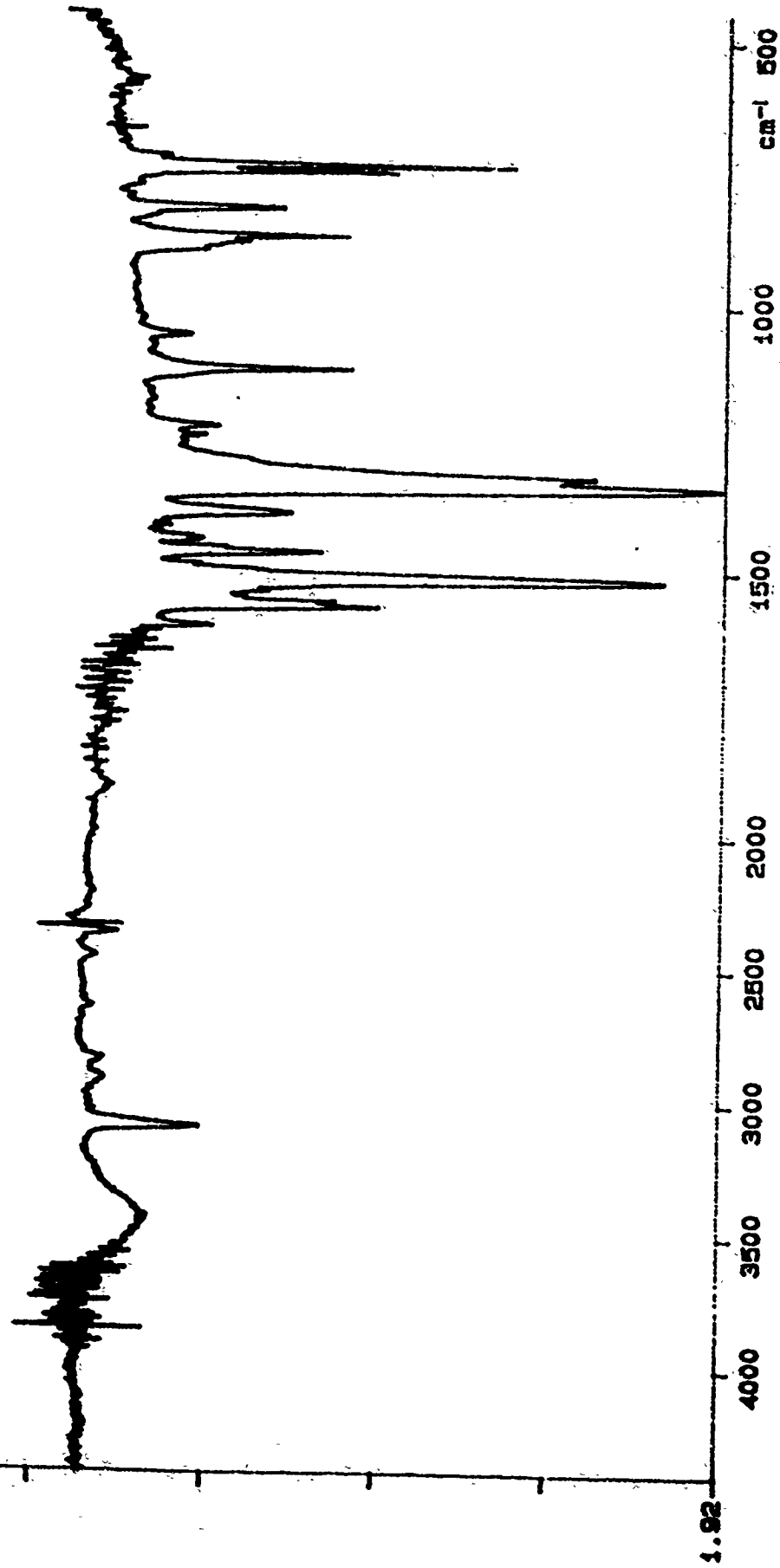
4000

28/5/90
J.C.



P-E

42.45
ST



90/08/13 12:32
X: 4 scans, 4.0cm-1, flat
3,7 Dinitrobenzothiophene

3,7-DINITRO-
DIBENZO THIAPHENE



DMF0 5
10mg/ml
THS
22.1°C

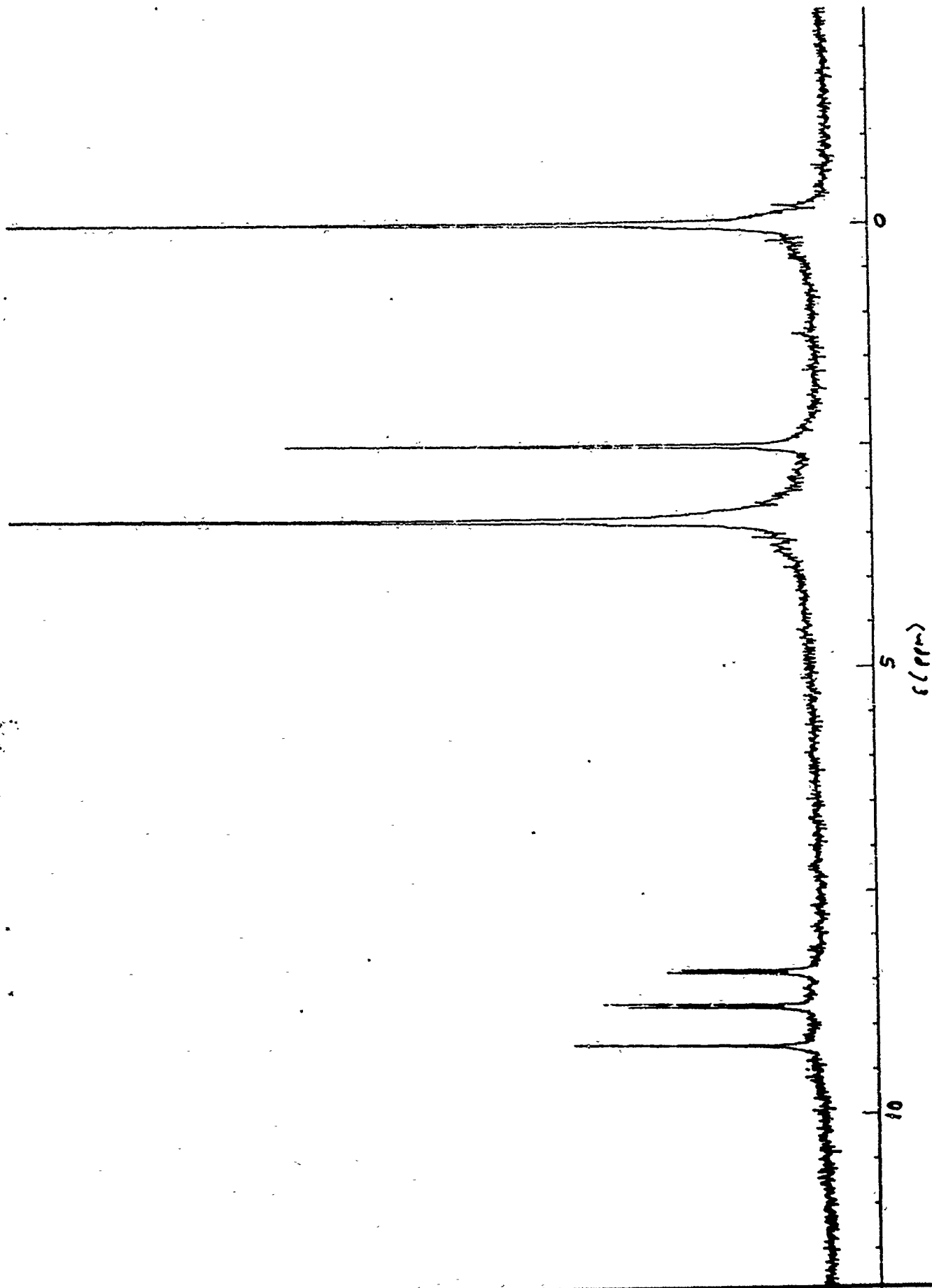
H₁

13.0

2.4

4000

28/6/90
J.C.



PE

49.30
ST

21.32

4000 3500 3000 2500 2000 1500 1000 500 cm^{-1}

90/08/13 12:53
X: 4 scans, 4.0cm⁻¹, flat
Dibenzothiophene S oxide

DIBENZOTHIOPHENE-

5-0-056



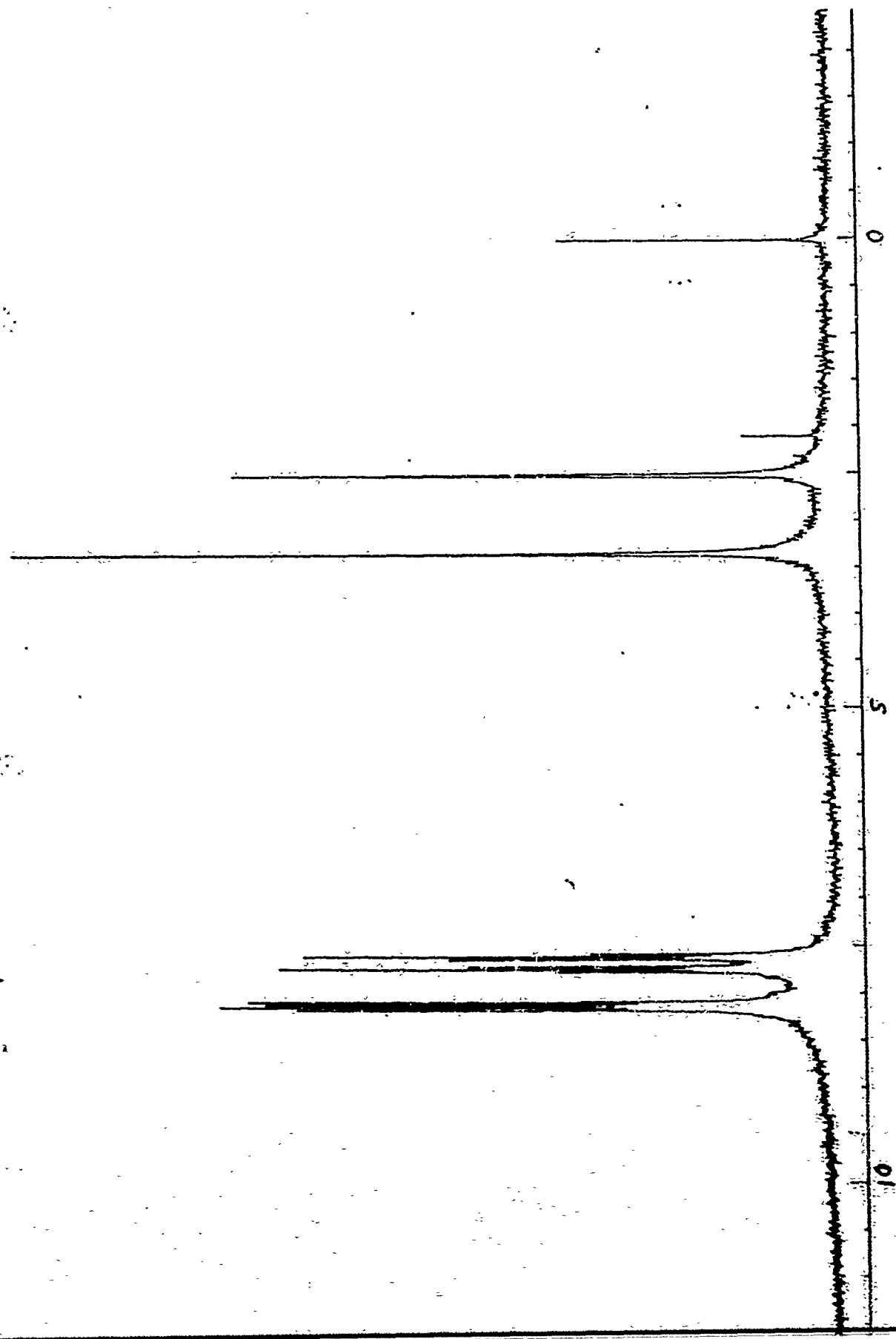
100% 5
7MS
22.0

4 ✓

83.0 ✓

24 4000

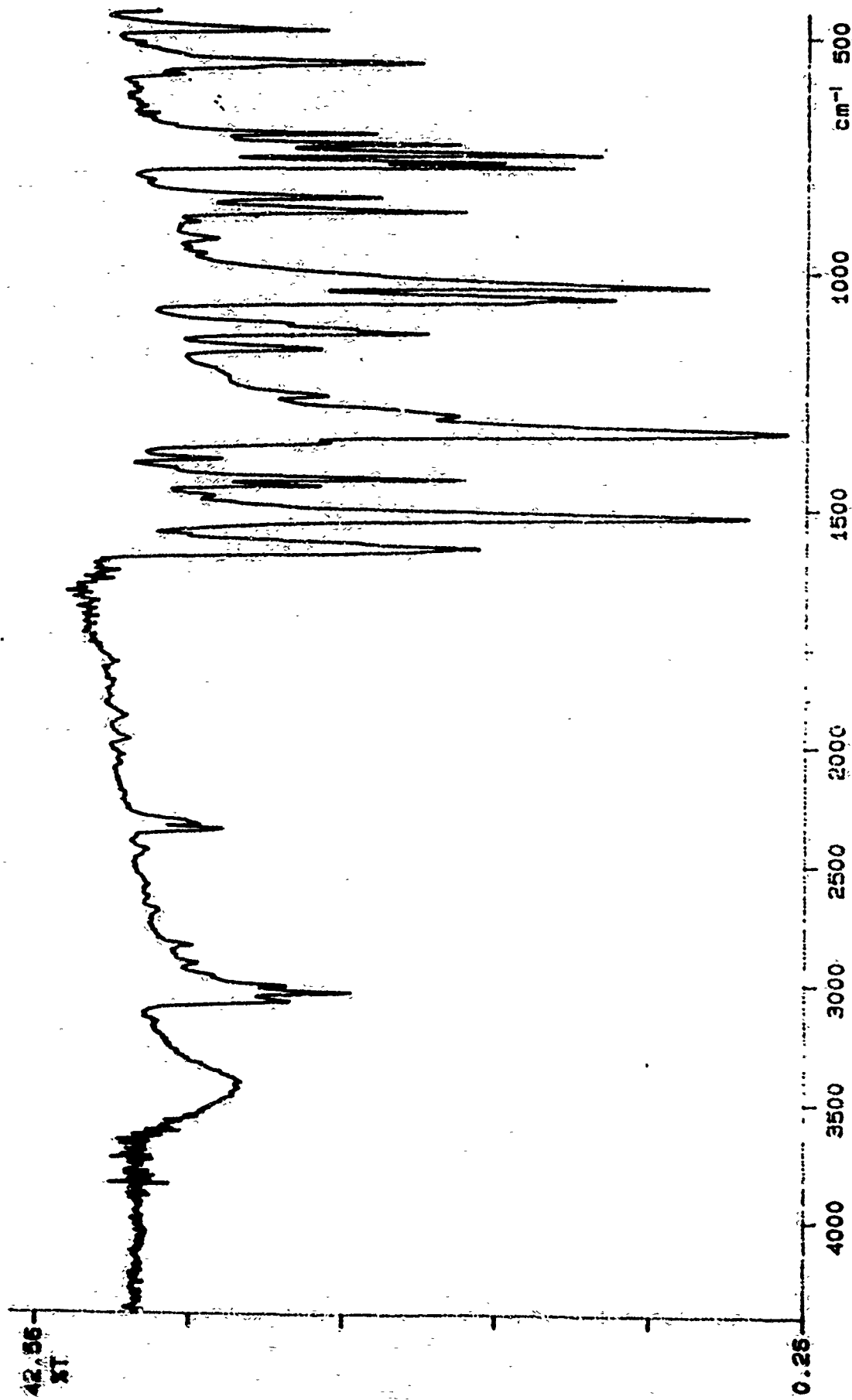
18/5/90
J.C.



8 (ppm)

P-E

42.86-
XT



90/08/13 14:16
X: 4 scans, 4.0cm⁻¹, flat
3 Nitrobenzothiophene 5 oxide

FX

3-NITRO-1,4-DITHIO-
-5-OXIDE



15430 S
100%
743

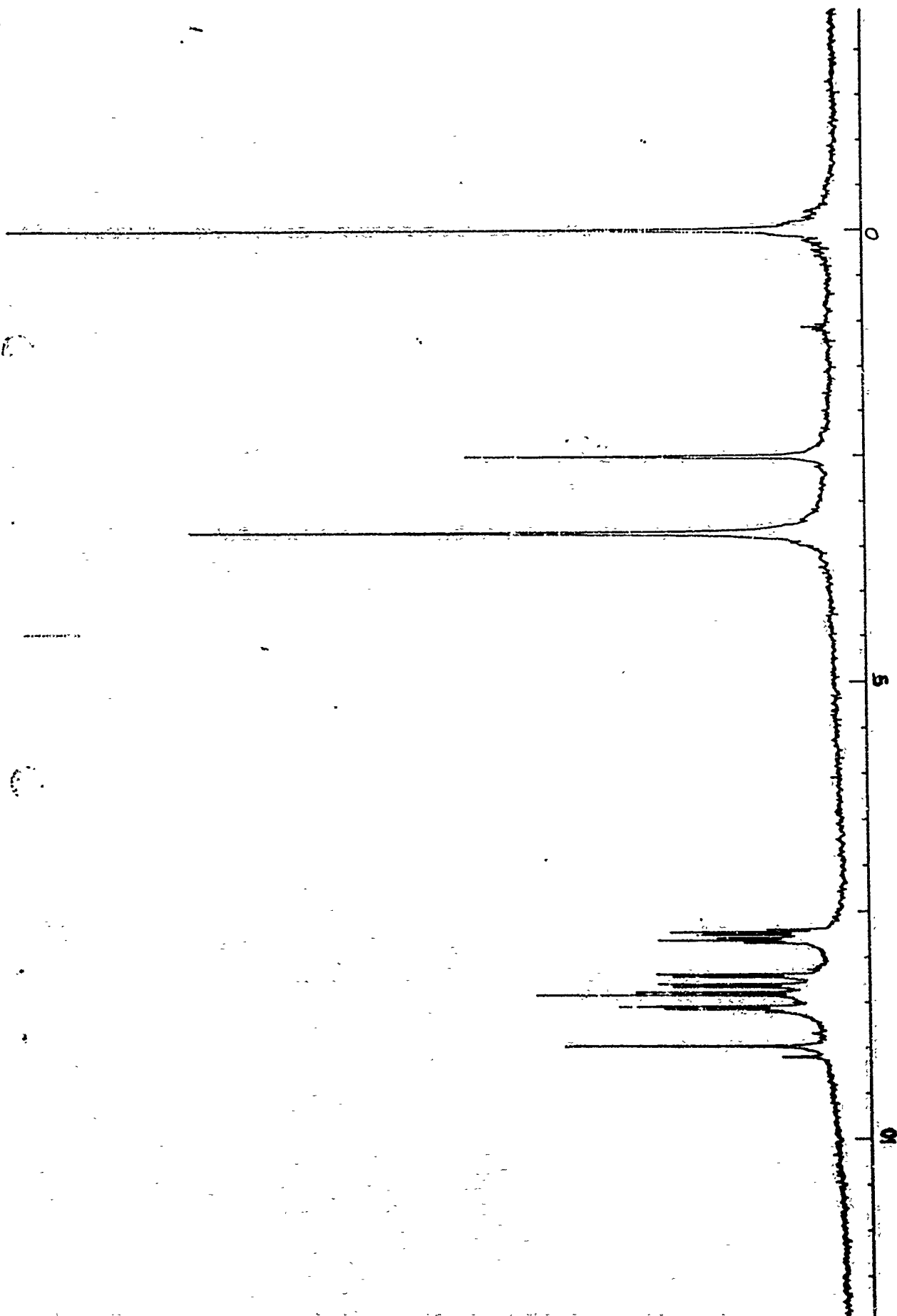
N

23.0

24

1000

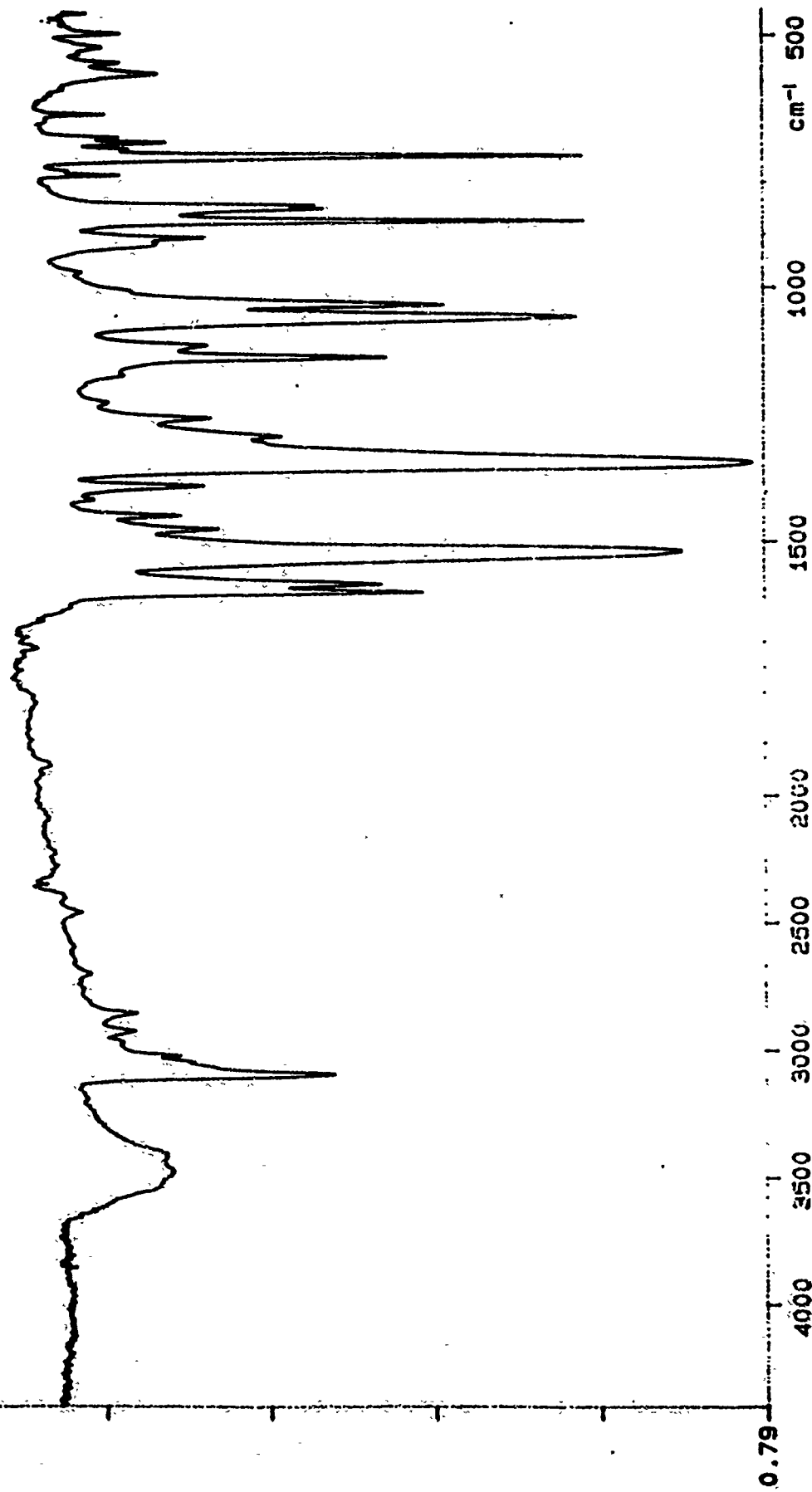
5.0



P-E

71.86

XT



90/08/13 14: 43

X: 4 scans, 4.0cm-1, flat

3,7 DINITROBENZ-2-THIOPHENE - S - OXIDE

1X

3,7-DINITRODIBENZO-
THIOPHENE-S-OXIDE



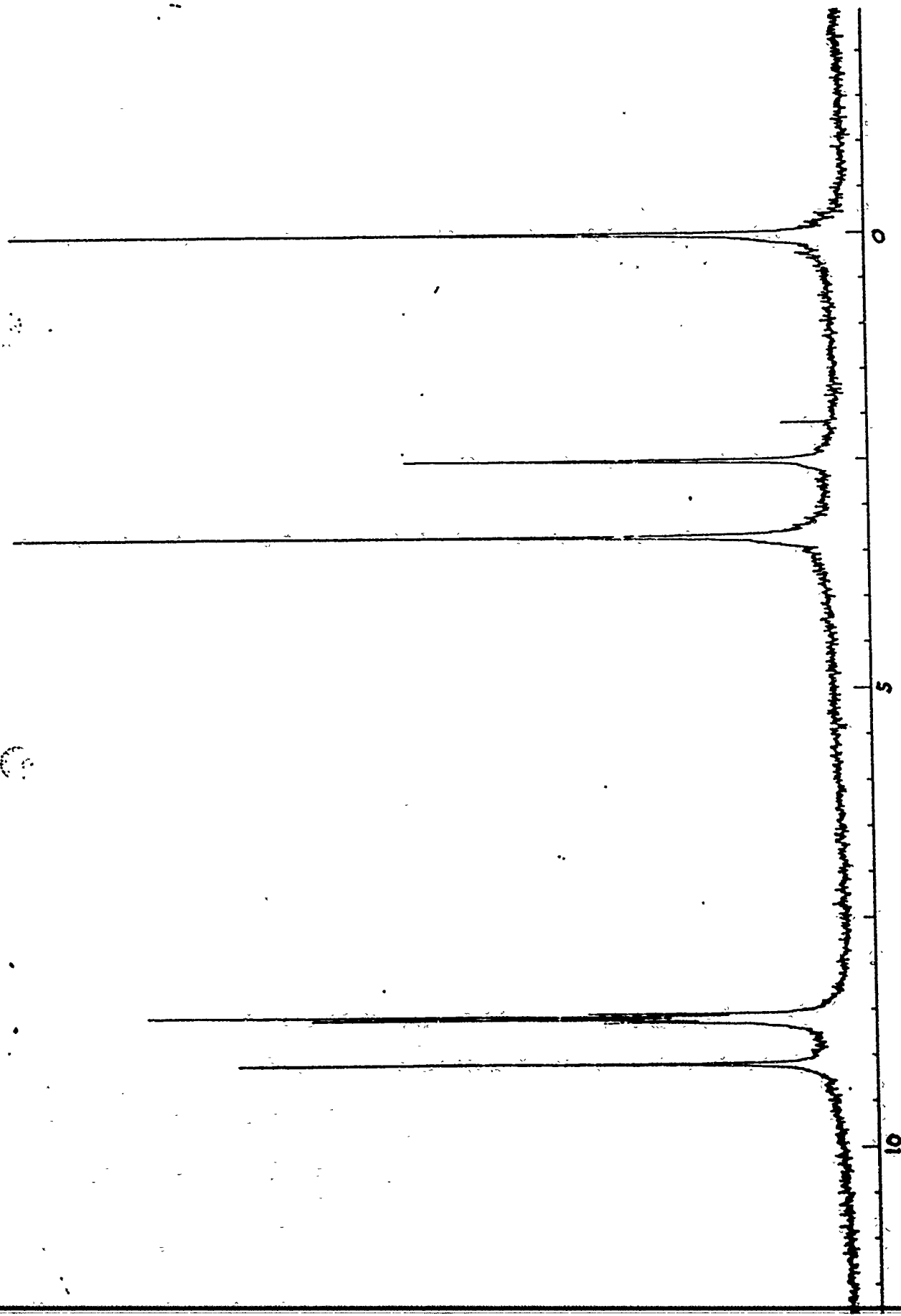
MSO
74.5 / 0.5 ml
21.9 °C

¹H

83.0

24
4000

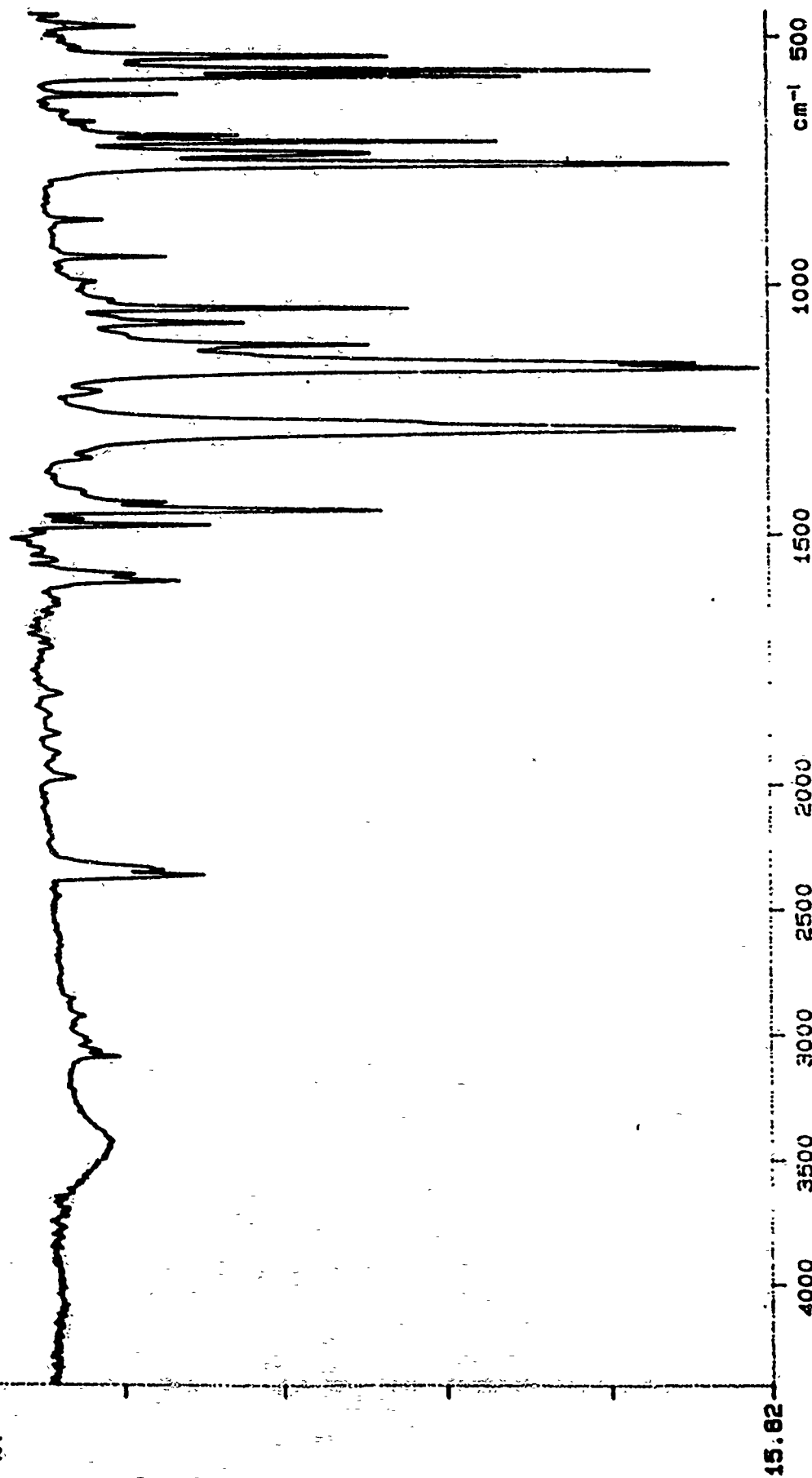
22/6/90
J.C.



δ (ppm)

P-E

77.16
ST



90/08/13 15:07
X: 4 scans, 4.0cm-1, flat
Dibenzothiophene 5,5 dioxide

FX

DIBENZO THIOPHENE
-S,S-DIOXIDE

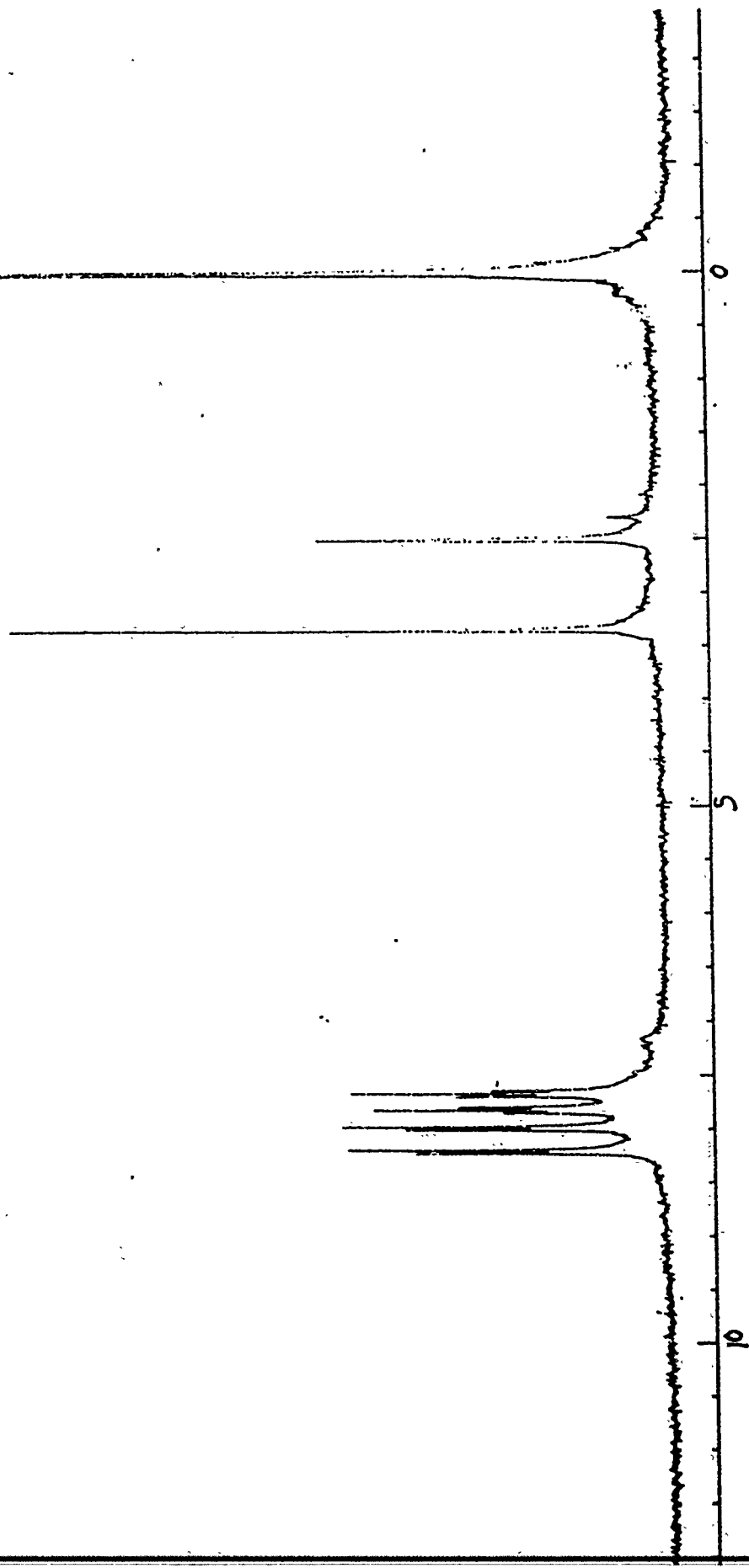


5
100%
74.5
20.62

H

24
4000

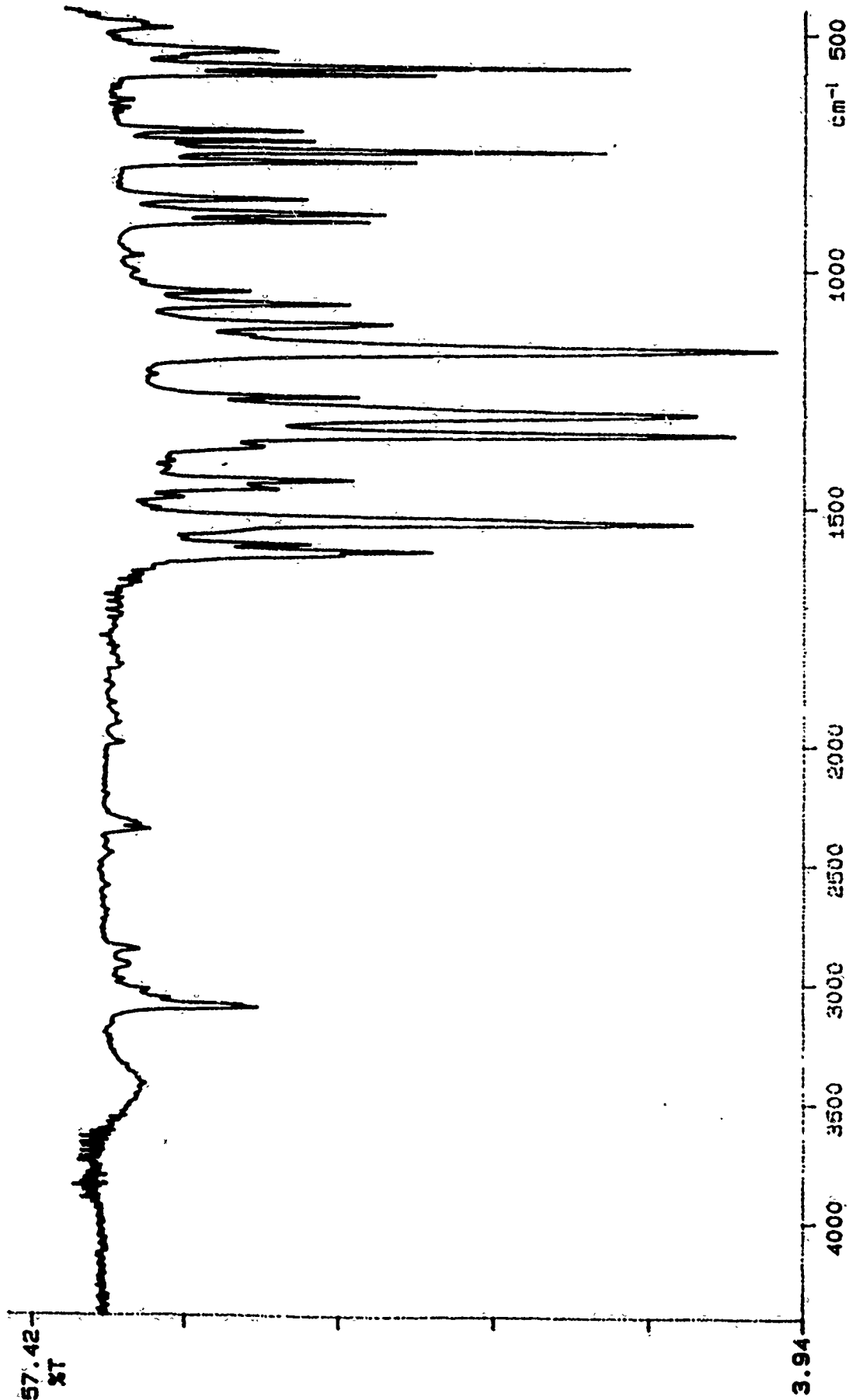
12/6/90
J.C.



$\delta(\text{ppm})$

P-E

57.42
XT



90/08/13 15:25
X: 4 scans, 4.0cm-1, flat
3 Nitrobenzothioephene 5,5 dioxide

FX

3-NITROBENZOTHIOPHENE 5,5-DIOXIDE

FX

3-NITRODIBENZO-
THIOPHENE-5,5-
DIOXIDE



NO₂

100%
TMS
20.6°C

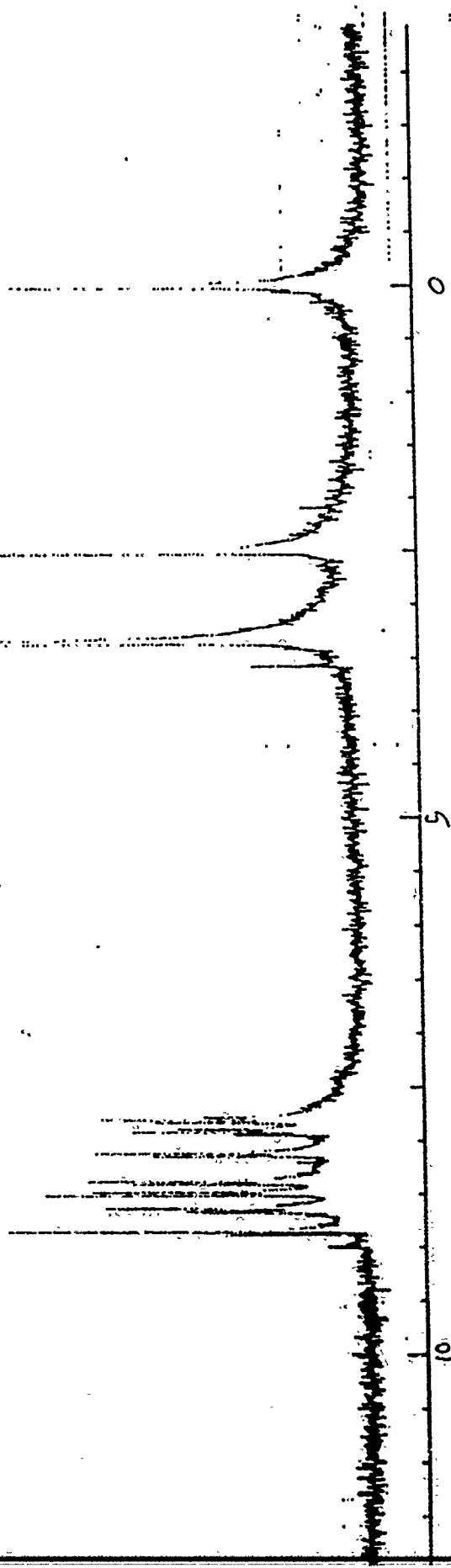
¹H

83.0

24

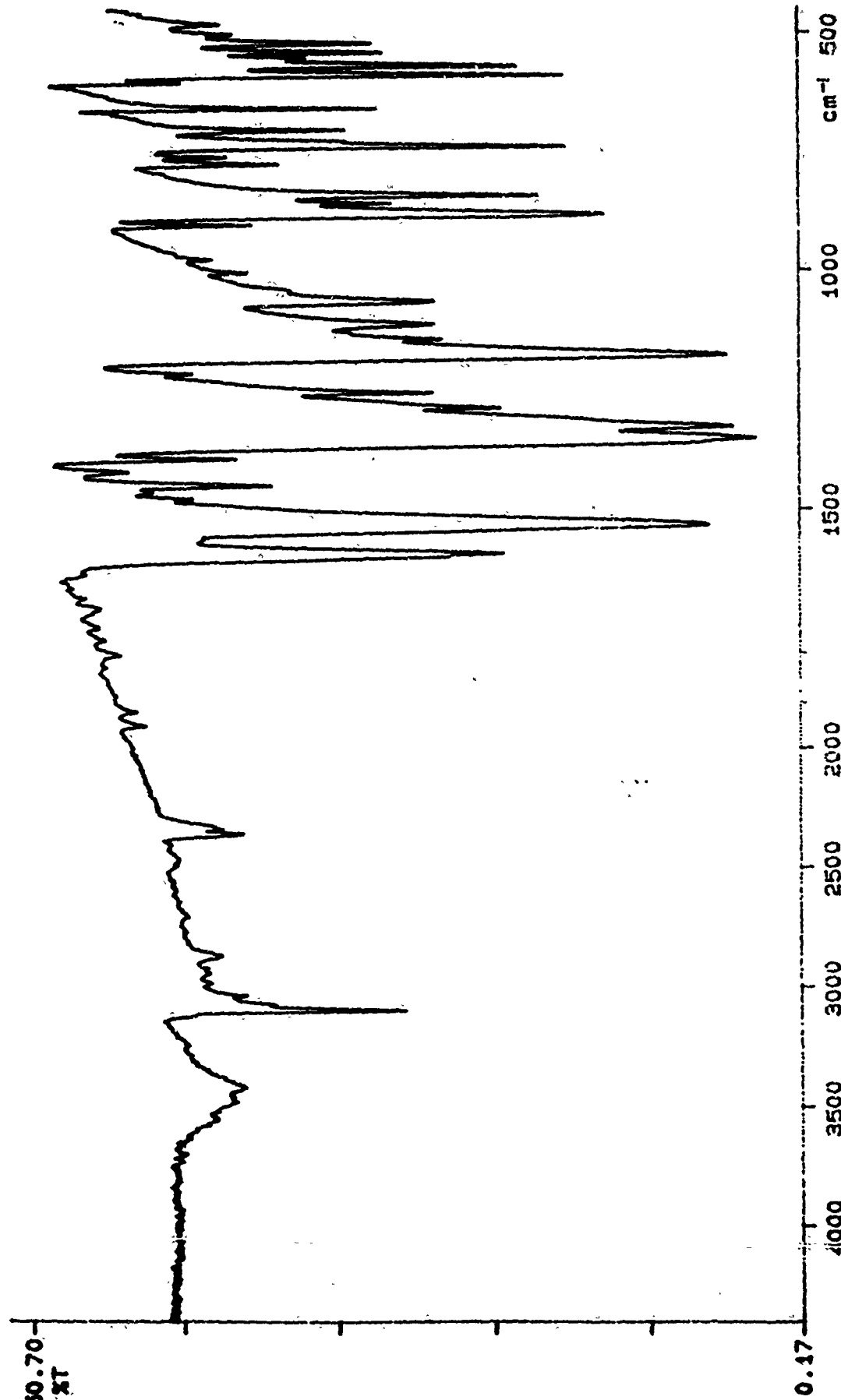
4000

12/6/90
J.C.



P-E

50.70
ST



90/08/13 15:44
X: 4 scans, 4.0cm-1, flat
3,7 Dinitrobenzothiophene 5,5 dioxide

3,7-DINITROBENZOTHIOPHENE-5,5-DIOXIDE



15000 5
1000/44
74.5
20.6

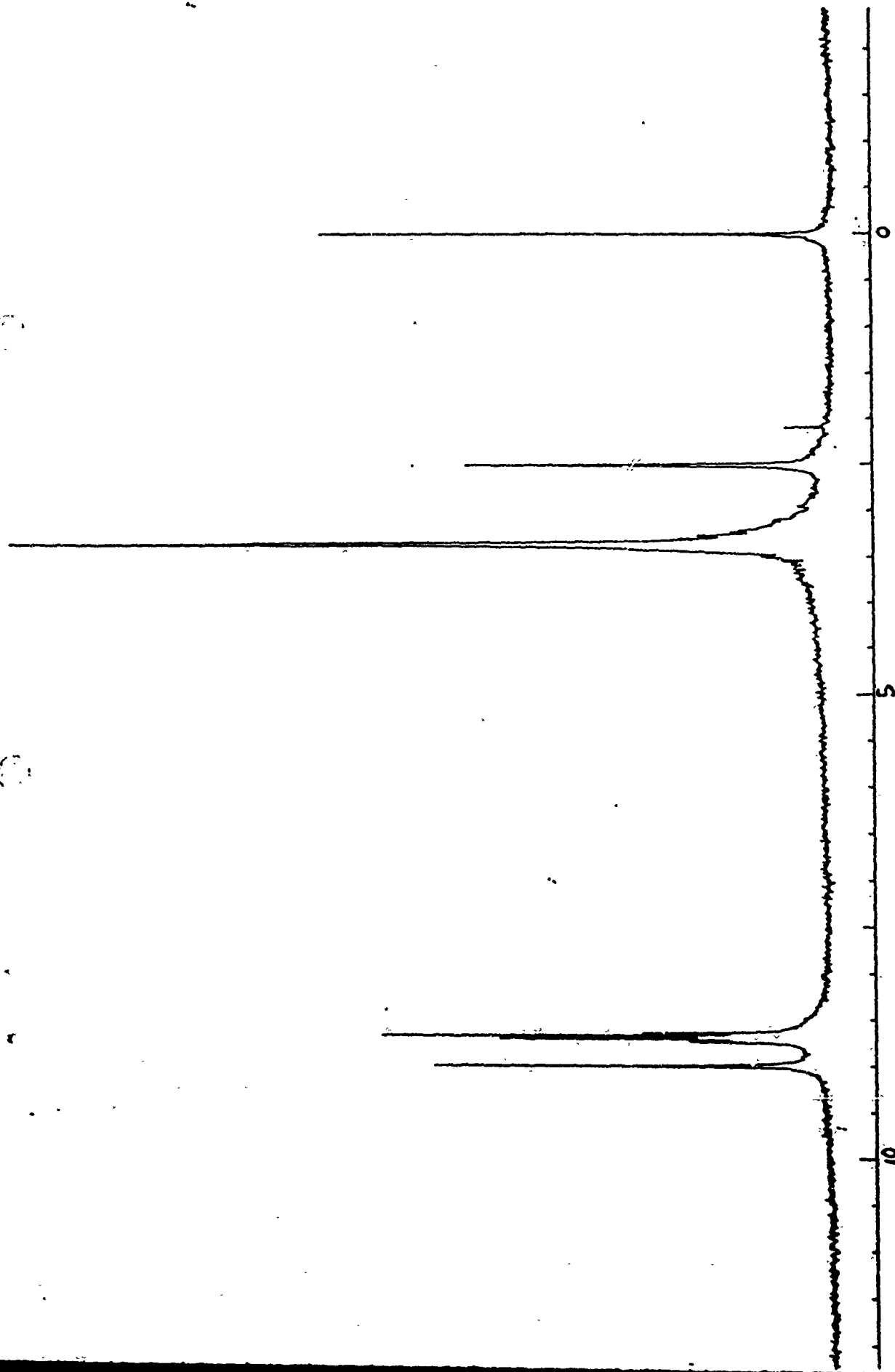
H

83.0

24

4000

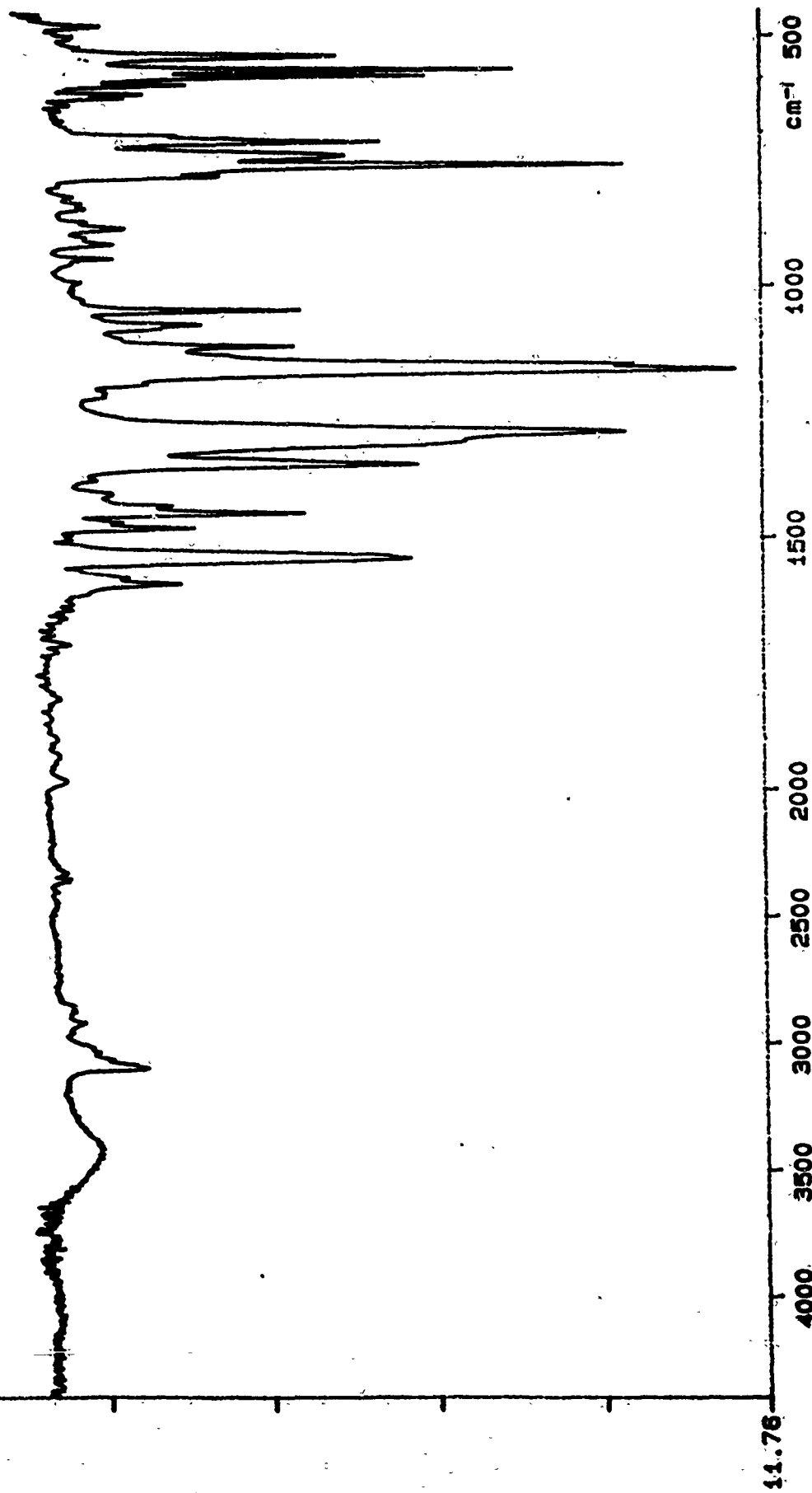
12/6/90
J.C.



δ (ppm)

P-E

76.10
XT



90/08/13 16: 01
X: 4 scans, 4.0cm-1, flat
2 Nitrodibenzothiophene 5,5 dioxide

2-NITRODIBENZO-
THIOPHENE-3,5-DIOXIDE
11.76

2-NITRODIBENZO-
THIOPHENE-2,5-DIOXIDE



5
10mg/ml
THF
25°C

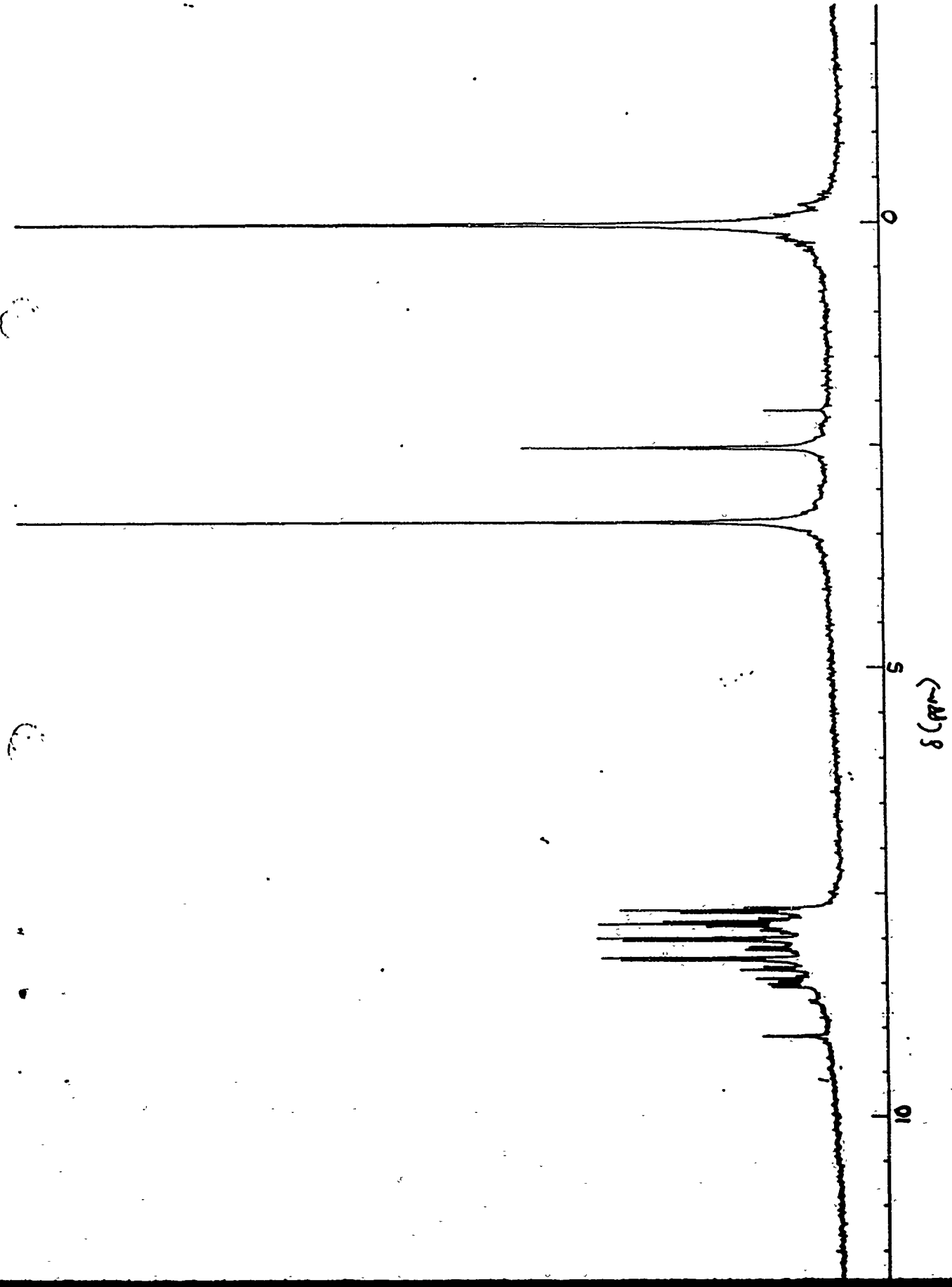
1H

82.0

24

4000

28/6/90
J.C.



1,3,7-TRINITRODIBENZO-
THIOPHENE-2,5-DIOXIDE

1,3,7-TRINITROBENZENE
TRICHLORO-S,S-DIOXANE



5
d₆-H₂O

50mg
TMS
23°C

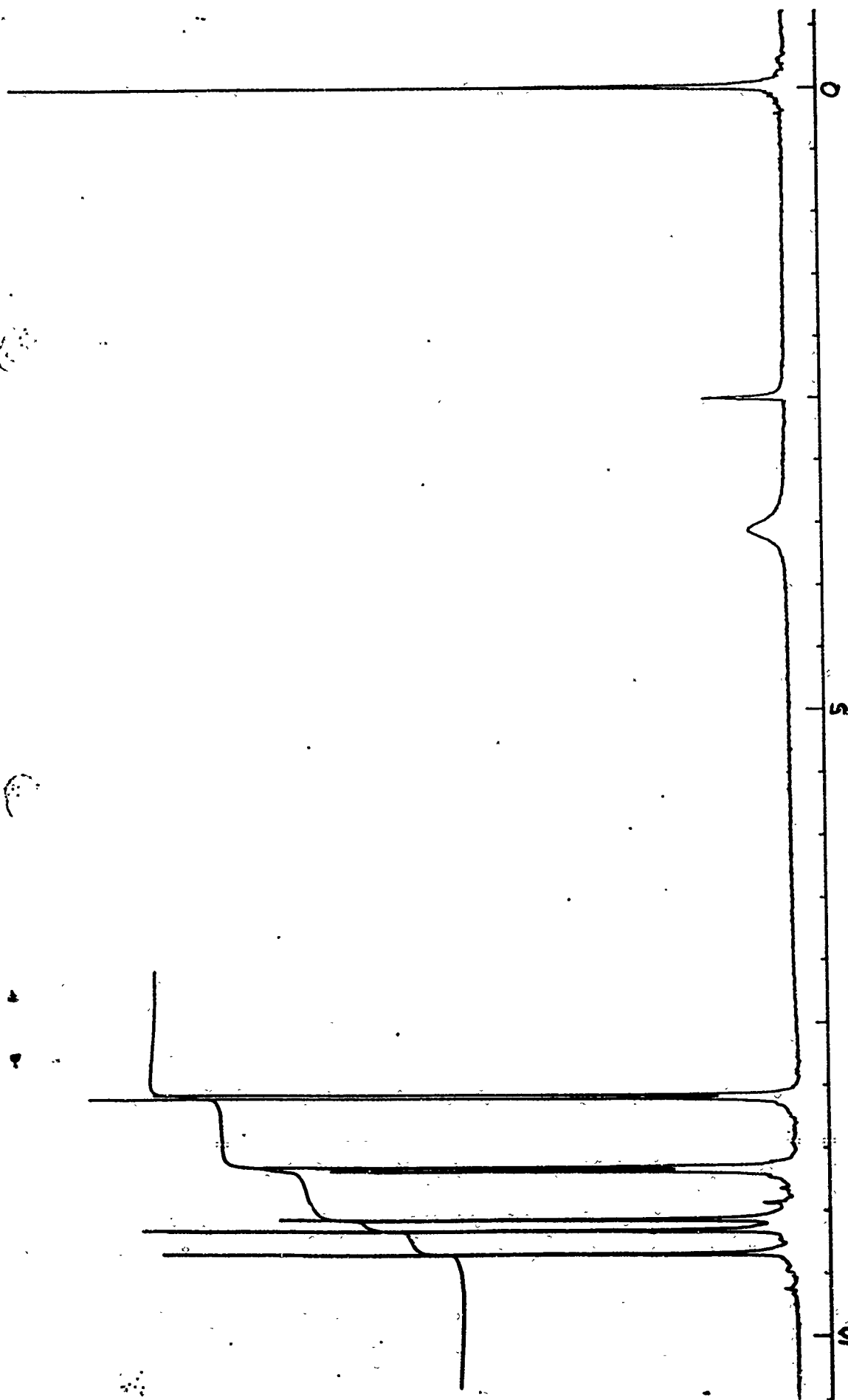
H

82.0

2 X 2

3000

5/10/90
J.C.



δ (ppm)