CHAPTER - 2

The versatility of antioxidants is discussed in Chapter I. In this chapter we discuss the synthesis and characterization of some new antioxidants based upon hindered phenols Since the present study pertains to hindered phenolic antioxidants, as a prelude to the present work, prior work in this field is reviewed here.

Phenolic Antioxidants :

The synthesis and applications of phenolic antioxidants based on US patents since 1972 is reviewed by Johnson[1].

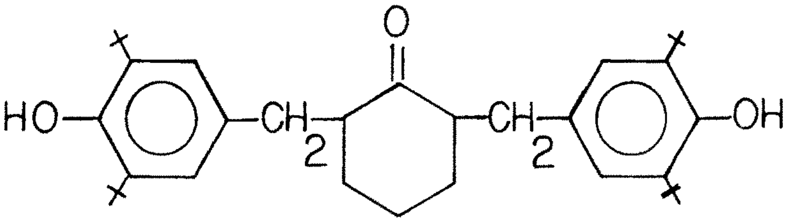
Antioxidants for multipurpose applications ranging from foods to fuels and plastics, as well as ultraviolet absorbing agents have been put forward by Morris et al.[2]. These are basically esters of 3,5-di-alkyl-4-hydroxy benzyl alcohols which on treatment with adipoyl chloride gave the corresponding adipate which showed the antioxidant activity.

Condensation of p-tert-alkyl phenol with formaldehyde in presence of HCl gave poly (p-tert-alkyl) phenol which was found to be effective as antioxidant for polypropylene[3].

Polyolefins were stabilised by Krueger[4] by employing 2,6-bis(3,5-di-tert-butyl-4-hydroxy benzyl) cyclohexanone **1** as antioxidant **1** was prepared by refluxing 1-(N-pyrolidinyl) cyclohexene with 3,5-di-tert-butyl-4-hydroxy benzylchloride.

Phenolic antioxidants as stabilisers for organic materials were synthesised by Yamada and Tanide [5] They carried out the reaction of 2,6-di-tert-butyl-phenol with $NaBH_4$ in DMF followed by treatment with benzylacrylate to get benzyl 3,5-di-tert-butyl-4-hydroxy phenyl propionate **2**. [$R = (CH_2)_m\ XC_6H_4R^1$, $R^1 = H, X = 0, n = 1, 2, m = 1\text{-}10$]

Song and Henry[6] have reported synthesis of 4-tert-butyl-3-hydroxy-2,6-dimethyl benzyl esters by esterification of 4-tert-butyl-3-hydroxy-2,6-dimethyl benzyl alcohol or chloride with carboxylic acid and its salts or acid chloride. They have also reported synthesis of 4-tert-butyl-3-hydroxy-2,6-dimethyl benzyl stearate **3** ($Z = C_{1\text{-}18}$ alkyl, $n = 1\text{-}4$) as suitable antioxidant for polyolefins by the reaction of 4-tert-butyl-3-hydroxy-2,6-dimethyl benzyl chloride, stearic acid and triethylamine.[7]



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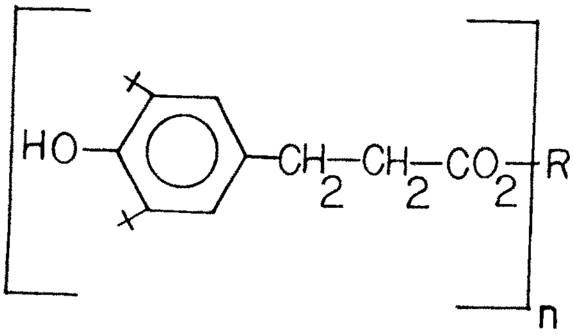

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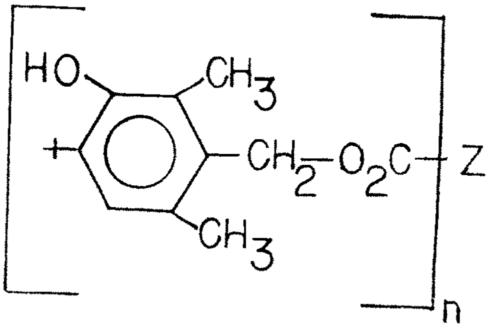

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Phenol derivatives **4** (R = H, CMe_3, R^1 = isopropyl or octadecyl, m = 1 or 2 and n = 1 or 2) were prepared by Mayer et al.[8] by the reaction of isopropyl 3-(2-oxocyclohexyl) propionate, o-tert-butyl-phenol and dodecyl mercaptan in presence of HCl and they were used as stabilisers for synthetic polymers.

Acetoxy derivatives of 2,4,6-tris (4-hydroxy benzyl) phenol useful as antioxidants for polyolefins were synthesised by Molt[9] by the reaction of resorcinol with 3,5-di-tert-butyl-4-hydroxy benzyl alcohol, naphtha and subsequent acetylation of the product with AC_2O.

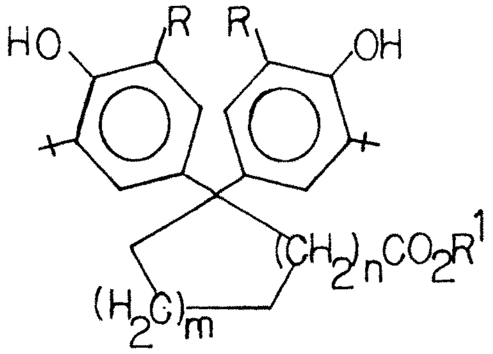
The reaction of dialkylphenol with dicyclopentadiene in presence of BF_3 gave bisphenol such as dicyclopentylene [2,2'-bis (4-methyl-6-tert-butyl phenol)] **5** as reported by Mueller and coworkers [10] as antioxidant for polymers. Similar bisphenols have been used as antioxidant by Takahashi et al.[11] Methylene bis (alkyl-tert-butyl phenol) monocarboxylate ester **6** ($R = CH_2 = CHCO$) was synthesised by the reaction of **6** (R = H) with carboxylic acid.

Uchida and Sato[12] reported 2-alkyl-4,6-di-tert-butyl resorcinol useful as antioxidant. The compound was prepared by treating 4,6- di-tert-butyl resorcinol with HCHO, $BuNH_2$, MeOH and Pd/C under hydrogenation catalyst.

Noburu et al.[13] synthesised phenolic polymer **7** (n = 2-75, isopropylidene groups in the repeating unit are meta or para to each other) useful as antioxidant for thermosetting resins. This was prepared by treating p-cresol with 1,3-bis-(1-hydroxy-1-methylethyl) benzene in toluene in presence of $p\text{-}MeC_6H_4SO_3H$ and subsequent stirring with α - methylstyrene.

Everly and Roper[14] prepared p-alkyl phenols as intermediates for phenolic antioxidants for gasoline, lubricants plastics and rubber. A mixture of 2,6-di-tert-butyl phenol, Me_2CHCHO, Me_2NH in Me_2CHOH was refluxed under nitrogen gave **8**, which was oxidised in presence of $FeCl_3$ to yield 3,5-di-tert-butyl-4-hydroxy benzaldehyde.

Kuepper et al.[15] have carried out extensive studies on different esters of (3-tert-butyl-4 hydroxy phenyl) alkanoate with oxyethylated polyphenols. Their studies revealed that specifically 5-alkyl ester derivatives with oxyethylated polynuclear di-or trihydric phenols are nondiscoloring stabilisers for polyolefins. Heating 2,2'-[cyclohexylidene bis (p-phenyleneoxy)] diethanol and methyl 3-(3,5-di-tert-butyl-4-hydroxy phenyl) propionate gave the diester.



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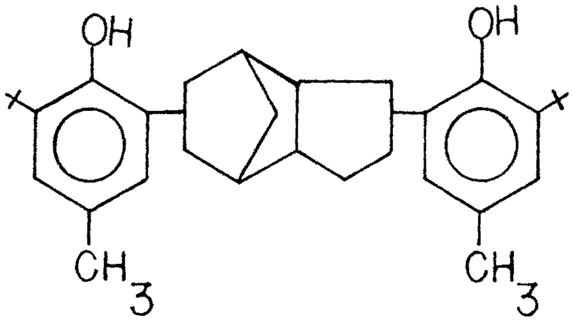

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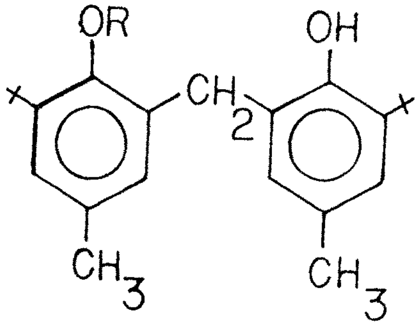

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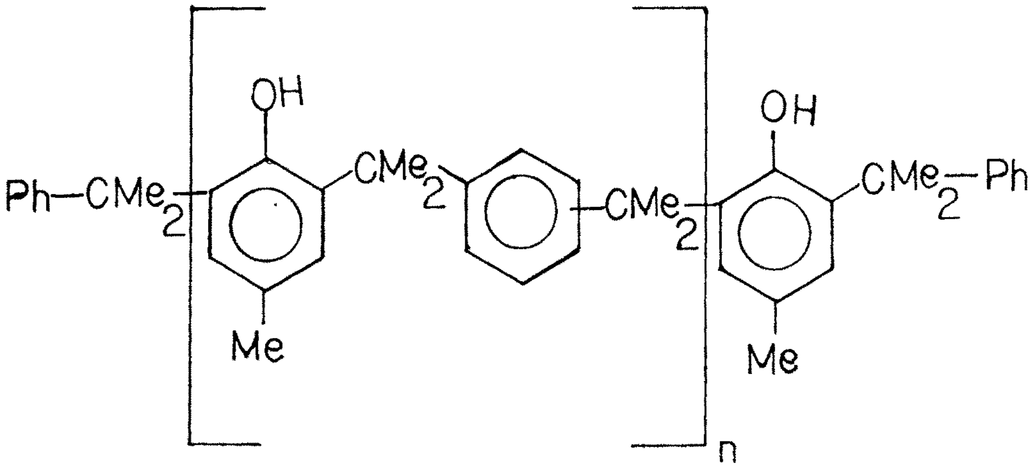

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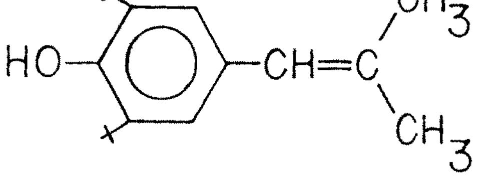

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Mina and Schell[16] reported the synthesis of derivatives of hindered phenols useful as antioxidants for plastics. The reaction of phenol with mesitylene in CH_2Cl_2 in presence of H2SO4 gave **9** which on further treatment with phenol in CH_2Cl_2 in presence of H_2SO_4, gave **10**. The antioxidant activity of **9** & **10** was tested with polypropylene by oven ageing test.

Takahashi and Narita[17] prepared tetrakis[3-(3,5-di-tert-butyl-4-hydroxy phenyl) propionyloxymethyl] methane by the transesterification of 3-(3,5-di-tert-butyl-4-hydroxy phenyl) propionic acid alkyl ester with 2,2,2-tris [3-(3,5-di-tert-butyl-4-hydroxy phenyl) propionyloxymethyl] ethanol.

Evans[18] has synthesised **12** (A=alkoxy, R^1, R^2, R^3 = alkyl, n=1-6) using hydroxy phenyl isobutyrates **11** (R=Me) and 1-octadecanol and Bu_2SnO which have been found to be effective antioxidants.

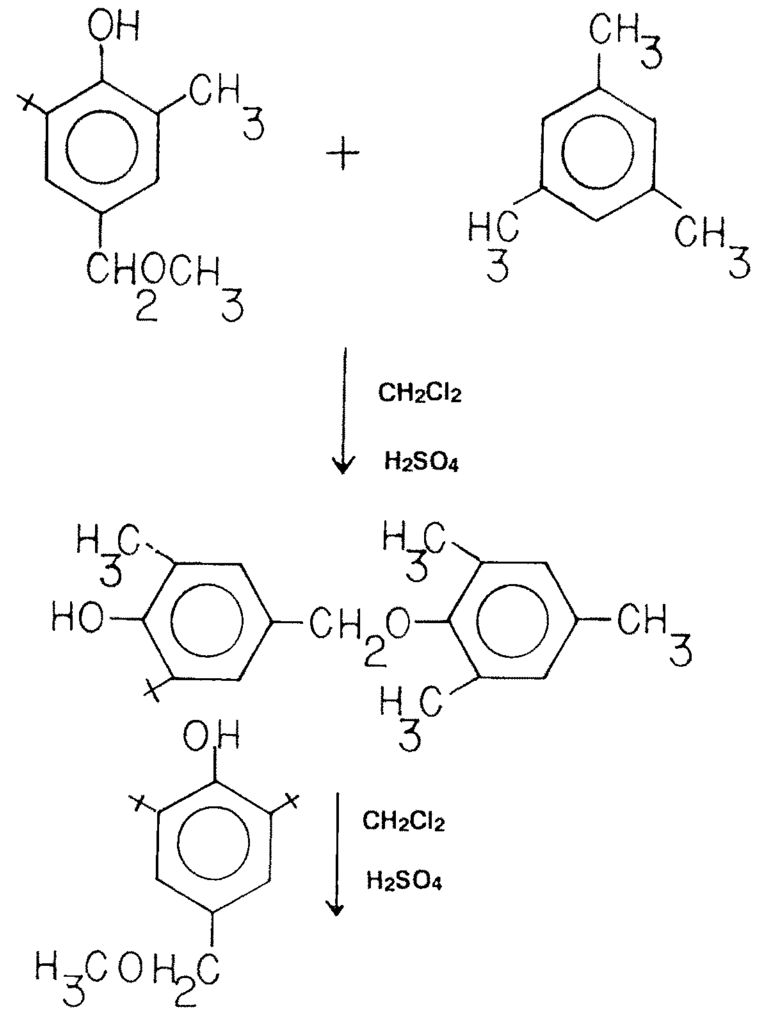
Alkyl β-(3,5-di-alkyl-4-hydroxy phenyl) propionates useful as antioxidants have been prepared by Marutani et al.[19] by adding alkylacrylates to 2,6-dialkylphenols in presence of alkali or alkaline earth phenoxides.

Recently, ageing resistant polyether rubber and polymeric antioxidant have been proposed by Shimizu[20]. Thus 4-hydroxy-3,5- di-tert-butyl phenyl glycidyl ether was prepared by reacting 2,6- di-tert-butyl hydroquinone, epichlorohydrin and $PhCH_2NMe_3Cl$

Sulphur containing Phenolic Antioxidants :

Tatsuji and Teruhisa[21] have reported the synthesis of 2,6-di-tert-butyl-α-(methyl thio) p-cresol useful as antioxidant by Williamson reaction of 2,6-di-tert-butyl-4-bromo phenol, NaOEt followed by reaction with alcoholic solution of MeSH.

Discoloration resistance in polypropylene was reported by Zaweski[22] using thiodimethylidyne tetrakis phenol **13**. Compound **13** was prepared by H_2S treatment of hemiquinone of a methylene bisphenol. These compounds were also found to be suitable antioxidants for rubbers and α,β-unsaturated polymers.



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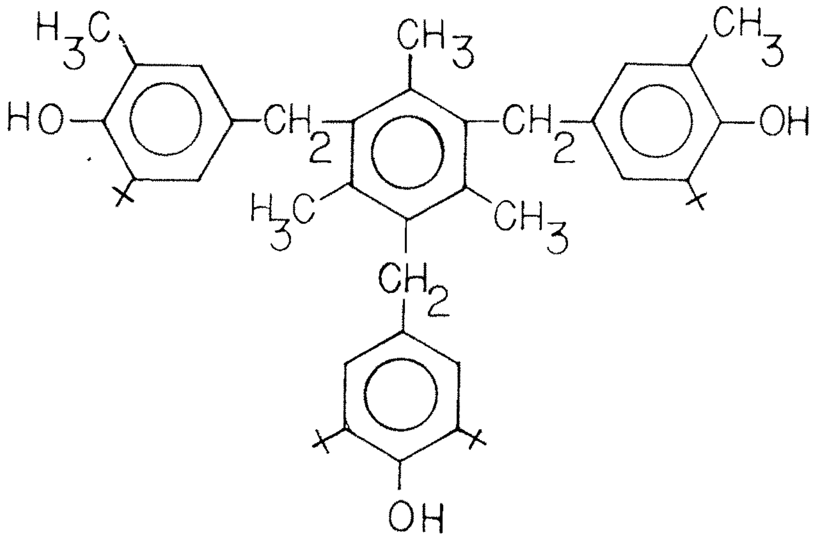

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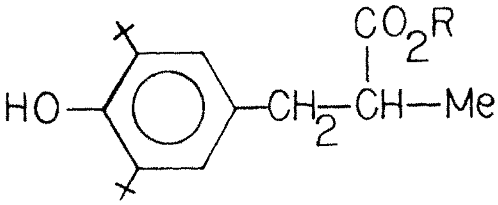

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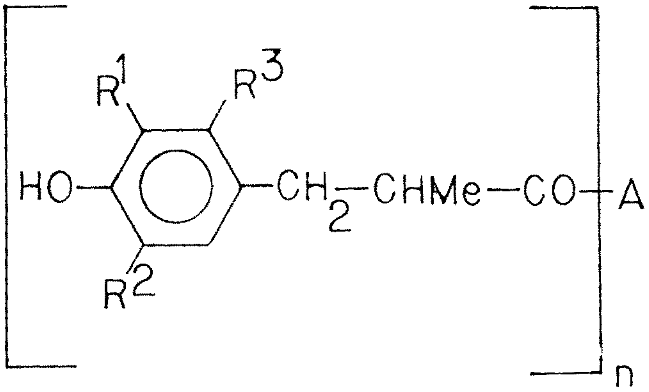

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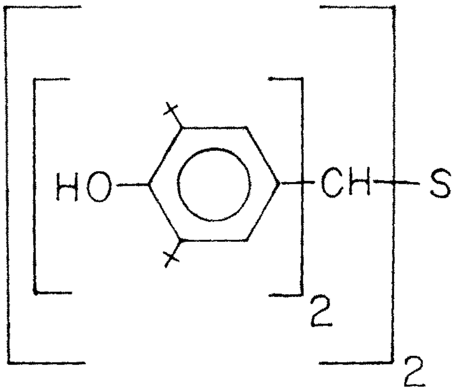


13

Thiomethyl phenol **14** [Q = $(CH_2)_2$, p-$(CH_2)_2C_6H_4$] useful as antioxidant for polypropylene was synthesised by Song[23] using 6,3,2,4 Me_3C $(HSCH_2)$ Me_2C_6HOH and p-$(Cl\text{-}CH_2)_2C_6H_4$ in Me_3COK.

Sulphur containing antioxidants were prepared by halogenation of **15** by Fujisawa and Katutani [24].

Treatment of 2,6-di-tert-butyl phenol with sulphur and KOH, S_2Cl_2 or Br_2 and KSCN gave **16,17**, which on further treatment with Zn gave thiophenol **18**. These were found to be effective antioxidants by Medvedev et al.[25].

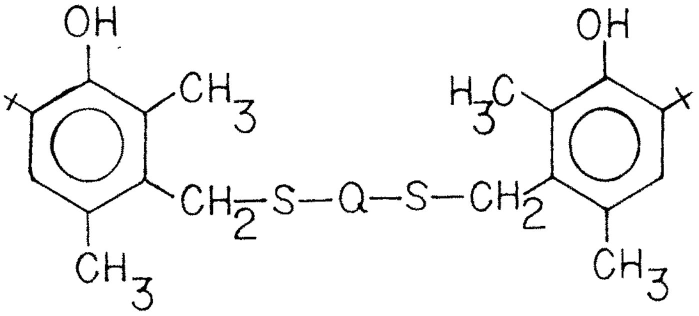
Antioxidants useful for diesel and lubricating oil have been synthesised by Nabiev and coworkers [26] by the condensation of alkyl halide glycidyl with 2,4-$HS(RCMe_2)C_6H_3OH$ (R = Me, Et).

Golubeva et al.[27] have condensed hydrazino-2,6-di-tert-butyl phenol derivatives with H_2S and isocyantes to give a series of compounds having higher antioxidant activity than Ional in T_6 jet air-craft fuel

Evans and Meier[28] synthesised 2,4,6 tri-functionalised phenols as stabilisers for polymers and lubricants. A mixture of 2,4,6-tris (dimethyl aminomethyl) phenol and $HSCH_2COOHCH_2$:CHEtBu were heated to give **19** (R = R^1 = $CH_2COOHCH_2CHEtBu$)

Jenkins [29] reported tris (substituted hydroxy phenyl thio) trithio ortho ester, as stabilisers for polymers. $(EtO)_3CH$ and 3,5-di- tert-butyl-4-hydroxy-1-mercapto-benzene in presence of HCl gave **20** tris (3,5-di-tert-butyl-4-hydroxy phenylthio) methane **20**

Onoue et al [30] reported 4,4'-monothiobisphenols **22** as antioxidant which were prepared by reaction of phenol derivatives **21** with SCl_2 using halogen catalyst in non-polar solvents These compounds have found use in intermedites for polymer modifiers, developers for thermal-recording papers.



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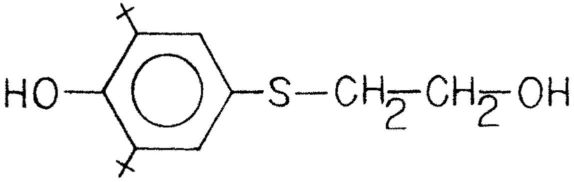

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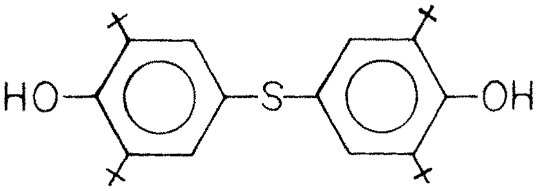

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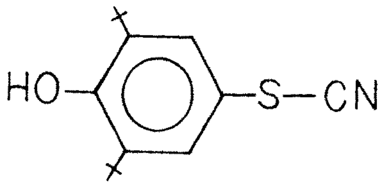

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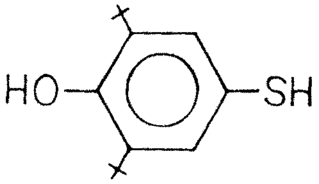

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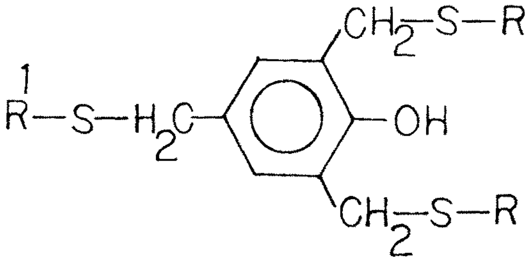

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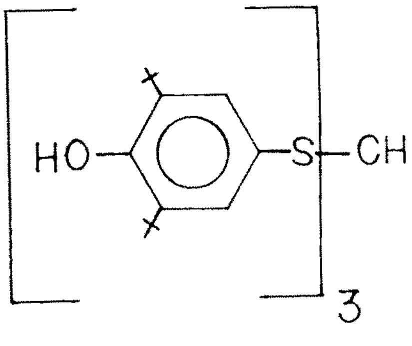

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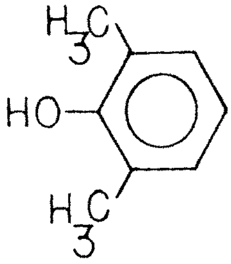

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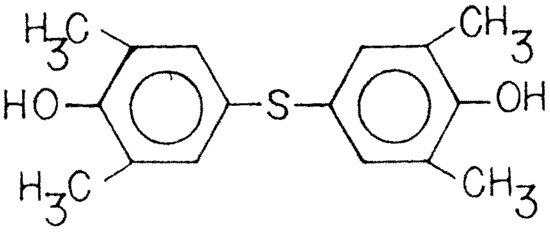


22

Pitteloud and Dubs[31] have synthesised substituted phenols containing sulphide linkage for their application as heat stabilisers. Adding Et_3N to a mixture of 3,5-bis(chloromethyl) mesitol, $HSCH_2COOCH_2CHEtBu$ and EtOH to yield **23** ($R = R^1 = CH_2COOHCH_2CHEtBu$)

Substituted phenols **24** and **25** ($R^1 = R^2 = R^3 =$ alkyl, $Z_2 =$ alkyl), have also been shown to have antioxidant activity by Evans and coworkers[32]. 4-Tert-butyl-2,6-bis-(octyl)thiomethyl phenol was prepared from paraformaldehyde, octane thiol and 4-tert-butyl phenol.

Polysulfides useful as antioxidants for plastics and lubricating oil were prepared recently, as reported by Born et al[33] by condensing $PhCH_2SNa$ with 2,6-di-tert-butyl-4-chloromethyl phenol.

Recently heat and light stabilisers of type 26 have been prepared by Meier et al.[34] 2,4,Bis(octylthiomethyl)-6-methyl phenol was stirred with H_2O_2 in Me_2CO to give **26** [$R^1 = Me$, $R^2 =$ octyl, $R^3 = H, m = 1, n = 0$].

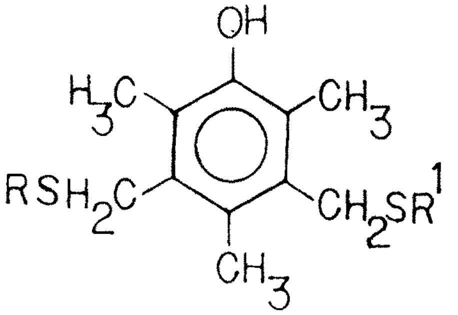
Nitrogen containing Phenolic Antioxidants :

Bruk and coworkers[35] synthesised N-substituted-3,5-di-tert-butyl- 4-hydroxy benzyl amines by the reaction of 3,5-di-tert-butyl-4-hydroxy benzyl bromide with primary and secondary amines and were found to be useful as antioxidants.

Hindered phenols on reaction with appropriate hexahydro-s- triazine yielded hexahydro-1,3,5-tris-(4-hydroxy phenyl)-s-triazines **27** which were reported as suitable antioxidants by Beears [36]

Dexter [37] reported synergistic compounds containing hindered phenolic and dimide as heat stabilisers for polymers. The reaction of 3,4,3',4'-benzophenone tetracarboxylic diimide with $4,3,5\text{-}HO(Me_3C)_2C_6H_3(CH_2)_n\text{-}NR_2$ in DMF gave N,N'-bis (3,5-di-tert-butyl-4-hydroxy benzyl) benzophenone-3,4,3',4'-tetracarboxylic diimide **28** ($n = 0,2,3$)

N,N'-Bis [β-(3,5-di-tert-butyl-4-hydroxy phenyl)propionyl] hydrazines **29** useful as antioxidants have been prepared by Nakinishi and Kirii[38] 3-(3,5-Di-tert-butyl-4-hydroxy phenyl) propionyl chloride in $CHCl_3$ was treated with MeNHNHMe.HCl and Et_3N in $CHCl_3$ and stirred to give **29** ($R^1 = Ph$, $R^2 = H$).



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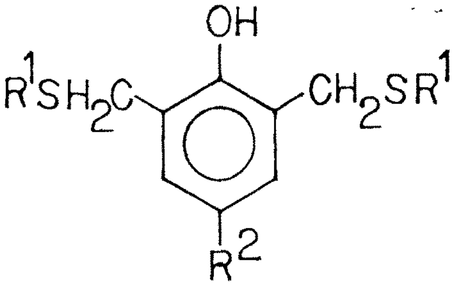

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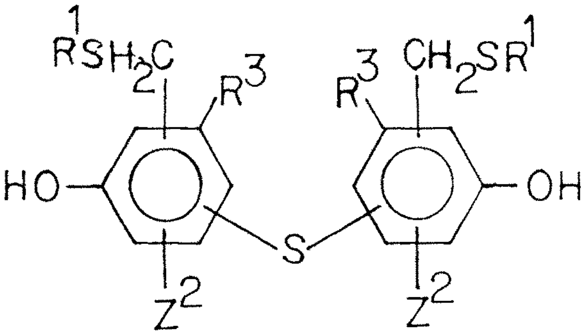

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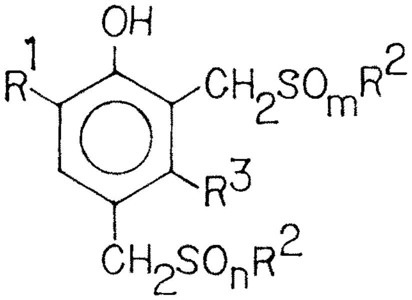

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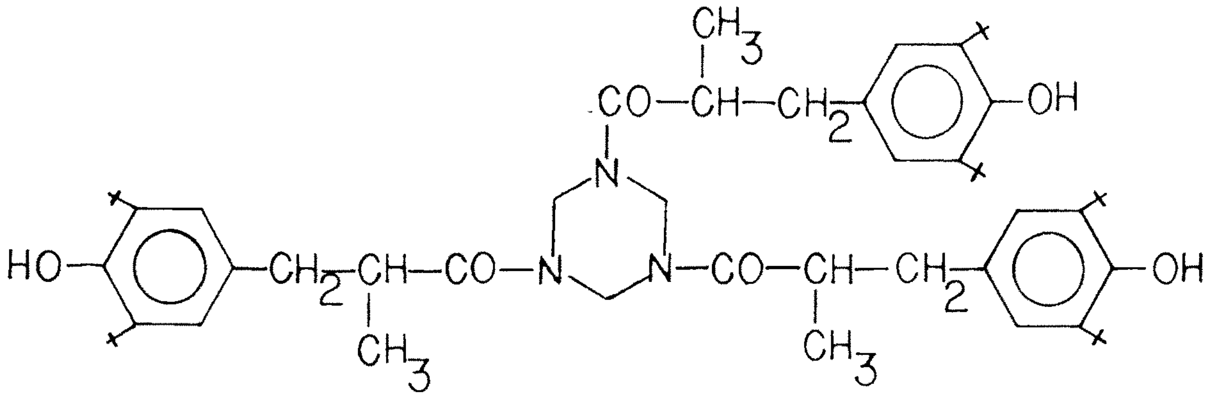

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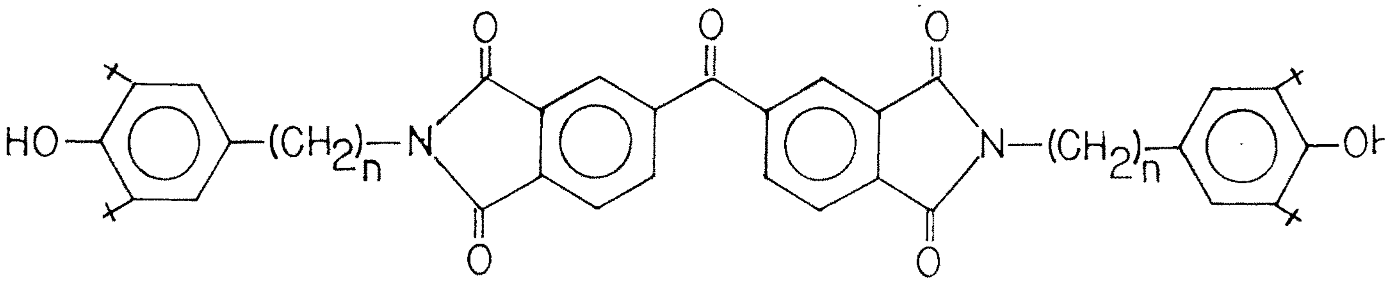

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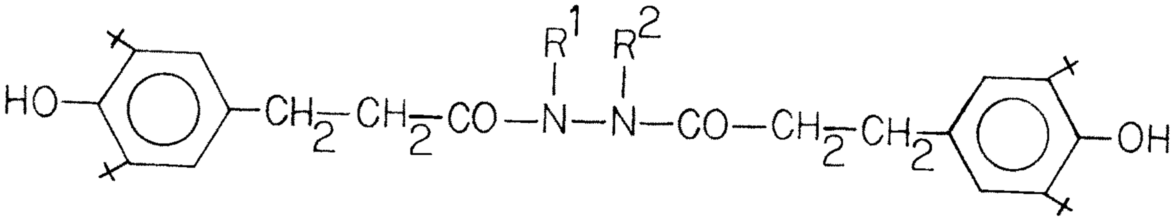

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Nitroalkane based antioxidants **30** useful for lubricants and polymers were put forward by Dounchis.[39] The compound **30** (R = $MeOCH_2$) was prepared by the condensation reaction of a nitroalkane with HCHO and 2,6-$(Me_3C)_2C_6H_3OH$)

A new process has been developed for the synthesis of N,N'-bis (3,5-di-tert-butyl-4-hydroxy phenyl) amine by Glebova et al.[40]. The compound was prepared by passing oxygen through 4-amino,2,6- di-tert-butyl phenol in toluene followed by reduction with Zr/AcOH, and found to be suitable as stabiliser for aviation fuels

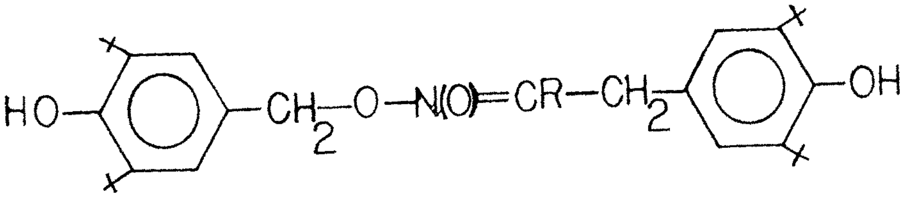
4-(α-Phenylethyl)3-hydroxydiphenylamines **31** were found to be useful antioxidants for lubricants by Baur and coworkers[41]. They synthesised **31** ($R = R^1$ =H,CHMePh) by alkylating 3-HOC $_6H_4$NHPh with styrene in presence of Friedal-Crafts catalyst.

Everly and Roper[42] synthesised 2-(3',5'-dihydrocarbyl-4'- hydroxybenzyl)-1,3-diketones **33** as antioxidants for polymers, gasoline and oil The compound **33** ($R^1 = R^2$ =hydrocarbyl) was prepared by reaction of benzylamines **32** (R^5,R^6 = alkyl,aryl) with 1,3-diketones $R^3COCH_2COR^4$-($R^3 = R^4$ =alkyl) in presence of an alkali or alkaline earth hydroxide

Polyolefins and organic materials have been stabilised by amino- alkylamide derivatives of (3,5-di-tert-butyl-4-hydroxy phenyl) propionic acid **34** as reported by Helwig and coworkers[43] **34** (R=2,3,5,6-tetrachloro-4-cyano phenyl) was prepared from pentachlorobenzonitrile and N-(2-amino ethyl)-3-(3,5-di-tert- butyl-4-hydroxy phenyl) propionamide.

p-(Octadecyloxycarbonyl) benzyl bromide was reacted with $HONH_2$ HCl in preparation of N,N-bis[p-(octadecyloxycarbonyl) benzyl] hydroxylamine by Ravichandran and Snead[44] as antioxidant for synthetic polymers.

Recently Luk'yanchuk et al[45] carried out cycloaddition reaction of tri-methyl-1,4-benzoquinone with 2-(cyanomethyl)-1-phenyl- 1,3,4-triazole in methanol containing piperidine to give 5- hydroxy-4,6,7-tri-methylbenzofurans **35** useful as antioxidants



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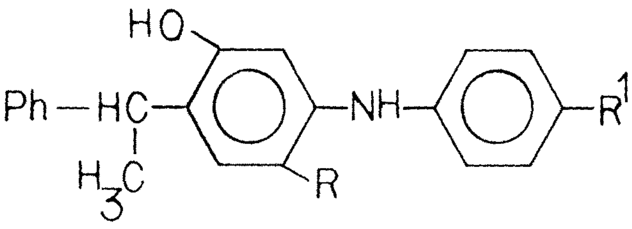

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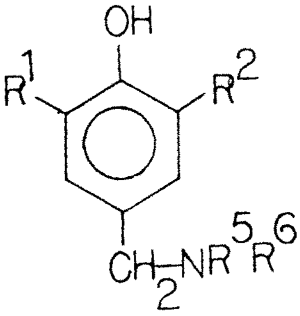

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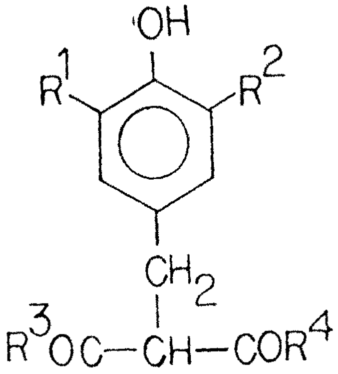

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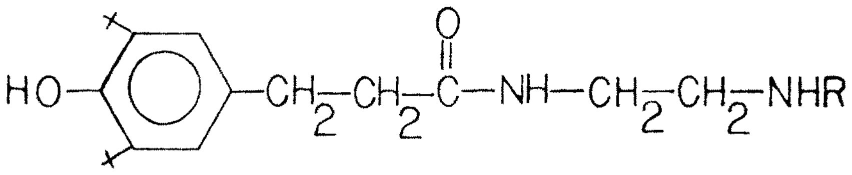

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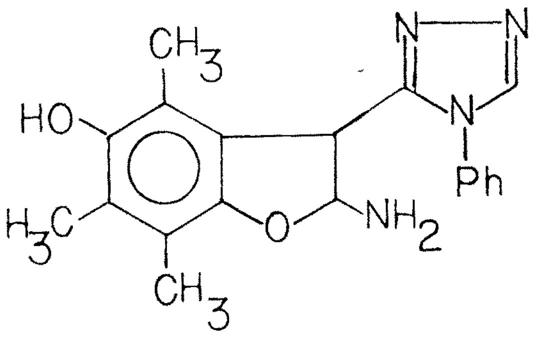

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Phosphorus containing Phenolic Antioxidants :

Heat stabilisers for various different polymers like nylon-6, polypropylene, urethane rubber were prepared by Schwarzenbach and Rosenberger[46]. They synthesised **36** by reacting 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo [2.2.2]octane with (3,5-di-tert-butyl-4-hydroxy phenoxy) acetyl chloride in $AcNMe_2$.

Sterically hindered phenolic phosphorous antioxidants have been investigated as stabilisers for polyethylene by Robin and Schulte[47] The phosphites **37** and **38** were prepared by heating 2,2'-methylene bis(4-methyl-6-tert-butyl phenol) with PCl_3 in o-dichlorobenzene.

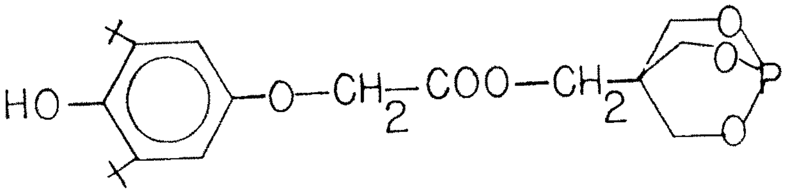
Metallic salts of α-hydroxybenzyl phosphonic acid were used as light and heat stabilisers for polypropylene as reported by Hopper and Tschenulin[48]. The acids $4,3,5\text{-}HO(Me_3C)_2C_6H_2CR(OH)PO(OH)_2$ (R=H or Me) were prepared by reaction of PCl_3 with $4,3,5\text{-}HO(Me_3C)_2COR$ followed by hydrolysis.

Spivack [49] reported poly (ol esters) of alkylated 4-hydroxy benzyl phosphinic acids **39** (R=trimethylene) as lubricants and stabilisers for rubber and polyolefins. They were prepared by reaction of Ph (3,5-di-tert-butyl-4-hydroxy benzyl) phenyl phosphinate and appropriate alcohol.

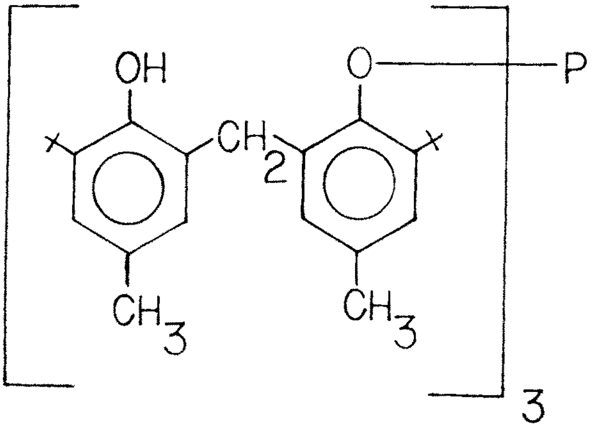
Akhmedzade et al.[50] synthesised phosphorous and sulphur containing antioxidants. They reacted $4,3,5\text{-}HO(Me_3C)_2C_6H_2CH_2Cl$ with Na_2S and $ClCH_2CH_2OH$ in EtOH to yield $4,3,5\text{-}HO(Me_3C)_2C_6H_2\text{-}CH_2SCH_2CH_2OH$ which on further reaction with PCl_3,$(PhO)_2PCl$, $PhOPCl_2$ and pyrocatechol chlorophosphite gave $(4,3,5\text{-}HO(Me_3C)_2C_6H_2\text{-}CH_2SCH_2CH_2O)_nPR_{3\text{-}n}$ (n=3, R=PhO, n=1,2, R=OC_6H_4O-o).

Dressler [51] prepared stabilisers and antioxidants for organic materials by treating 4,6-di-tert-butyl resorncinol, 2,4-lutidine and xylene with PCl_3 to give tris (4,6-di-tert-butyl-4-hydroxyphenyl)phosphite.

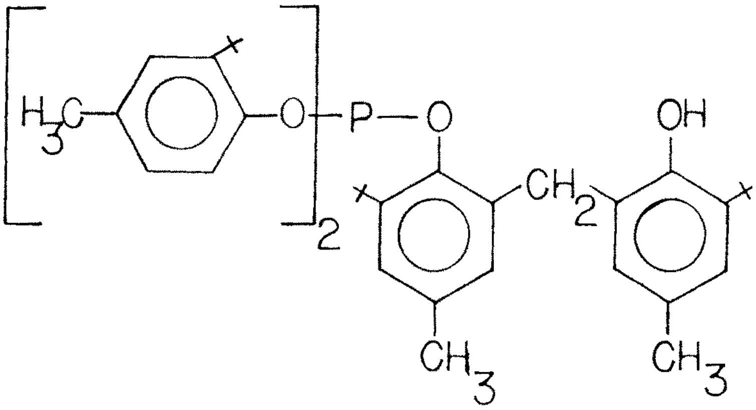
Polyester and vinyon fiber stabilisers have been prepared by Qizhang and Ruoying et al [52] They synthesised 3,5-di-tert-butyl-4-hydroxy benzyl phosphonic diethyl ester by reaction of N,N- dimethyl-3,5-di-tert-butyl-4-hydroxy benzylamine with diethylphosphonate.


HO
O
CH2
COO
CH2
O
O
P
O

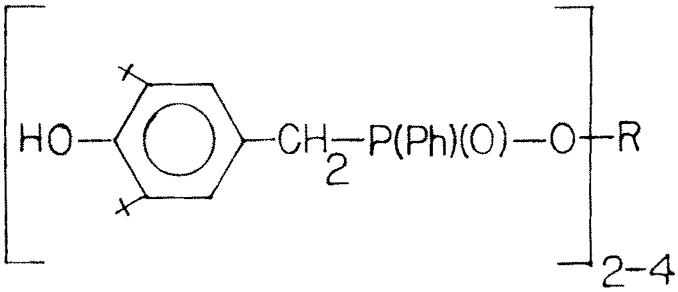
36


OH
O
P
CH2
CH3
CH3
3

37


H3C
O
P
O
2
OH
CH2
CH3
CH3

38


HO
CH2
P(Ph)(O)
O
R
2–4

39

Sulphur and Nitrogen containing Phenolic Antioxidants :

Fitten et al[53] reported the synthesis of 4-hydroxy 3,5-di-tert-butyl benzyl piperidine -1-carbodithioate **40** by reaction of CS_2 with a mixture of (4-hydroxy-3,5-di-tert-butyl benzyl) piperidine and was evaluated as antioxidants

3,5-(Dihydrocarbyl)-4-hydroxy phenyl-3-(hydrocarbyl)-4-hydroxy-5-(dialkyl amino methyl) benzyl sulphide **41** (R, R^1 & R^2 = hydrocarbyl) R^3=H, Me) was prepared by the reaction of 3- hydrocarbyl -4-hydroxy -5-(dimethyl amino) benzyl N,N'-dimethyl dithiocarbamate with a 4-mercapto phenol under alkaline condition as reported by O'shea[54] The antioxidant activity of **41** for rubbers plastics, fats and petroleum products was also reported.

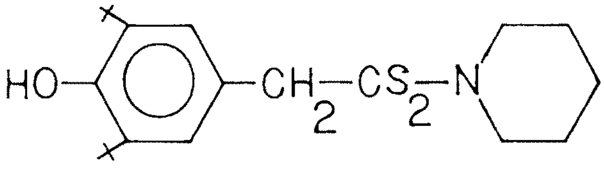
Alkyl hydroxybenzyl amides useful as antioxidants were prepared by Knell[55] by treatment of $4,3,5\text{-}HO(Me_3C)_2C_6H_2CH_2\text{-}NHCOR$ (R=Me, $CH=CH_2$) with RSH to yield $4,3,5\text{-}HO\text{-}(Me_3C)_3 - C_6H_2CH_2NHCOCH_2CH_2SR^1$ (R^1=Octyl).

Dunski and coworkers[56] synthesised thioamidophenol isocyanurate stabilisers for polyolefins. Stirring of N-(4-hydroxy-3,5-di- tert-butyl phenyl) acrylamide, tris [2-{(3-mercapto propionyl)oxy} ethyl] isocyanurate, $PhCH_2Me_3^+ \, OH^-$ in $CHCl_3$ gave phenolic isocyanurate.

Dunski et al.[57] also reported dithiodialkanoamido-phenol stabilisers for organic materials and plastics. Catalytic hydrogenation of 2,6-di-tert-butyl-4-nitroso phenol followed by reaction with dithiodiacetyl chloride in presence of Et_3N gave diamide **42**. [n=1-10, $R^1 = R^2 = C_{1\text{-}8}$ alkyl]

Steinburg and Cortolono[58] reported stabilisers containing sulphur and hindered phenol group for lubricating oils, plastics, resins and polymers. The reaction of 3-(3,5-di-tert-butyl-4-hydroxy phenyl) propionic acid, $4\text{-}MeC_6H_4SO_3H$ in PhMe with thioglycerol gave thiiranes **43** ($R^1 = R^2 = C_{1\text{-}6}$ alkyl, R^3=H, β=hetroatom, m=0-6, n=1-6]

Thorwart and coworkers[59] carried out the synthesis and evaluation of 5-(3-alkyl-5-tert-butyl-4-hydroxyphenyl)-2-amino-6H-1,3,4-thiadiazines **44** useful as inhibitors, antioxidants and pharmaceuticals. 2-Bromo-1-(3,5-di-tert-butyl-4-hydroxy phenyl) ethanone was refluxed with $Me_2NCSNHNH_2$ in EtOH to give **44** (R^1,R^2 = $C_{1\text{-}3}$ alkyl, R^3, R^4 = 4-7 membered hetrocycle)



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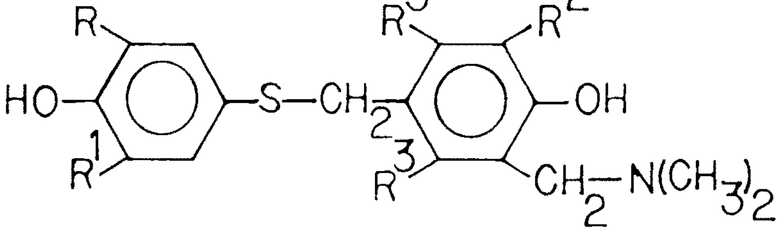

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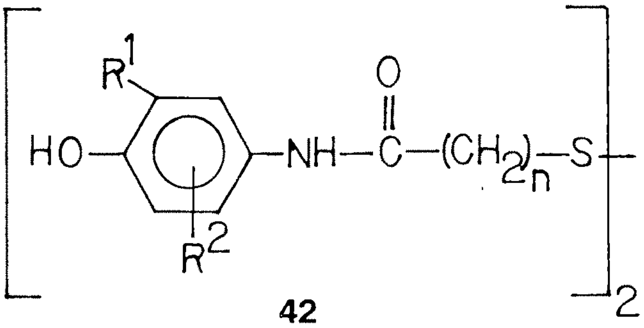

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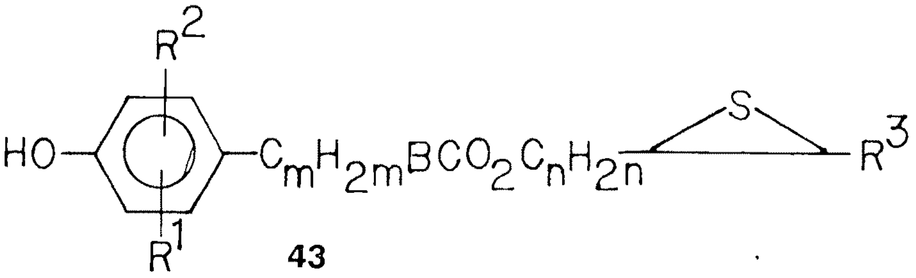

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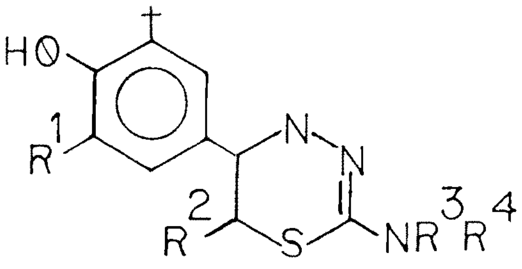


44

Recently Tochacek[60] reported bis (Phenyl propionyl hydrazinocarbonyl alkyl) thioethers **46** ($R^1 = R^2 = C_{1-24}$ alkyl, n = 1- 24) as antioxidants for plastics The compound **46** was prepared by acylation of $[H_2NNHCO(CH_2)_n]_2S$ with a phenyl propionate **45**. ($X = OR^3$, halo, $R^3 = C_{1-12}$ alkyl).

From the literature survey it is revealed that among the antioxidants based on hindered phenols, the combination of hindered phenol with acid hydrazones is less extensively studied, whereas the combinations of hindered phenol with thiosemicarbazones, oxadiazole, and pyrazole are apparently not reported. Many of the new antioxidants synthesised combine a hindered phenol group with another group containing nitrogen sulphides, triazines, phosphates and phosphites. These combinations would give active materials having the advantage of two or more stabilising moieties. So it is anticipated that the above mentioned combinations would give significant stabilisation efficiency.

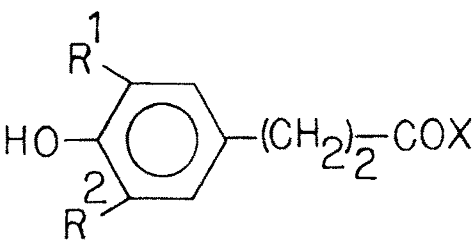
With these in view the following antioxidants are synthesised. The structures are assigned on the basis of elemental analysis, IR and NMR spectral studies.

Present Work :

3,5-Di-tert-butyl-4-hydroxy benzaldehyde is synthesised from 2,6-di-tert-butyl-4-methyl phenol (AO_1) according to reported procedure[61].

Synthesis of N' (3,5-di-tert-butyl-4-hydroxy phenyl) methylene-4-hydroxy benzohydrazine (AO_2).

3,5-Di-tert-butyl-4-hydroxy benzaldehyde on condensation with 4-hydroxy benzo hydrazide in ethanol gave N'(3,5-di-tert-butyl-4-hydroxy phenyl) methylene-4-hydroxy benzohydrazine (Scheme-1). The structure of AO_2 was established on the basis of its ^{1}HNMR spectra (Fig.2.1A) taken in DMSO which exhibited singlet at δ 1.5 for two tert-butyl groups at C-3 and C-5 positions of phenyl ring. The two doublets appearing at δ 6.9 and δ 7.9 (J = 8Hz) indicate aromatic protons of hydroxy phenyl ring Singlet at δ 7.5 showed the presence of two protons of phenyl ring Singlet at δ 8 3 indicate proton of CH = N group. The IR (KBr) spectra (Fig.2.2) showed band at 1610 cm^{-1} for C = N group. The strong band at 1640 cm^{-1} is due to > C = O of (CONHN = CH) group. The broad band observed at 3150-3250 cm^{-1} is for -NH group and band at 3700 cm^{-1} is for - OH group. The signal for aldehydic proton of 3,5-di-tert-butyl-4-hydroxy benzaldehyde appears at δ 9.8, that particular signal disappears in the case of N'(3,5-di-tert-



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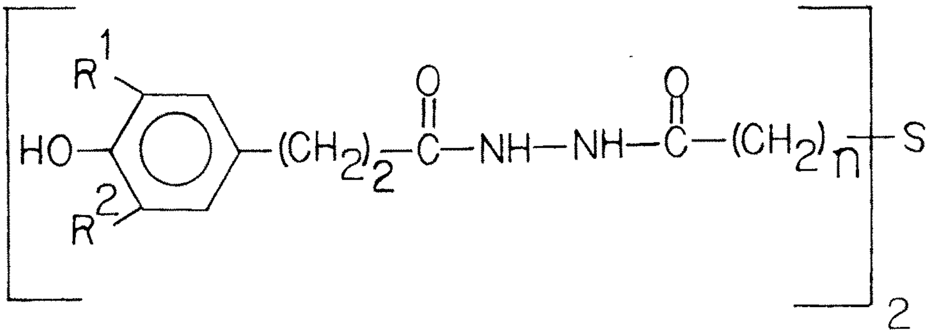
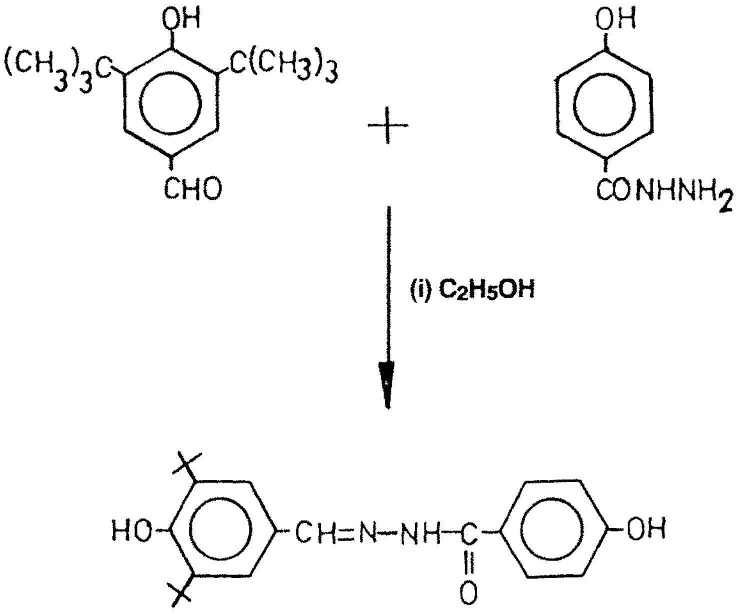


46

Scheme-1



AO2

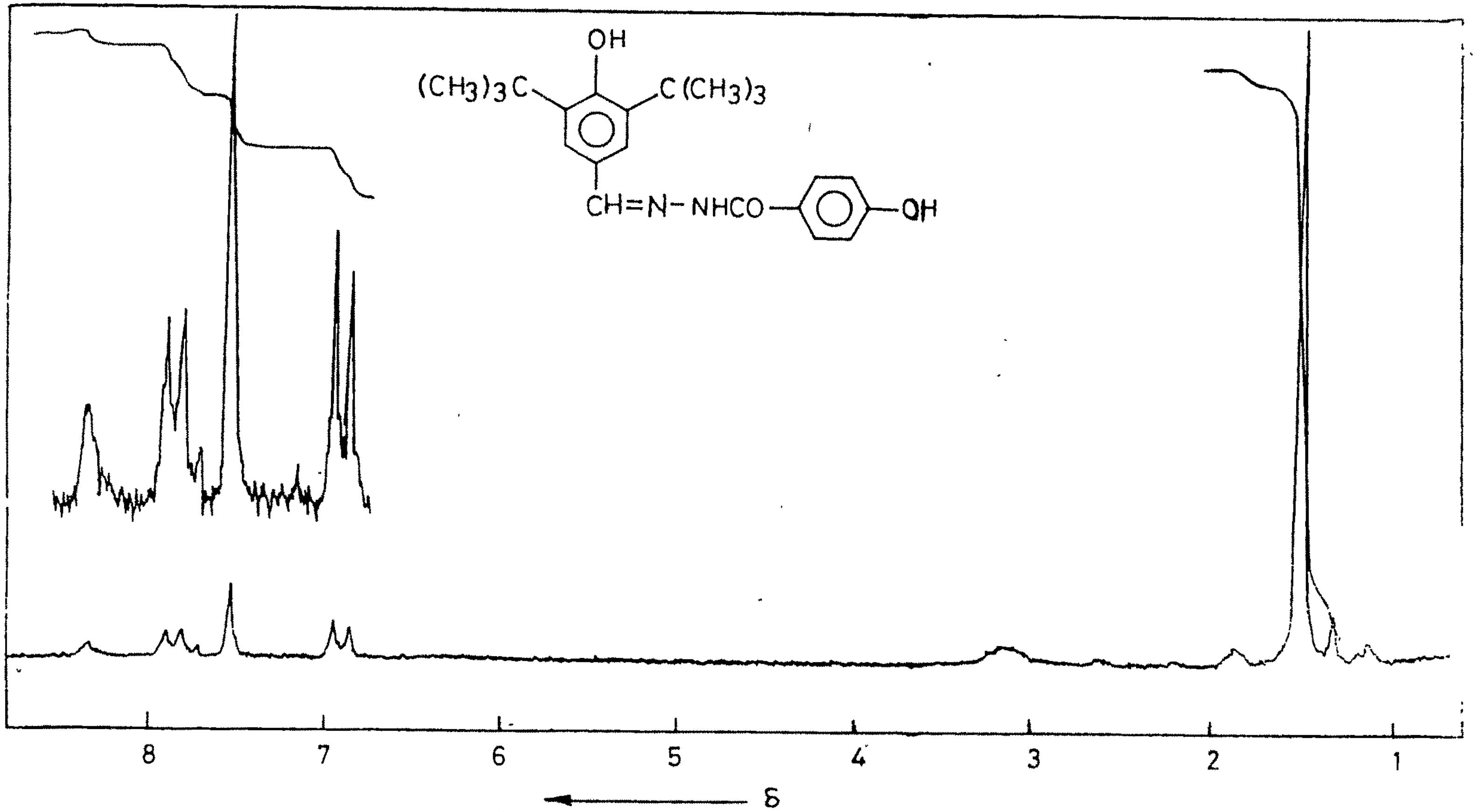


Fig. 2.1A ^{1}HNMR spectra of Compound AO_2

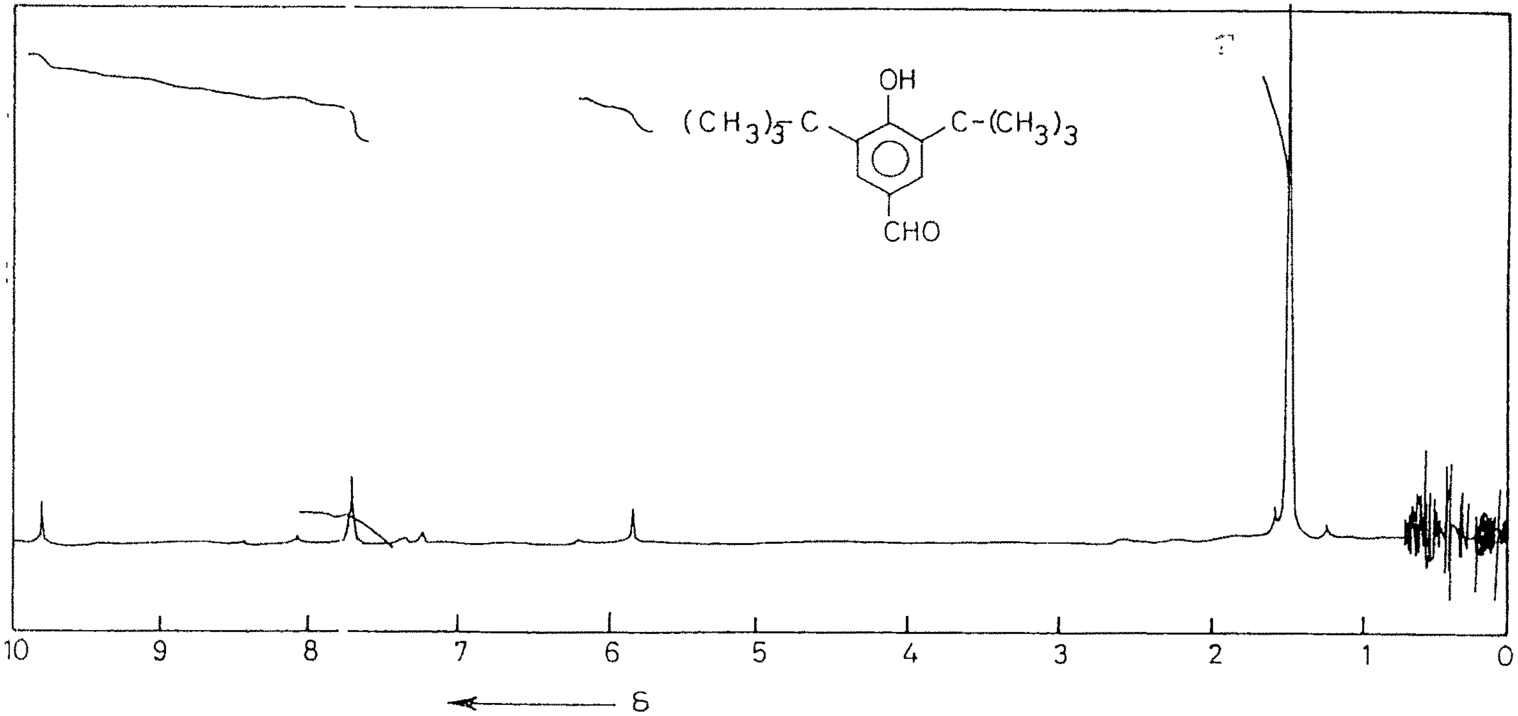


Fig. 2.1B ^{1}HNMR spectra of 3,5-di-tert-butyl-4-hydroxy benzaldehyde

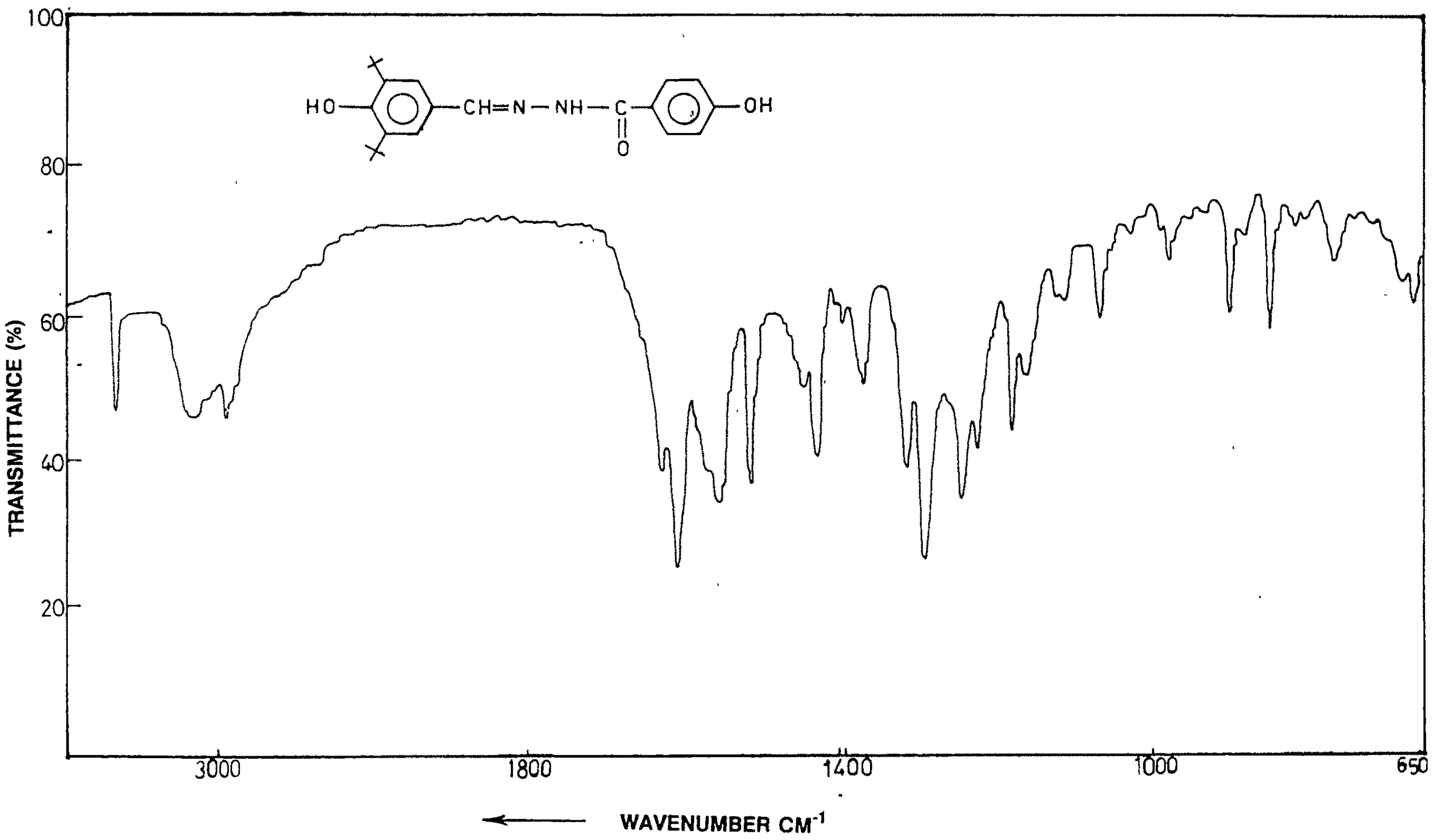


Fig. 2.2 IR spectra of Compound AO_2

butyl-4-hydroxy phenyl) methylene-4-hydroxy benzohydrazine and the new signal for CH=N appears at δ 8.3 (Fig. 2.1B).

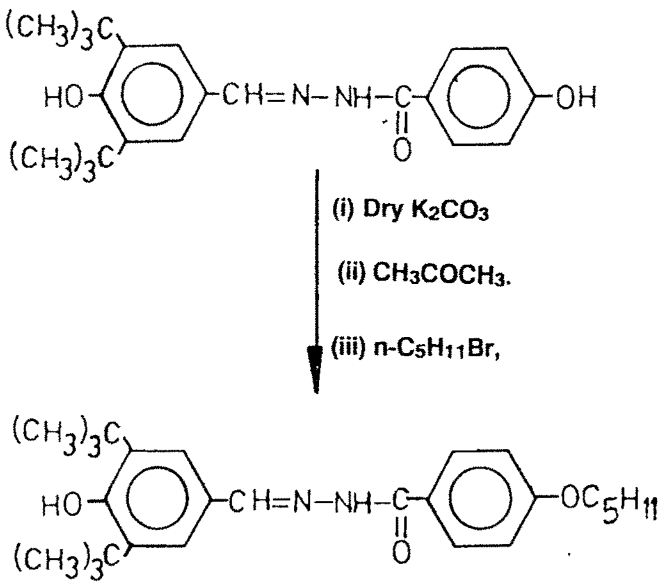
Synthesis of N'(3,5-di-tert-butyl-4-hydroxy phenyl) methylene-4-pentyloxy benzohydrazine (AO$_3$).

N'(3,5-di-tert-butyl-4-hydroxy phenyl) methylene-4-hydroxy benzohydrazine on alkylation with n-bromo pentane in presence of anhydrous potassium carbonate in dry acetone gave corresponding N'(3,5-di-tert-butyl-4-hydroxy phenyl) methylene-4-pentyloxy benzohydrazine, the structure of which was confirmed by the spectral studies (Scheme-2). The ^{1}HNMR spectra (Fig.2.3) taken in CDCl$_3$ exhibited a singlet at δ 1 35 for two tert-butyl groups of C-3,C-5 of phenyl ring and pentyl group at 4-position of the pentyloxy benzohydrazine Triplet at δ 4.0 is due to the methylene protons of the pentyloxy benzohydrazine Singlet at δ 5.4 is due to proton of hydroxy group. Two doublets which appeared at δ 6.9 and δ 7 9 (J=7Hz) indicated coupling of two aromatic protons located at C-2 and C-3 of pentyloxy benzohydrazine. Signal at δ 7.4 indicated a singlet for two aromatic protons at C-2 and C- 6 of the phenyl ring. The IR (KBr) spectra (Fig.2.4) showed a band at 1105 cm^{-1} for (C-O-C) linkage. The band at 1596 cm^{-1} is due to (C=N) group. The band at 1675 cm^{-1} is due to the > C=O of (CONHN=CH) group. The broad band at 3400-3500 cm^{-1} is due to the - OH group

Synthesis of N'(3,5-di-tert-butyl-4-hydroxy phenyl) methylene-4-octyloxy benzohydrazine (AO$_4$).

AO$_4$ was syhthesised by alkylation of N'(3,5-di-tert-butyl-4-hydroxy phenyl) methylene-4-hydroxy benzohydrazine with n-octyl bromide in presence of anhydrous K$_2$CO$_3$ in dry acetone (Scheme-3). The ^{1}HNMR spectra (Fig 2.5) was taken in CDCl$_3$ showed a singlet at δ 1.35 for two tert-butyl group at C-3, C-5 of phenyl ring and octyl group at 4-position of the octyloxy benzohydrazine. Signal observed at δ 3.9 exhibited a triplet for methylene proton of the octyloxy group of octyloxy benzohydrazine. Singlet at δ 5 4 is due to the hydroxyl proton of phenyl ring Two doublets located at δ 6 8 and δ 7.8 (J=8Hz) showed coupling of two aromatic protons at C-2 and C-3 of octyloxy benzohydrazine. Singlet at δ 7.4 indicated two aromatc protons at C-2 and C-6 of phenyl ring The IR (KBr) spectra (Fig.2 6) showed a band at 1164 cm^{-1} for ether (C-O-C) linkage The band at 1566 cm^{-1} is for C=N group. The band at 1651 cm^{-1} is due to the > C=O of (CONHN=CH) group. The band at 3293 cm^{-1} and 3634 cm^{-1} are due to -NH and -OH groups respectively.

Scheme-2



AO3

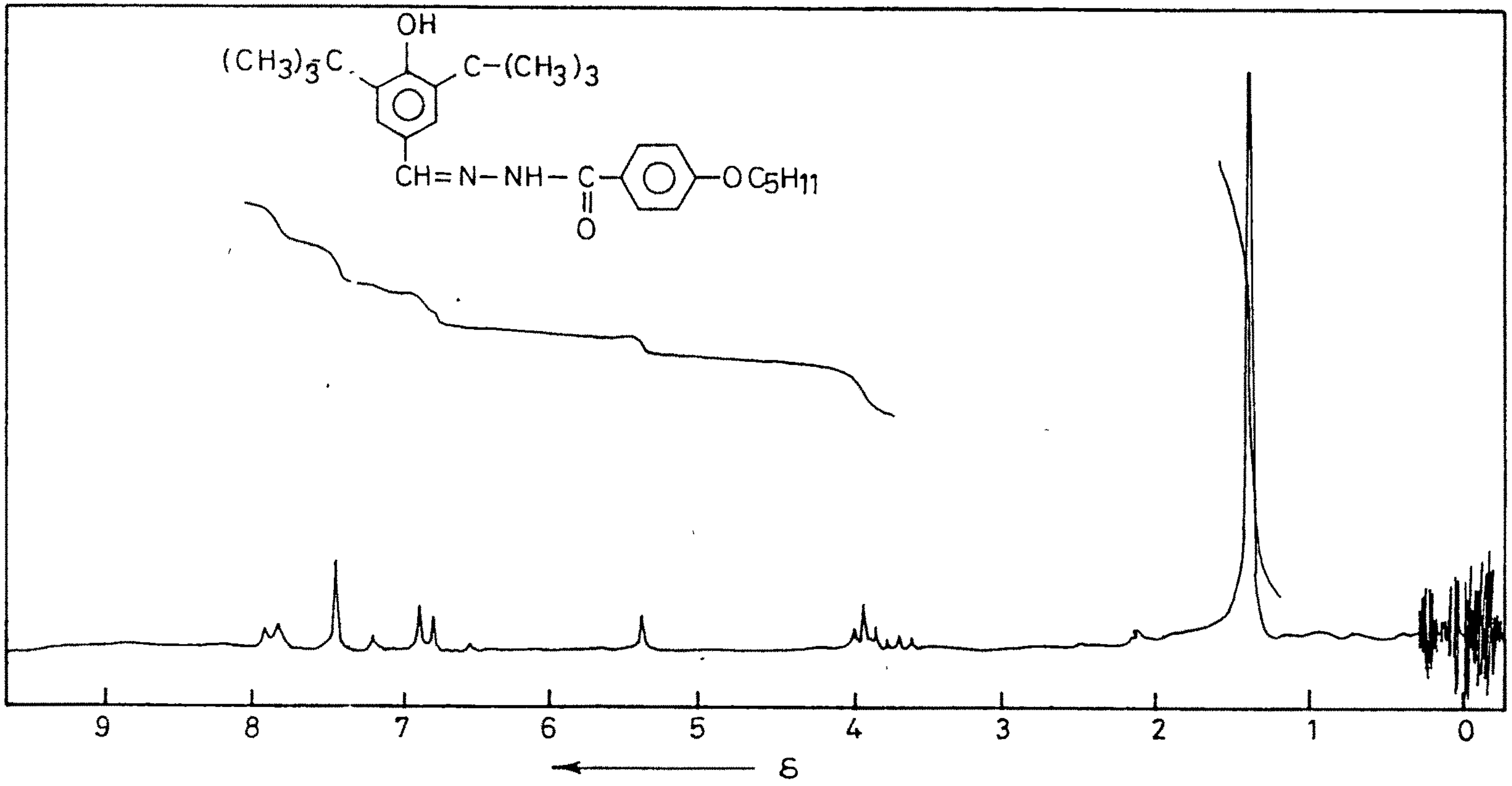


Fig. 2.3 ^{1}HNMR spectra of Compound AO$_3$

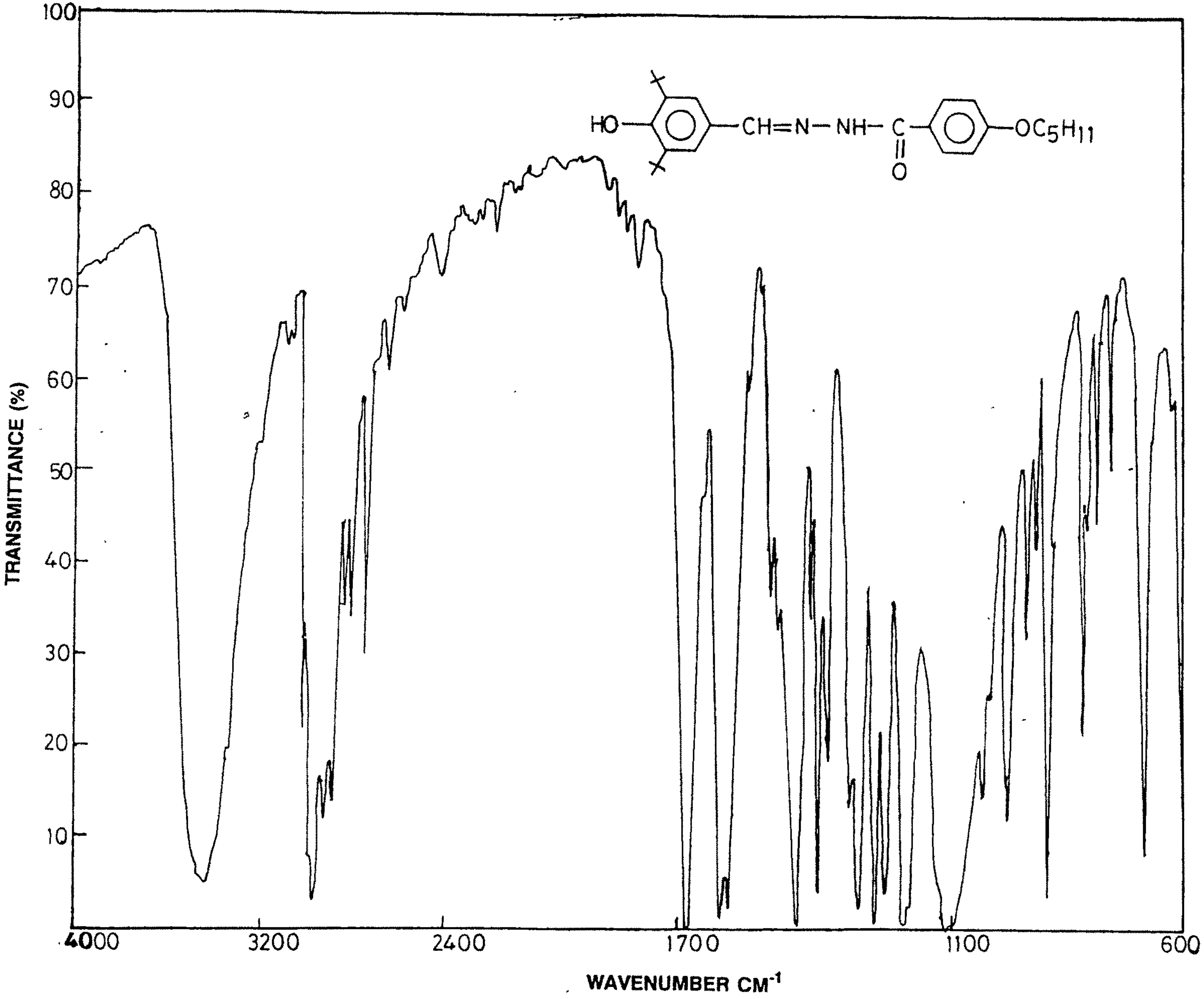
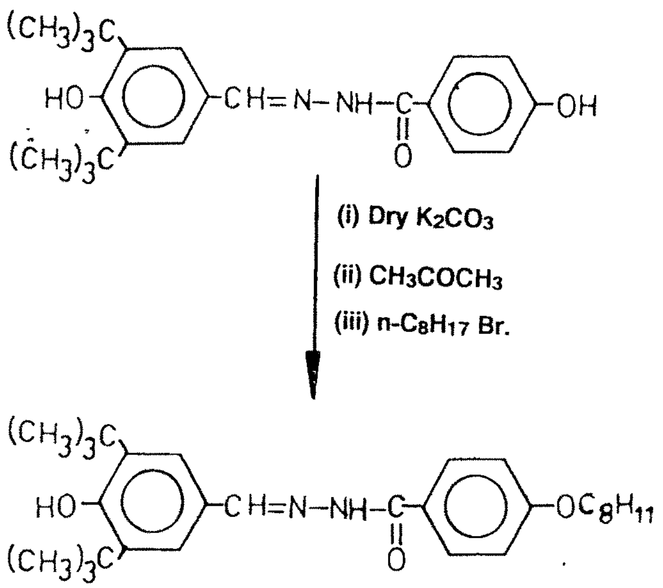


Fig. 2.4 IR spectra of Compound AO$_3$

Scheme 3


(CH3)3C
HO
(CH3)3C
CH=N-NH-C
O
OH
(i) Dry K2CO3
(ii) CH3COCH3
(iii) n-C8H17 Br.
OC8H11

AO4

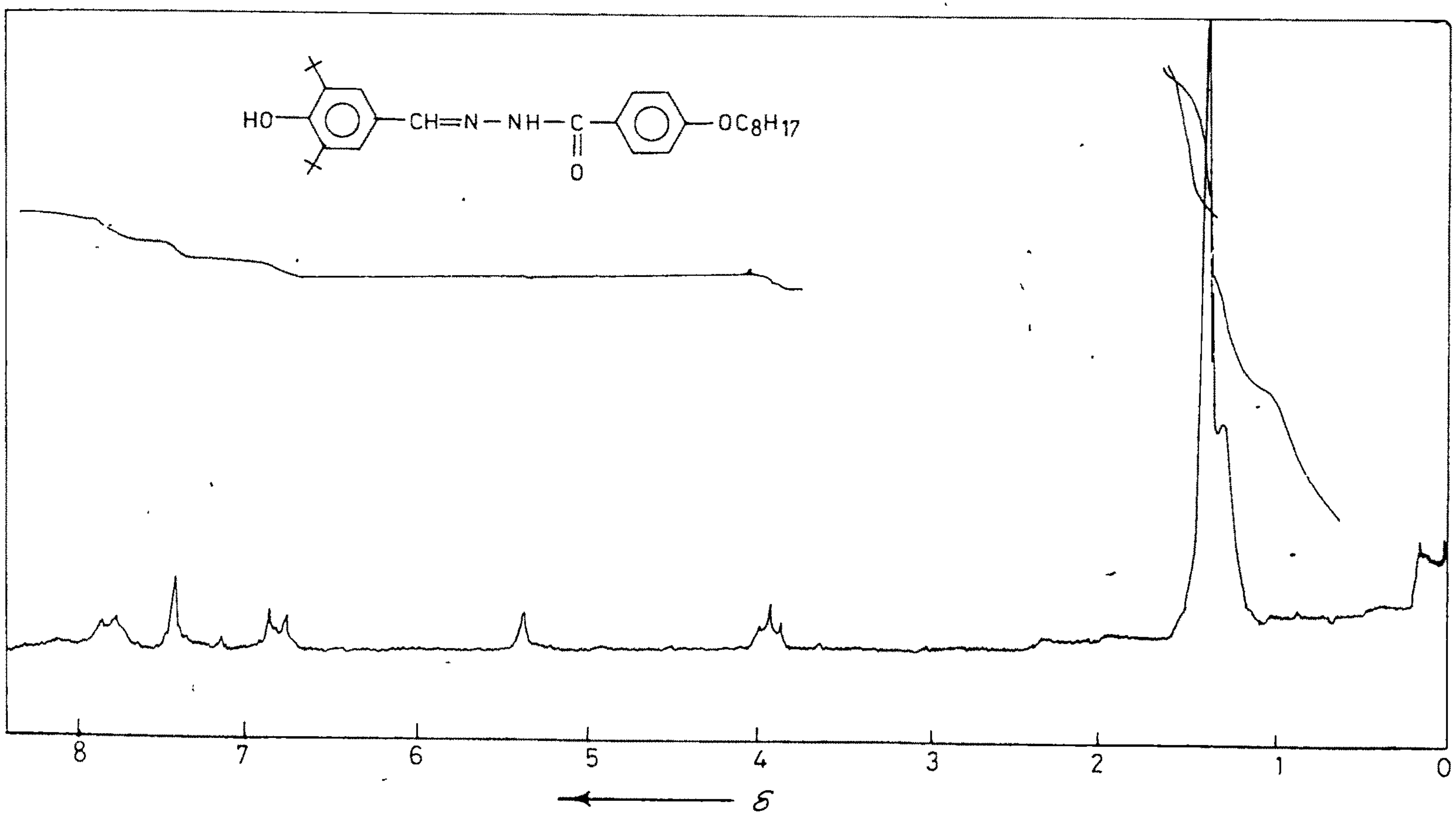


Fig. 2.5 ^{1}HNMR spectra of Compound AO$_4$

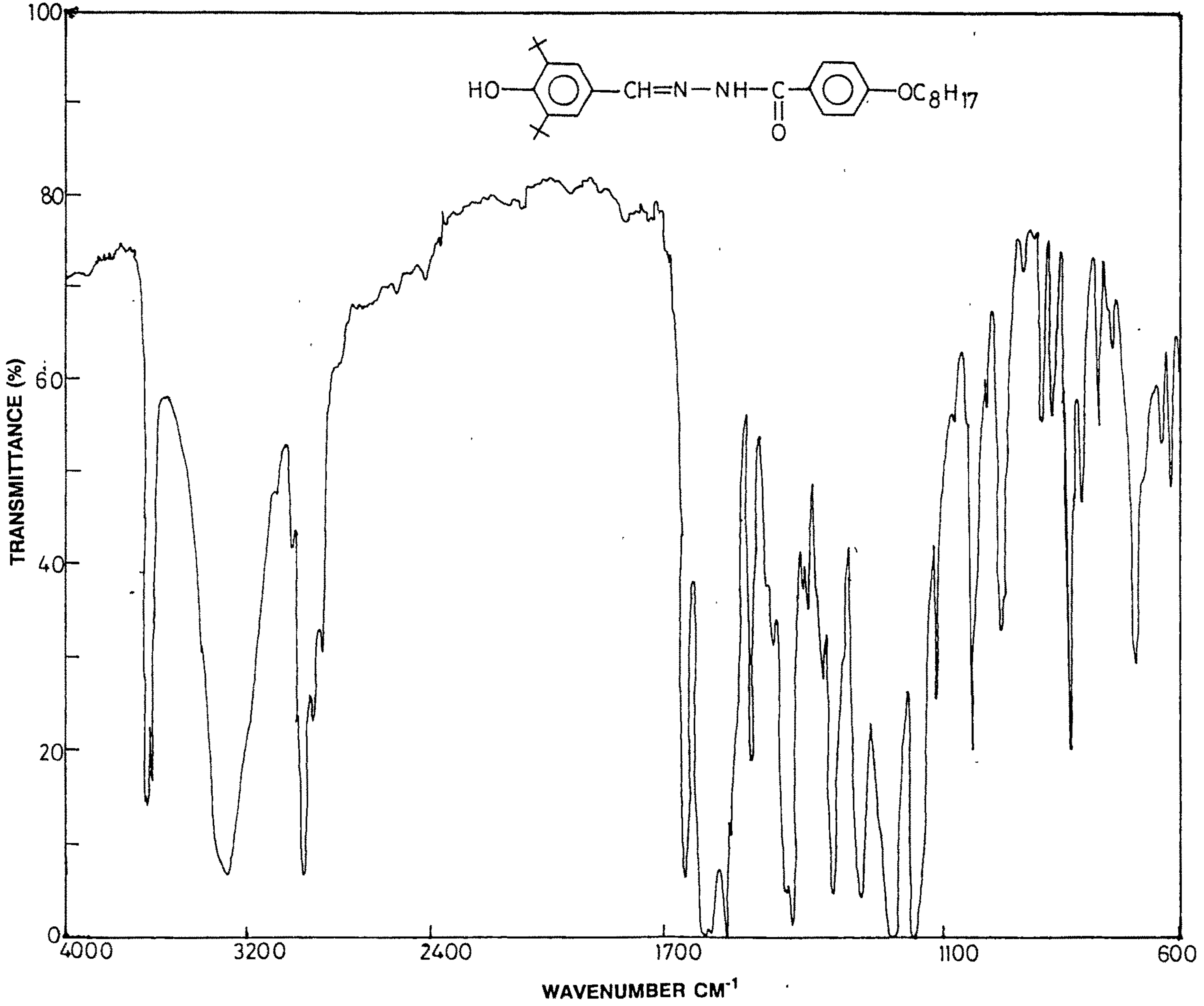


Fig. 2.6 IR spectra of Compound AO4

Synthesis of N'(3,5-di-tert-butyl-4-hydroxy phenyl) methylene-4-decyloxy benzohydrazine (AO_5).

N'(3,5-Di-tert-butyl-4-hydroxy phenyl) methylene-4-hydroxy benzohydrazine when subjected to alkylation with n-bromo decane in presence of anhydrous potassium carbonate in dry acetone gave N'(3,5-di-tert-butyl-4-hydroxy phenyl) methylene-4-decyloxy benzohydrazine (Scheme-4). The ^{1}HNMR spectra (Fig.2 7) of this compound taken in $CDCl_3$ showed a singlet at δ 1.35 for two tert- butyl groups at C-3, C-5 of phenyl ring and protons of decyl group at 4-position of decyloxy benzohydrazine. Triplet appeared at δ 3.9 is for the methylene proton of the decyloxy group. Singlet at δ 5.4 is due to the hydroxyl proton Signals at δ 6 8 and δ 7.9 (J=8Hz) showed two doublets indicating the coupling of two aromatic protons located at C-2 and C-3 of octyloxy benzohydrazine. Singlet at δ 7.4 indicated two aromatic protons at C-2 and C-6 of phenyl ring. The IR spectra (Fig.2.8) taken with KBr Pellet, showed an ether linkage (C-O-C) at 1165 cm^{-1} The band observerd at 1606 cm^{-1} indicated the presence of C=N group. The strong band at 1730 cm^{-1} is due to the > C=O (CONHN=CH) group. The broad band at 3225 cm^{-1} showed the presence of -NH group.

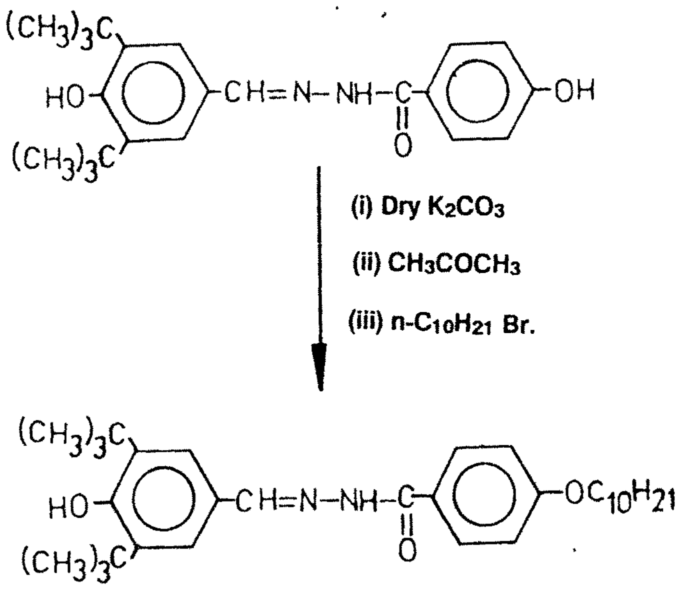
Synthesis of 2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carboxamide (AO_6).

3,5-Di-tert-butyl-4-hydroxy benzaldehyde in ethanol on condensation with semicarbazide hydrochloride in presence of sodium acetate gave 2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carboxamide (Scheme-5). The structure was established on the basis of its ^{1}HNMR spectra (Fig.2 9) taken in $CDCl_3$ + 2 drops of DMSO, which exhibited singlet at δ 1.45 indicating the presence of two tert-butyl groups at C-3 and C-5. Singlet at δ 5.6 for three protons of two different groups $-NH_2$ and -OH Singlet at δ 7.35 indicated two aromatic protons at C-2 and C-6. Singlet at δ 7 7 indicated the proton of CH=N group. The IR (KBr) spectra (Fig.2.10) showed band at 1571 cm^{-1} is for C=N group The band at 1683 cm^{-1} is due to >C=O of (CONHN=CH) group The band at 3301 cm^{-1} indicated presence of $-NH_2$ group The bands at 3481cm^{-1} and at 3628 cm^{-1} are due to -NH and -OH groups respectively.

Synthesis of 2-amino-5-(3,5-di-tert-butyl-4-hydroxy phenyl) 1,3,4-oxadiazole (AO_7).

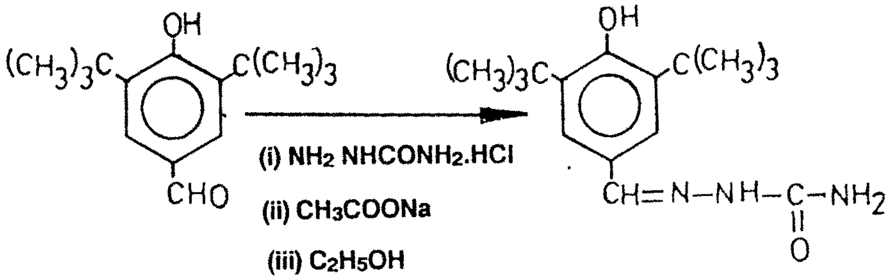
2-[(3,5-Di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carboxamide on cyclization with bromine and acetic acid in presence of sodium acetate gave 2-amino-5(3,5-di-tert-butyl-4-hydroxy phenyl) 1,3,4-oxadiazole (Scheme-6), the structure of which was established by its ^{1}HNMR spectra (Fig.2 11) taken in $CDCl_3$. Singlet at δ 1 45 indicated the presence of two

Scheme-4



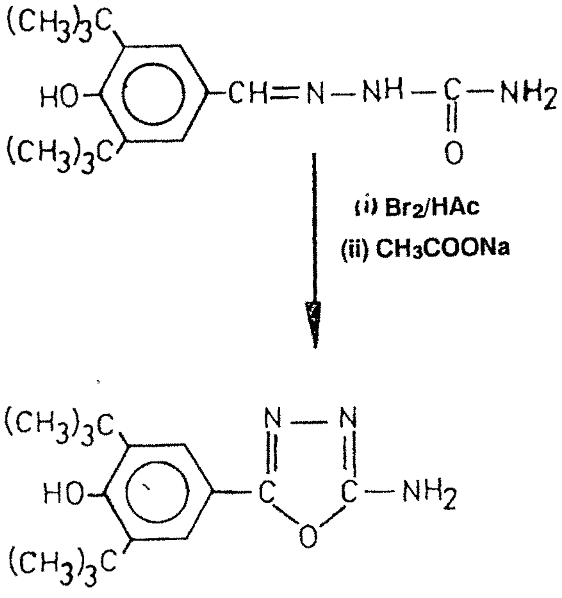
AO_5

Scheme-5



AO_6

Scheme-6



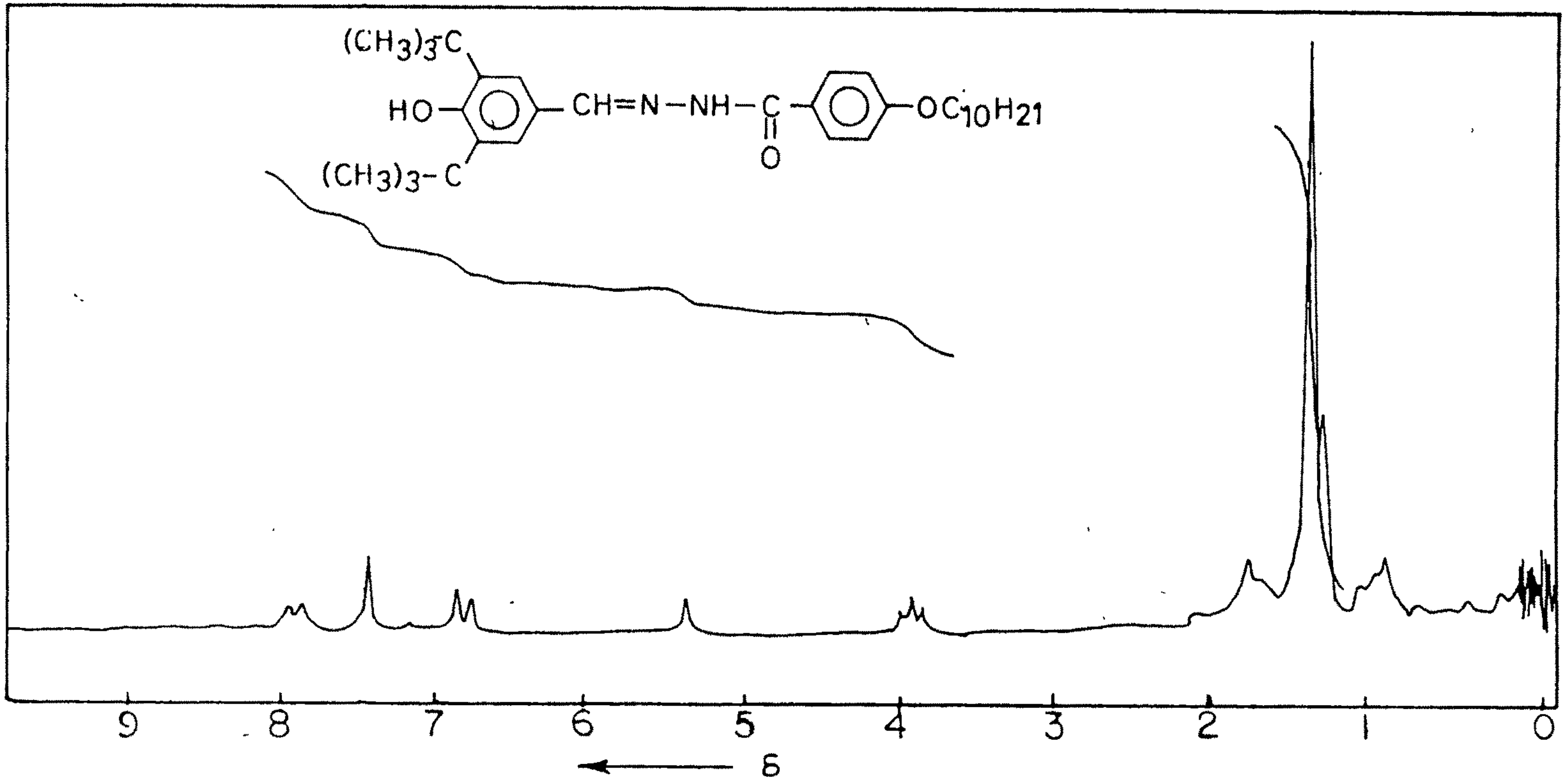
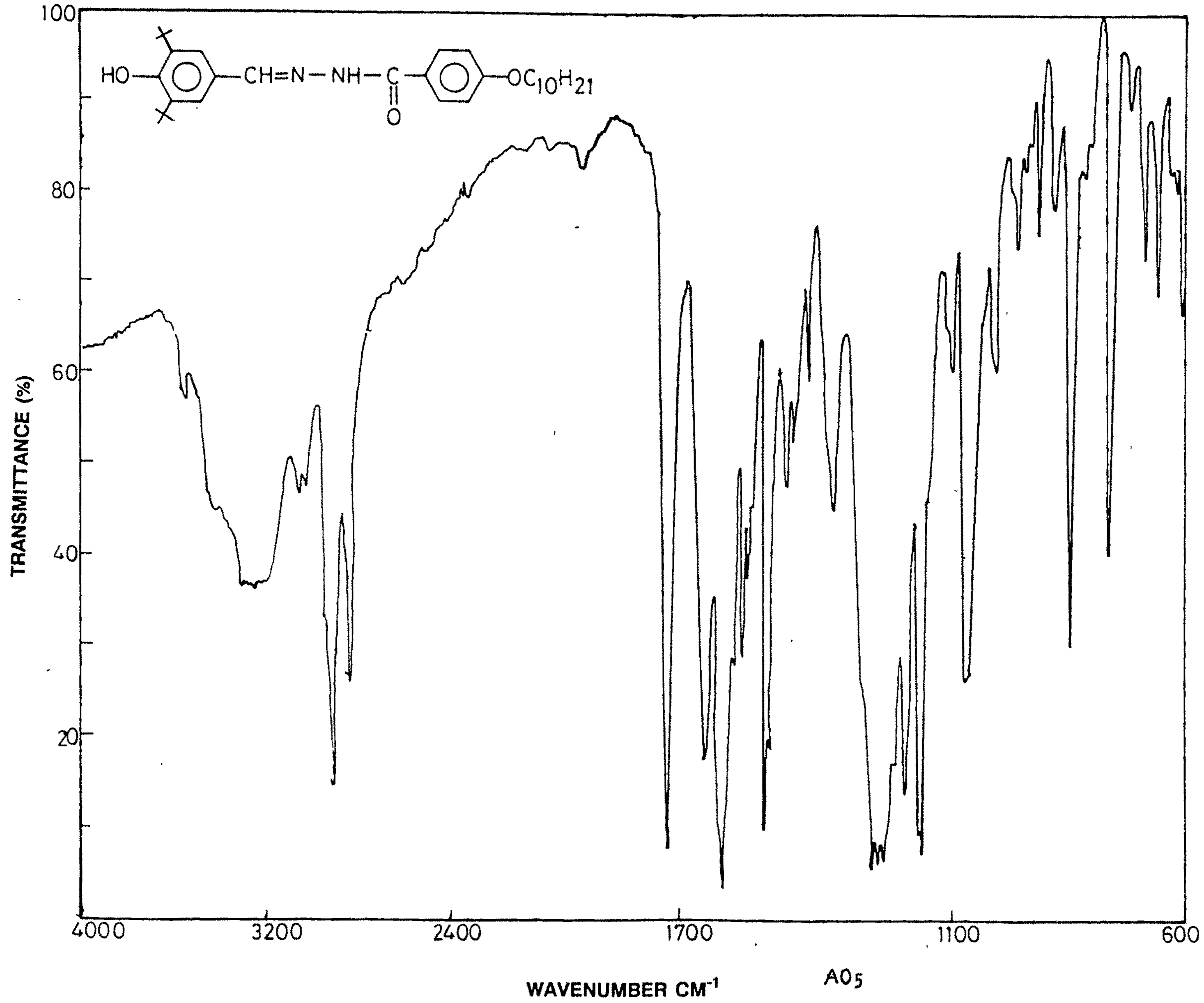


Fig. 2.7 ^{1}HNMR spectra of Compound AO$_5$



A05

Fig. 2.8 IR spectra of Compound AO_5

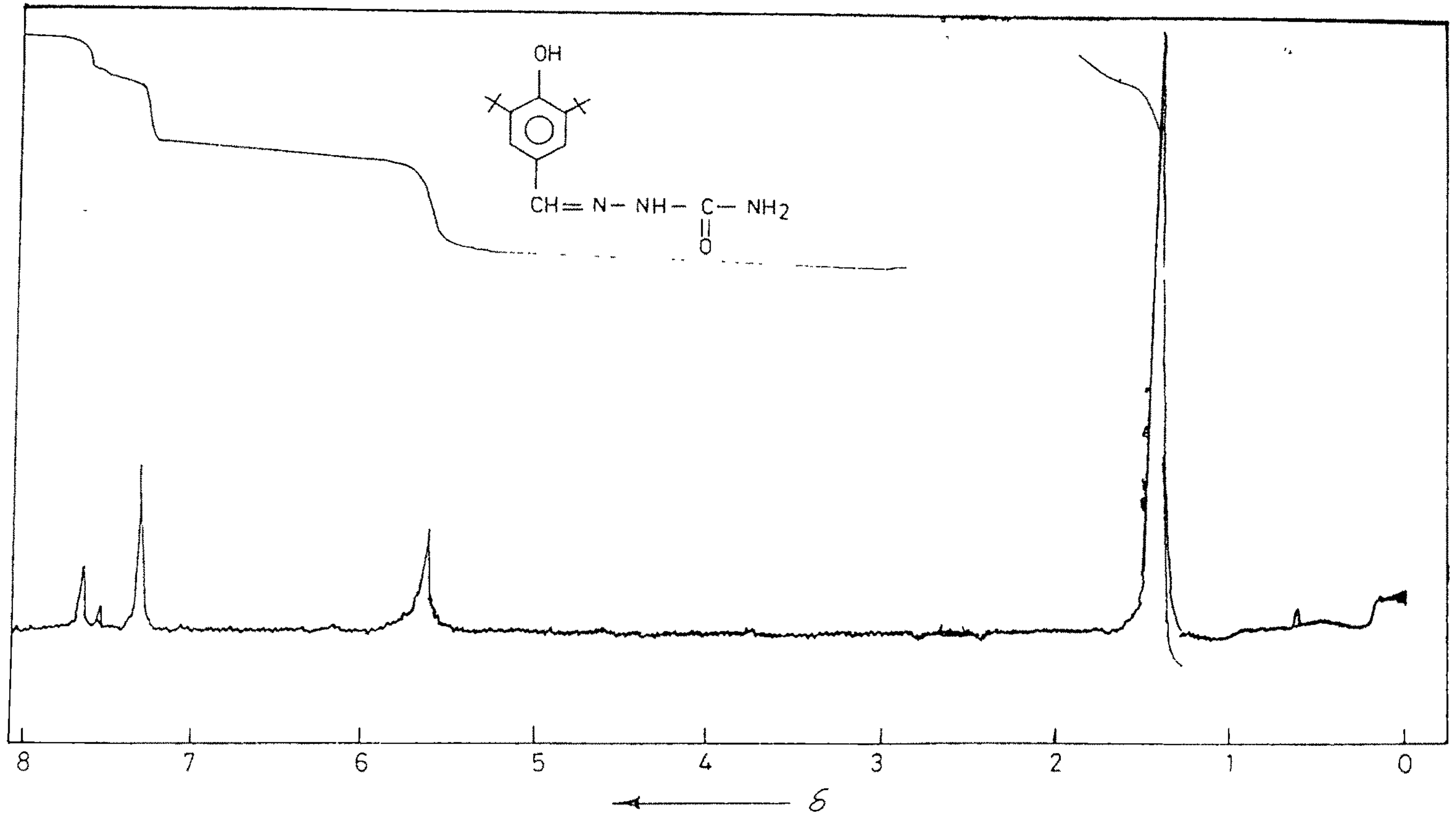


Fig. 2.9 ^{1}HNMR spectra of Compound AO_6

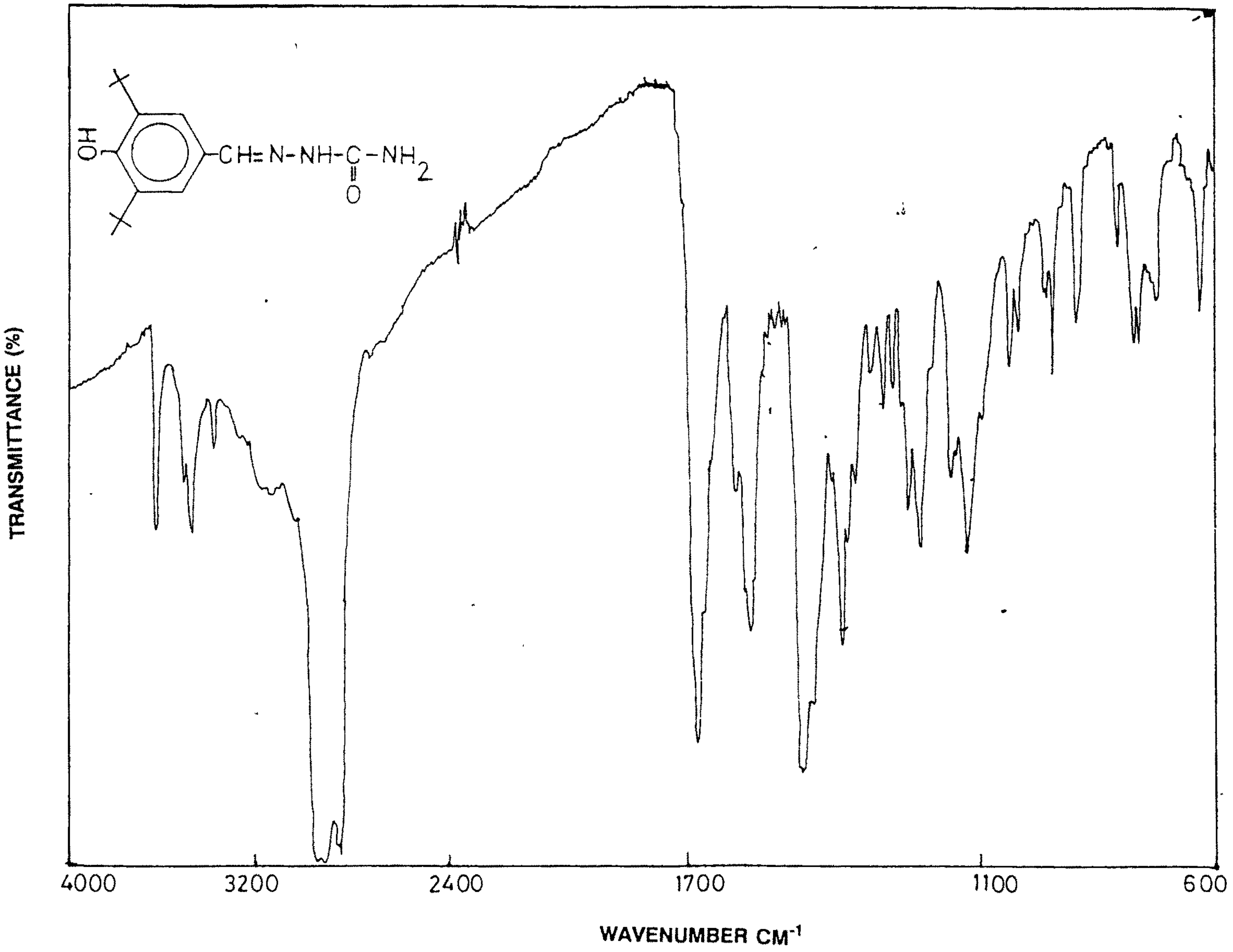


Fig. 2.10 IR spectra of Compound AO_6

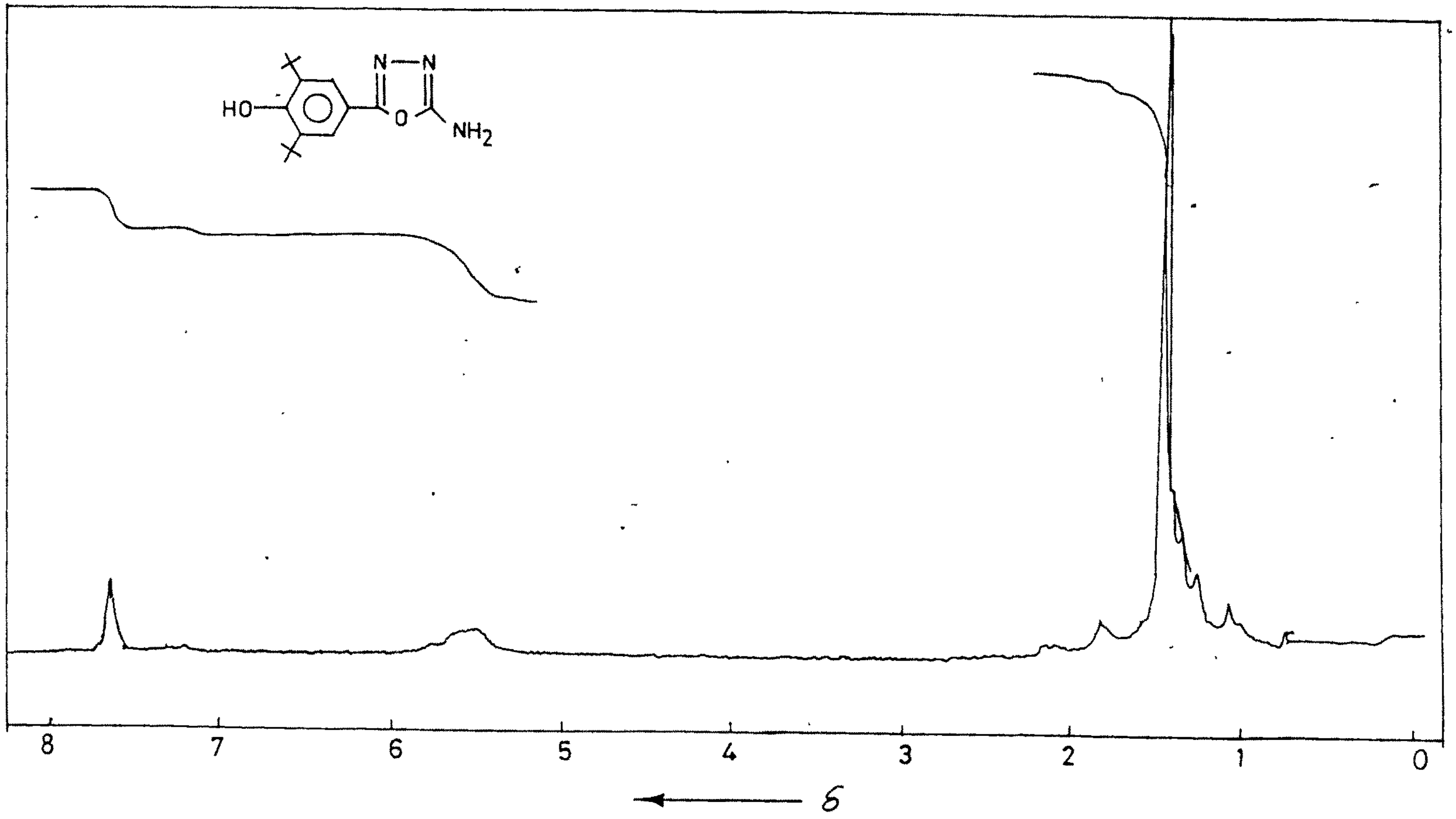


Fig. 2.11 ^{1}HNMR spectra of Compound AO_7

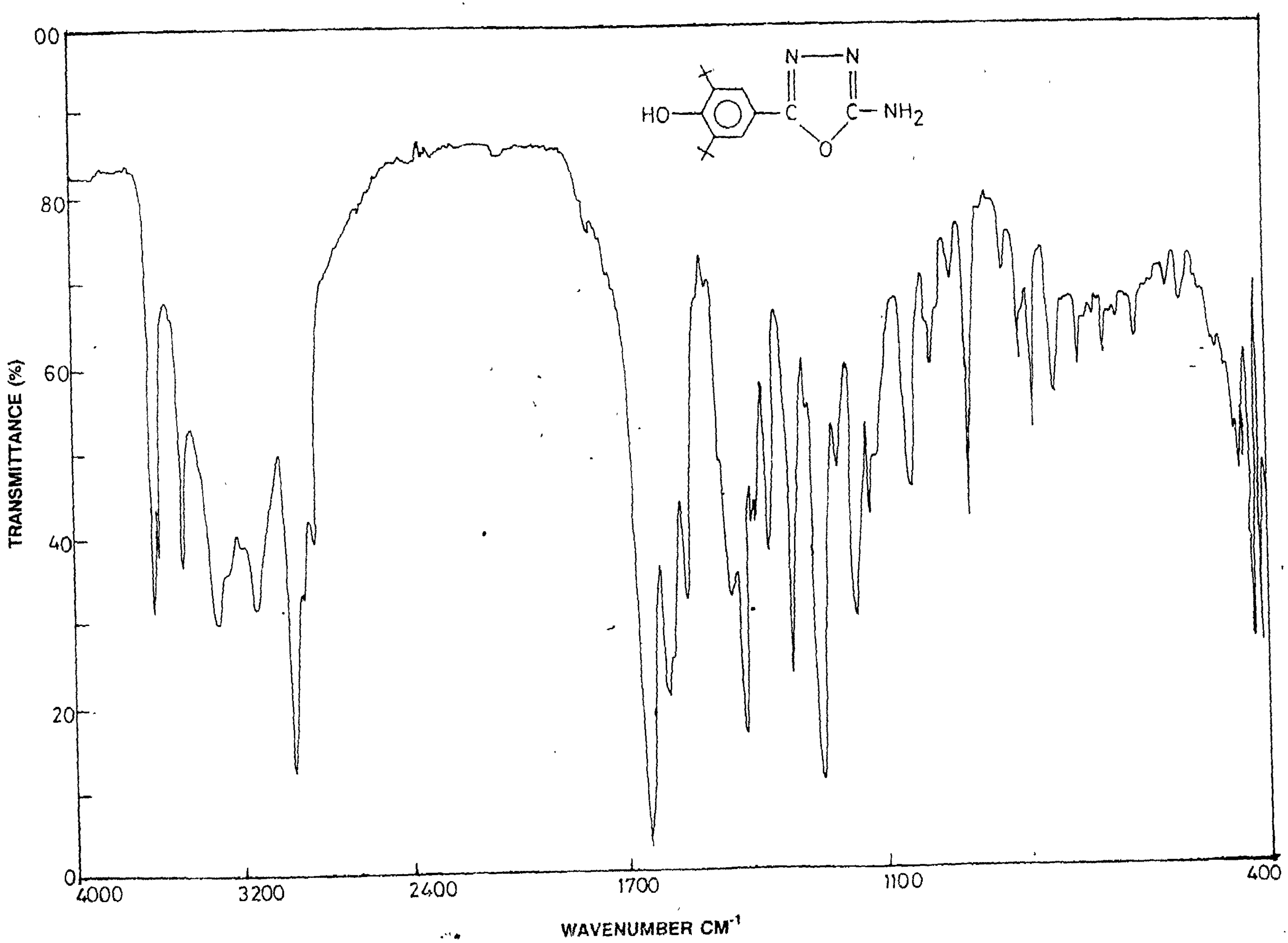


Fig. 2.12 IR spectra of Compound AO$_7$

tert-butyl groups at C-3 and C-5. Broad singlet at δ 5.6 is due to the presence of three protons of two different groups -NH_2 and -OH Singlet at δ 7.65 indicated two aromatic protons at C-2 and C-6. IR (KBr) spectra (Fig.2.12) showed a band at 1240 cm^{-1} due to ether linkage (C-O-C) The bands 3321 cm^{-1} and 3517 cm^{-1} are due to -NH_2 and -OH groups respectively

Synthesis of 2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamide (AO$_8$).

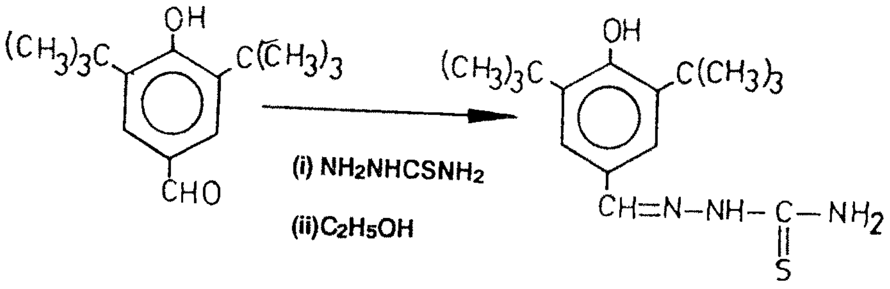
3,5-Di-tert-butyl-4-hydroxy benzaldehyde on condensation with thiosemicarbazide in ethyl alcohol gave 2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamide (Scheme-7). The structure of this compound was established by its ^{1}HNMR spectra (Fig.2.13) taken in $CDCl_3$. Singlet at δ 1.4 indicated the presence of two tert-butyl groups at C-3 and C-5. Hydroxy proton appeared as a singlet at δ 5.4 Singlet at δ 7.3 corresponding to the two aromatic protons. Singlet at δ 7.8 is due to the proton of azomethine group The IR (KBr) spectra (Fig.2.14) showed band at 1300 cm^{-1} due to C=S group. The band at 3150cm^{-1} and 3500cm^{-1} are due to -NH_2 and -NH group respectively The band at 3650cm^{-1} is due to -OH group.

Synthesis of 2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene]- N-phenyl hydrazine carbothioamide (AO$_9$).

4-Phenyl-3-thiosemicarbazide was synthesised from aniline as per reported procedure.[62]

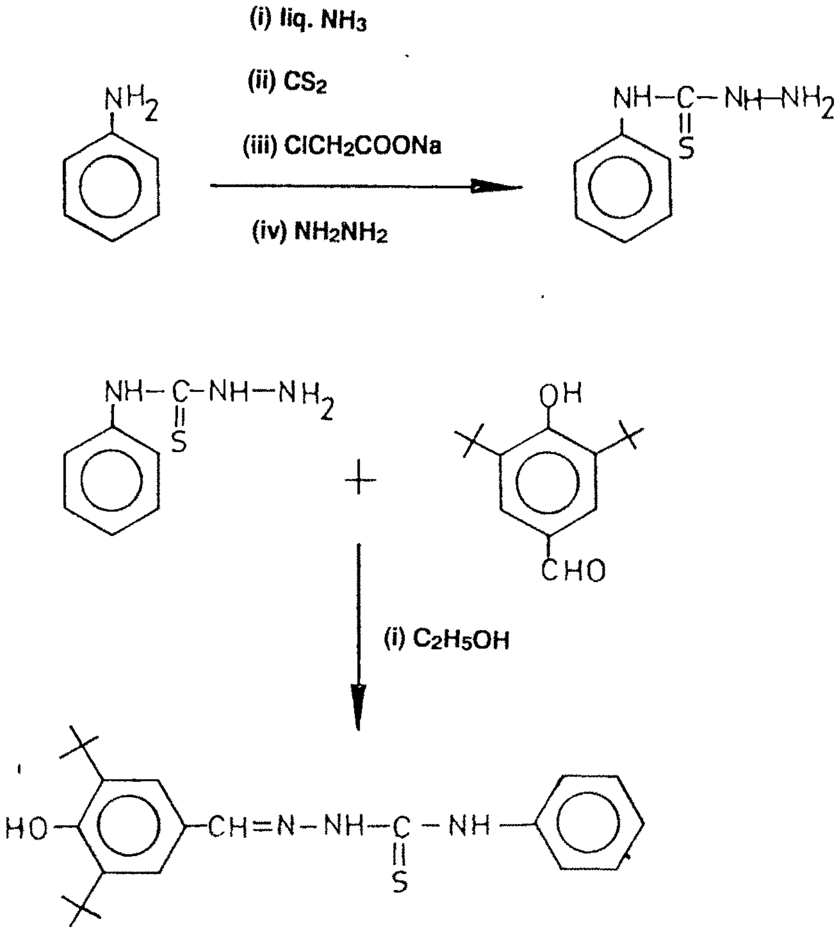
3,5-Di-tert-butyl-4-hydroxy benzaldehyde on condensation with 4-phenyl-3-thiosemicarbazide in ethanol gave 2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene]-N-phenyl hydrazine carbothioamide (Scheme-8). The structure of this compound was established by its ^{1}HNMR spectra (Fig.2.15) taken in $CDCl_3$ The singlet at δ 1.45 for eighteen protons indicated the presence of two tert-butyl groups at C-3 and C-5 of phenyl ring, singlet at δ 5.5 is due to the proton of -OH group. Multiplet from δ 7 2 to δ 7.7 indicated seven aromatic protons. Singlet at δ 7.80 is due to the presence of (CH=N) group. Two singlets at δ 9.2 and δ 9 55 indicated two -NH protons. The IR (KBr) spectra (Fig.2.16) showed a band at 1270 cm^{-1} for C=S group Band at 1550 cm^{-1} is due to the presence of (C=N) group. The band at 3300 cm^{-1} and 3670 cm^{-1} are due to -NH and -OH groups respectively

Scheme-7



AO$_8$

Scheme-8



AO$_9$

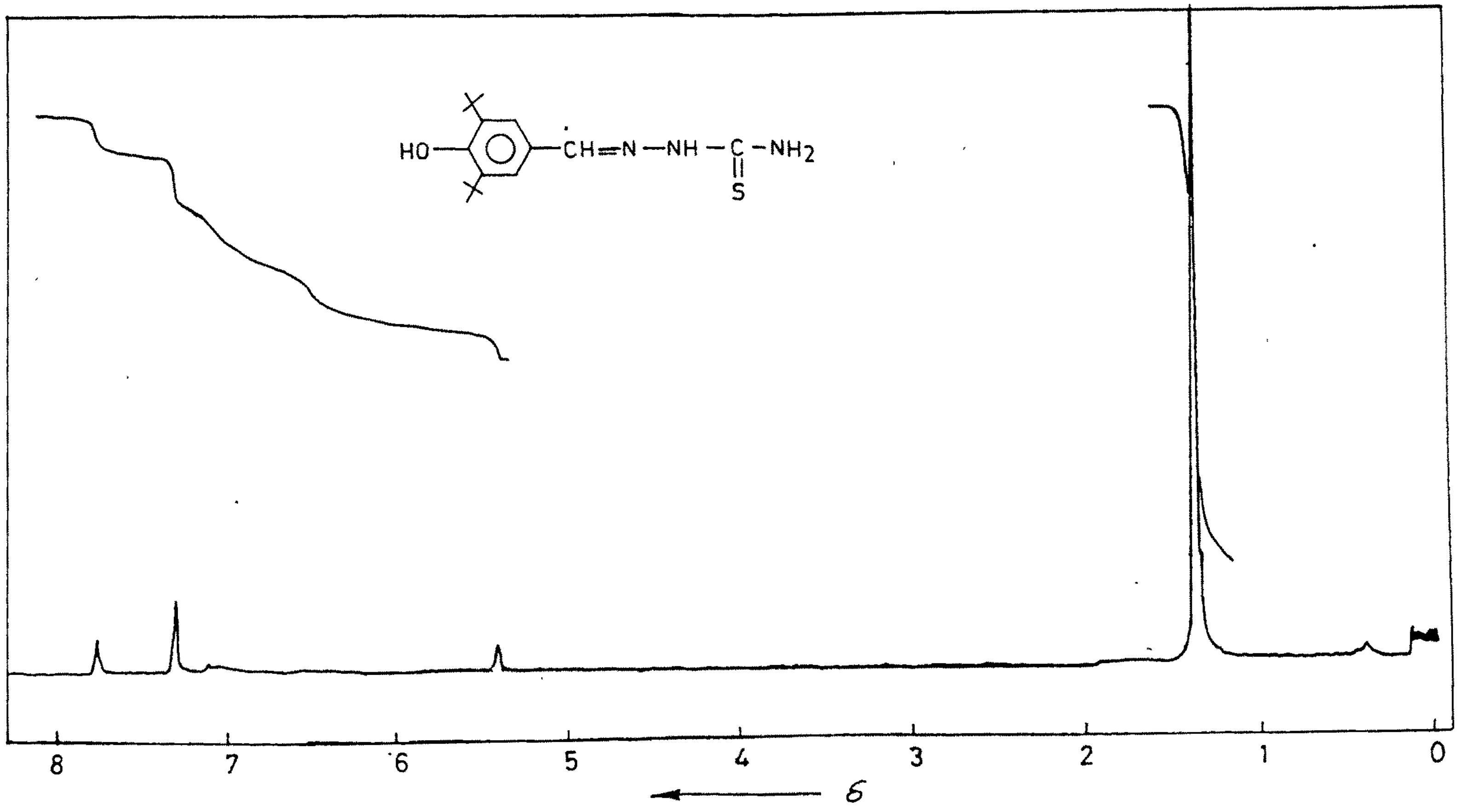


Fig. 2.13 ^{1}HNMR spectra of Compound AO_8

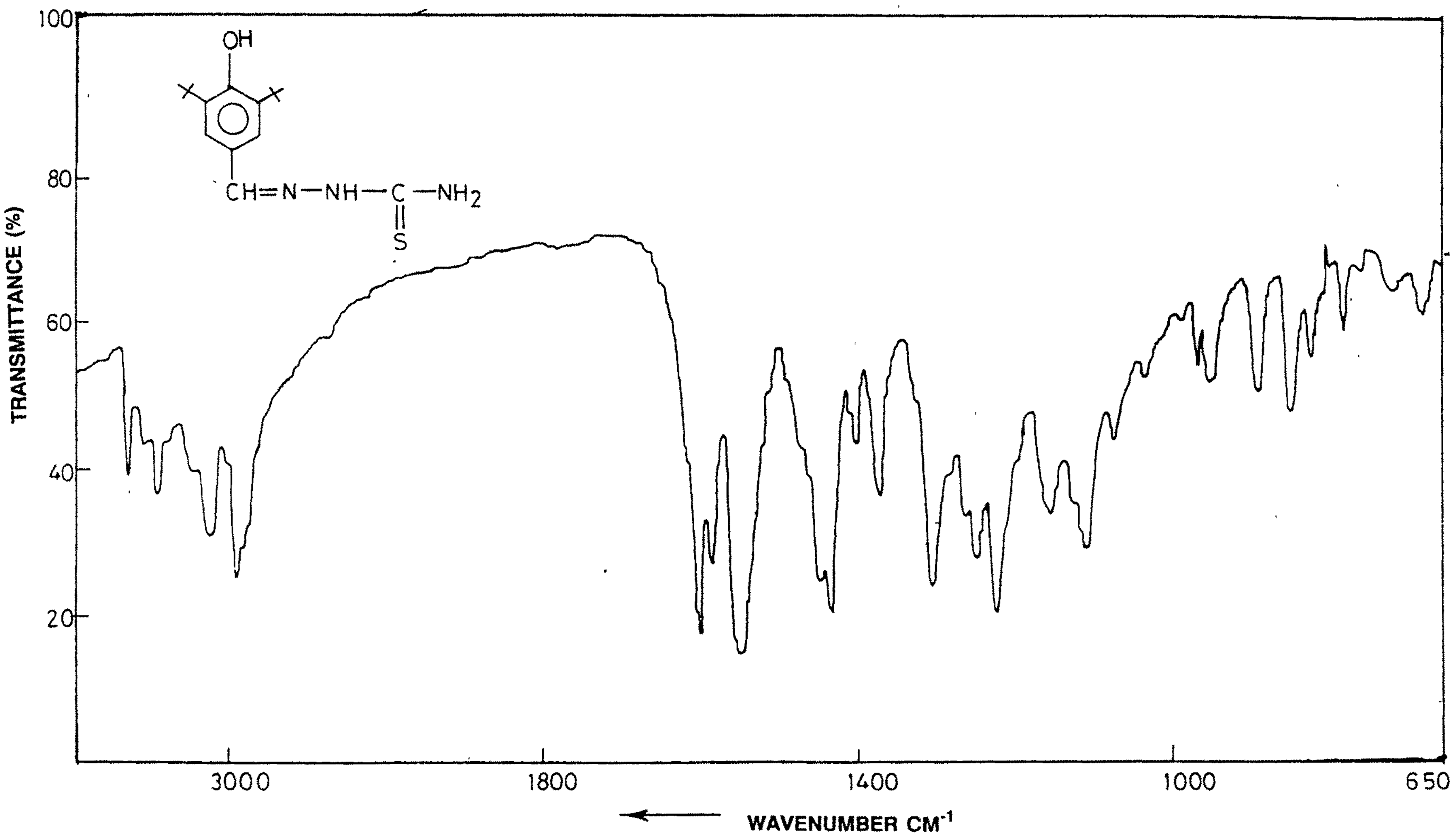


Fig. 2.14 IR spectra of Compound AO_8

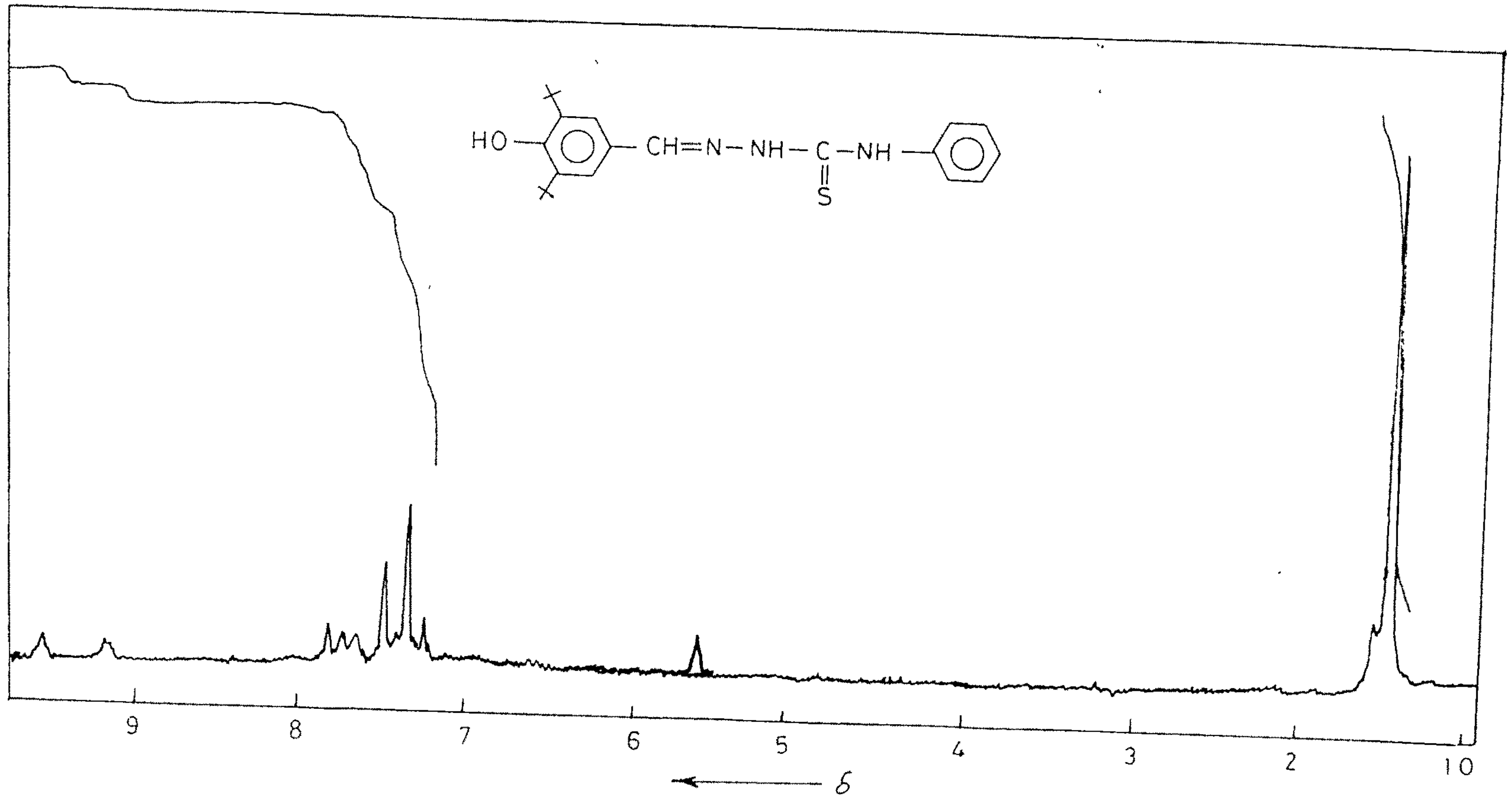


Fig. 2.15 ^{1}HNMR spectra of Compound AO_9

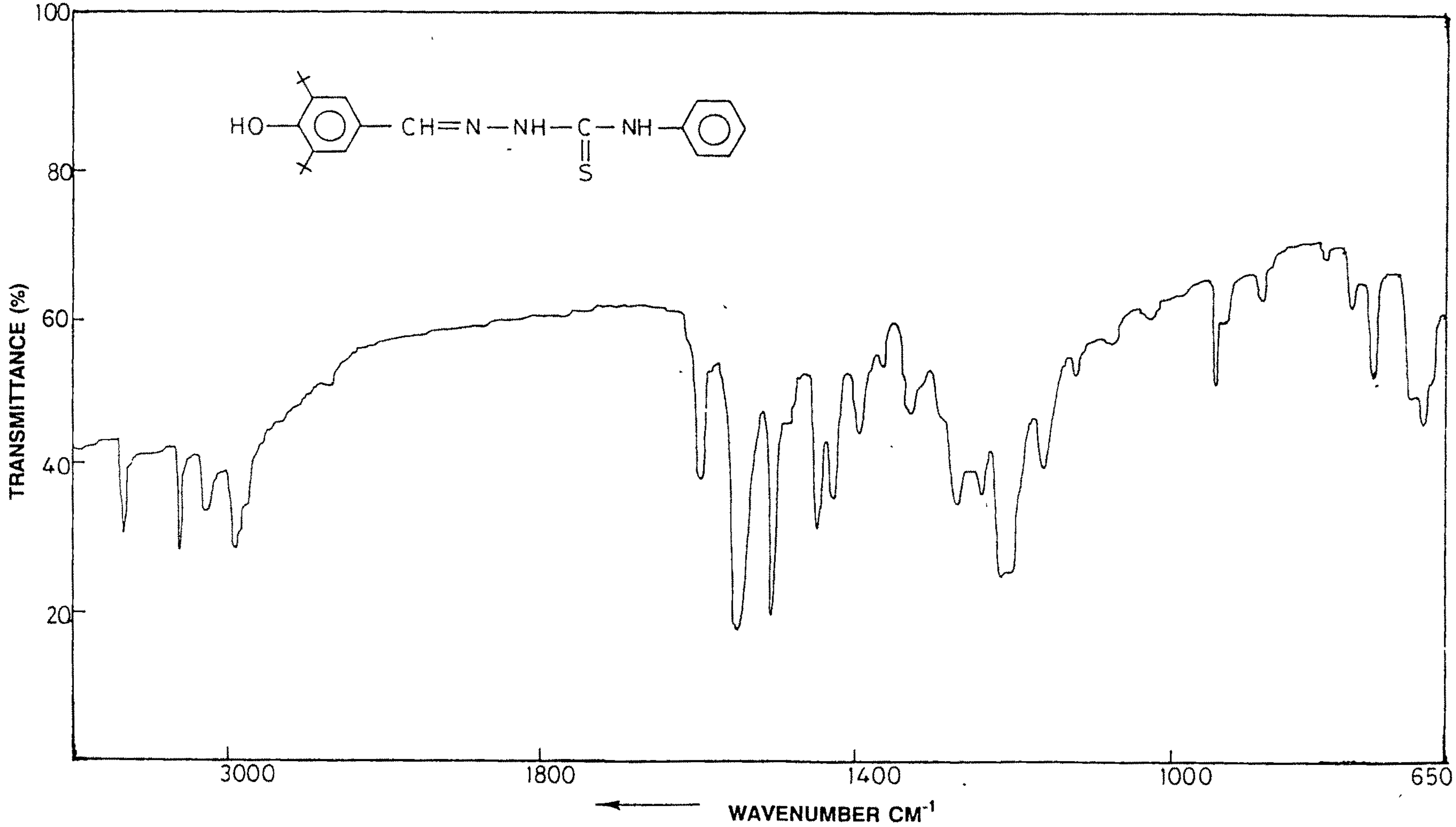


Fig. 2.16 IR spectra of Compound AO_9

Synthesis of 2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene]-N-4-(methyl phenyl) hydrazine carbothoamide (AO_{10}).

4-(4-Methyl phenyl) -3-thiosemicarbazide was synthesised from p- toludine according to the method reported in literature.[62]

3,5-Di-tert-butyl-4-hydroxy benzaldehyde on reaction with 4-(4-methyl phenyl) 3-thiosemicarbazide in ethyl alcohol gave 2-[(3,5- di-tert-butyl-4-hydroxy phenyl) methylene]-N-(4-methyl phenyl) hydrazine carbothioamide (Scheme-9) The structure of the compound was established on the basis of ^{1}HNMR spectra (Fig 2.17) taken in $CDCl_3$. The singlet at δ 1 45 exhibited 18 protons of two tert-butyl group at C-3 and C-5 positions of the phenyl ring The singlet at δ 2.35 indicated methyl group at C-4 position of 4- methyl phenyl ring Singlet at δ 5.5 is due to the proton of the -OH group. The multiplet from δ 7 2 to δ 7 3 indicated four aromatic protons of 4-methyl phenyl ring. Singlet which appears at δ 7 5 indicated two aromatic protons of phenyl ring. Singlet at δ 7.8 is due to the presence of proton of CH=N group Two singlets at δ 8.95 and δ 9 2 indicated two protons of two different -NH groups The IR (KBr) spectra (Fig.2.18) showed band at 1215 cm^{-1} for (C=S) group. The band observed at 1540 cm^{-1} for (C=N) group. The bands at 3325 cm^{-1} and 3675 cm^{-1} are for -NH and -OH groups respectively

Synthesis of 1,2-di-[2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamido] ethane (AO_{11}).

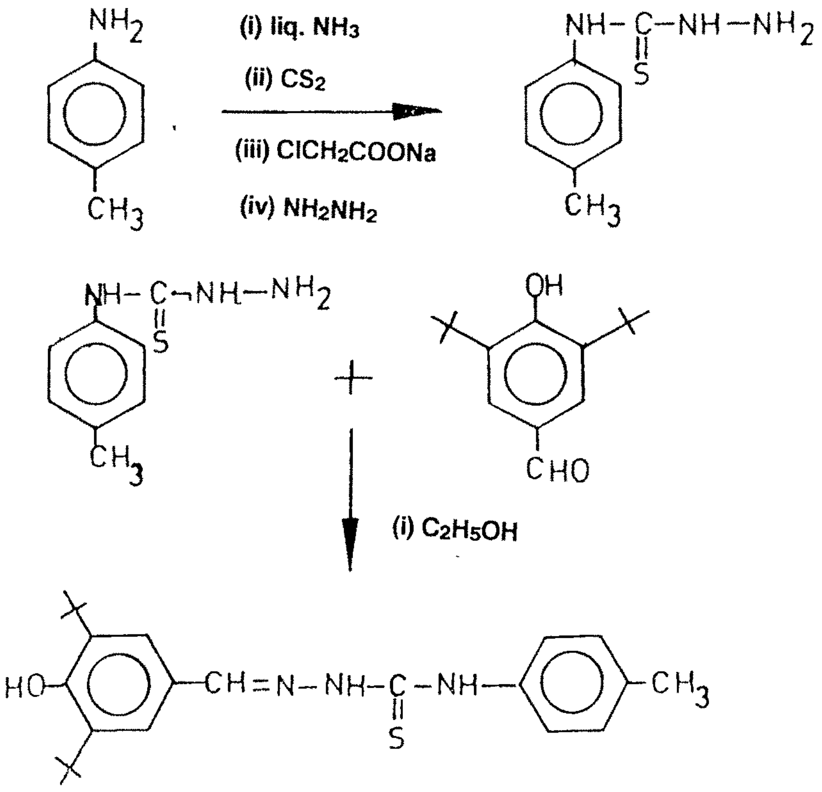
1,2-Di-(3-thiosemicarbazide) ethane was prepared from 1,2-diamino ethane according to method reported in literature[62].

3,5-Di-tert-butyl-4-hydroxy benzaldehyde in ethanol when allowed to react with 1,2-di-(3-thiosemicarbazide) ethane by refluxing, gave 1,2-di-{2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamido} ethane (Scheme-10). The IR (KBr) spectra (Fig.2 19) showed a strong band at 1270 cm^{-1} due to C=S The band at 1595 cm^{-1} is due to the presence of (C=N) group. The bands at 3200 cm^{-1} and 3650 cm^{-1} are due to the -NH and OH groups respectively

Synthesis of 1,4-di-{2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamido} benzene (AO_{12}).

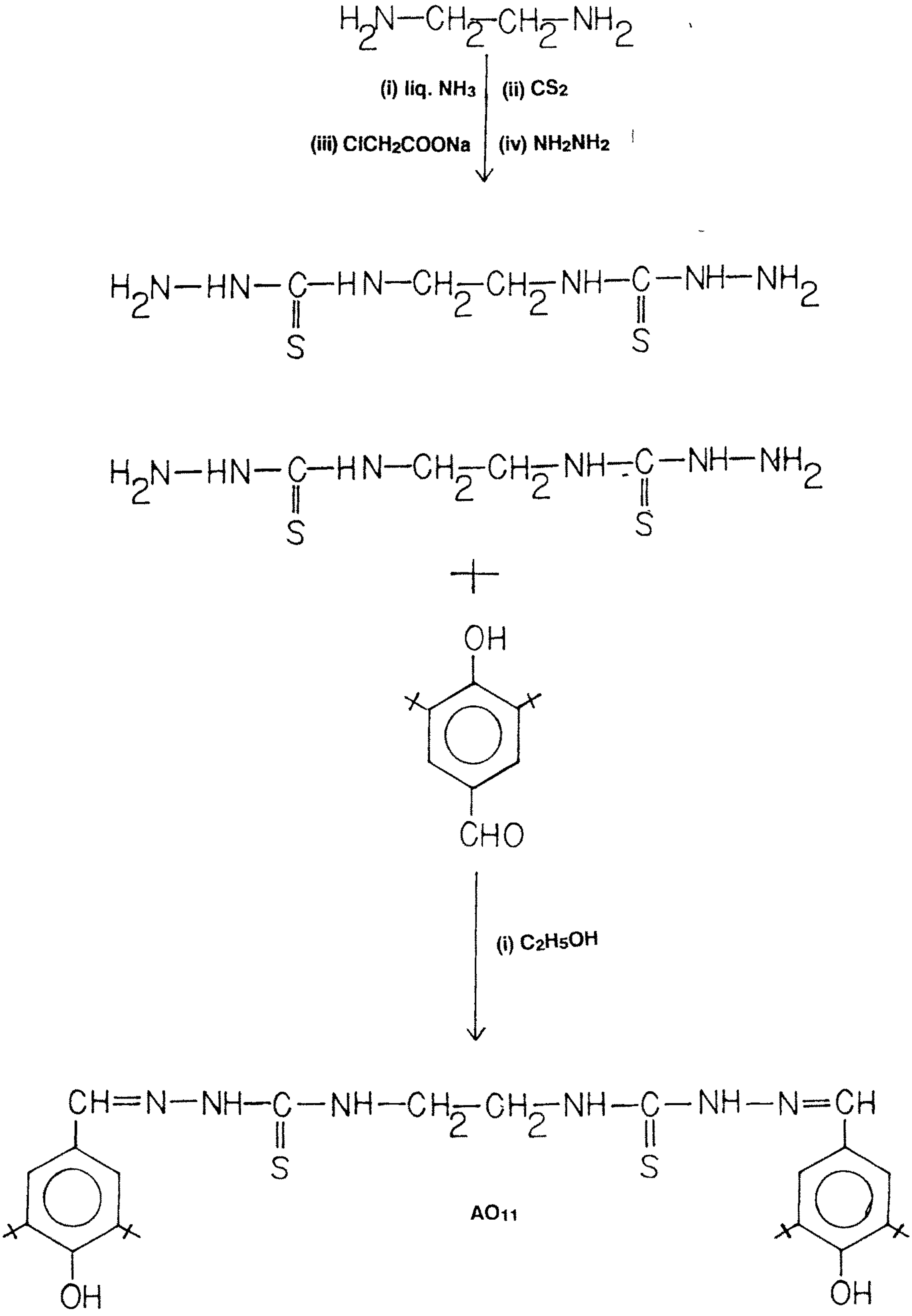
1,4-Di-(3-thiosemicarbazide) benzene was synthesised from 1.4-phenylene diamine according to the method reported in literature[63]

Scheme-9



AO$_{10}$

Scheme-10



AO11

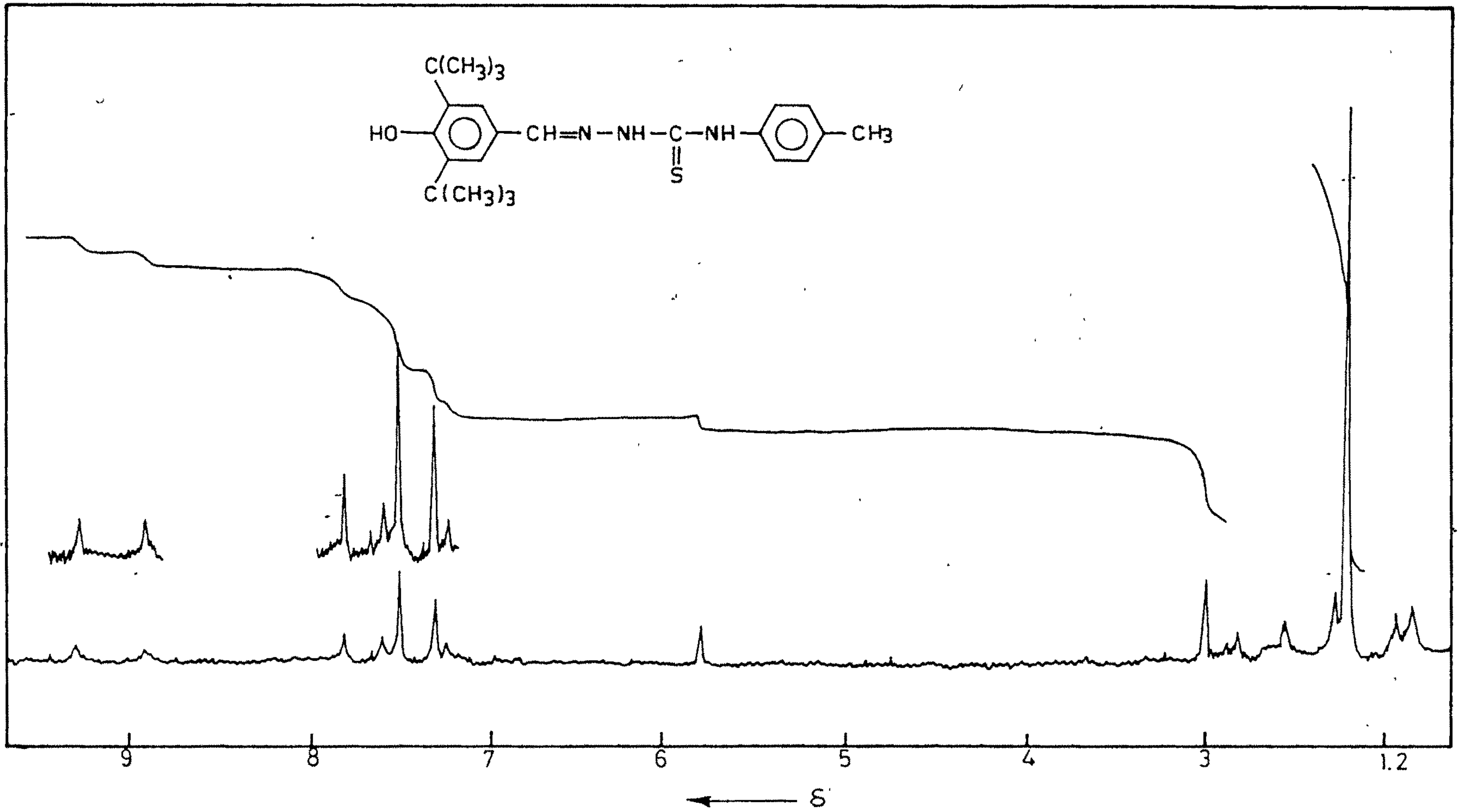


Fig. 2.17 ^{1}HNMR spectra of Compound AO$_{10}$

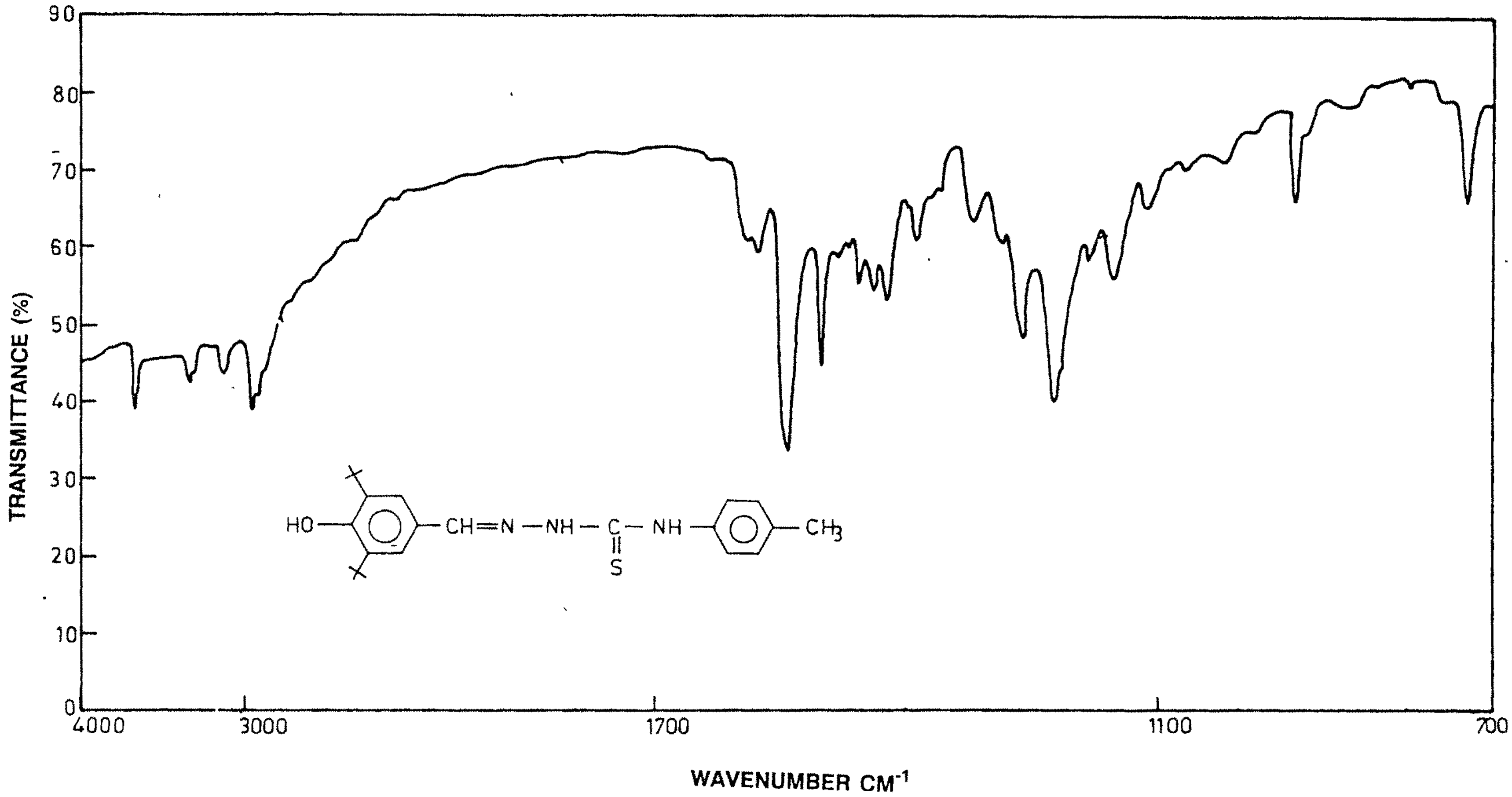


Fig. 2.18 IR spectra of Compound AO$_{10}$

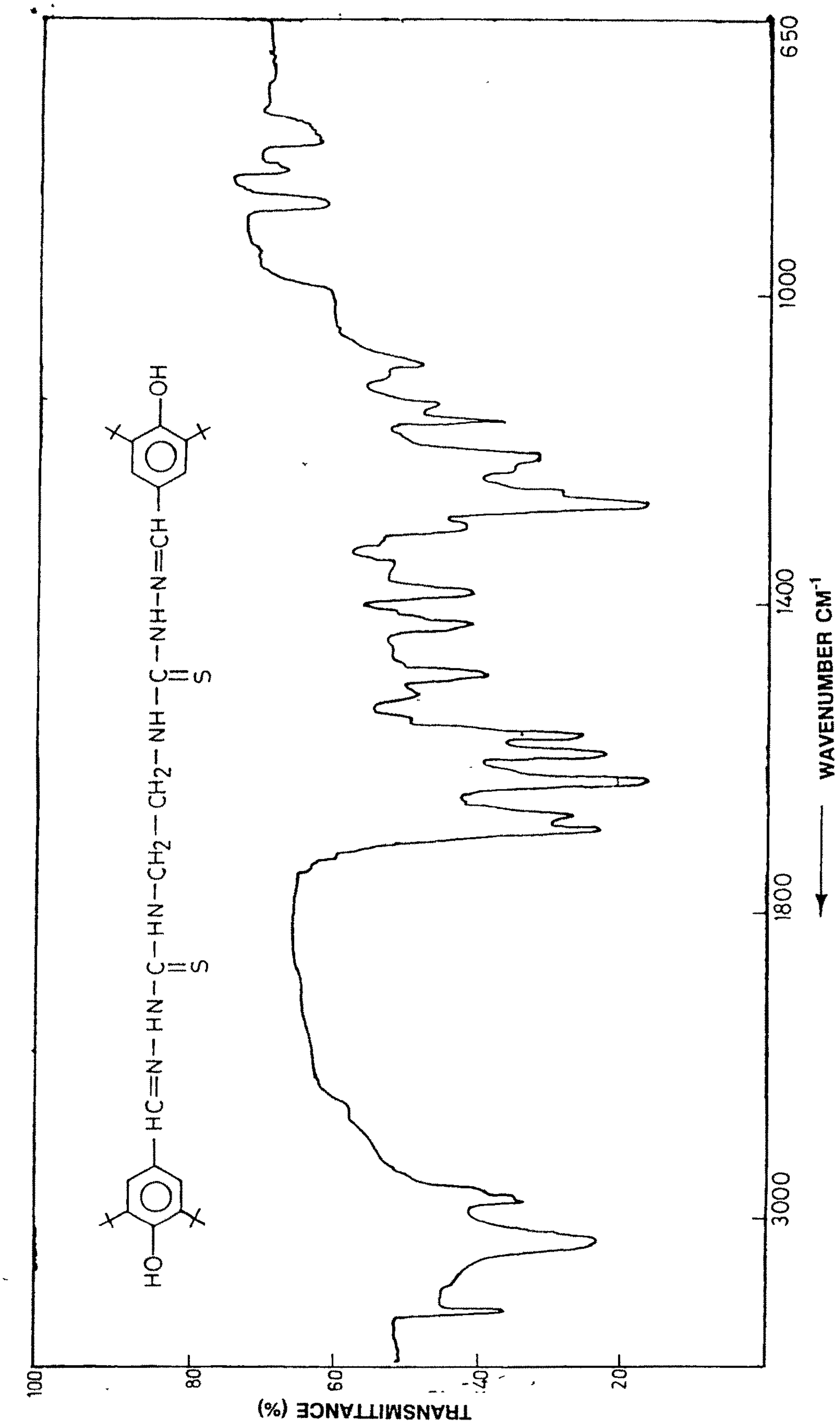


Fig. 2.19 IR spectra of Compound AO_{11}

3,5-Di-tert-butyl-4-hydroxy benzaldehyde on condensation with 1,4-di-(3-thiosemicarbazide) benzene in ethyl alcohol gave 1,4-di-{2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamido} benzene (Scheme-11) The IR (KBr) spectra (Fig.2.20) showed band at 1320 cm^{-1} for C=S group The band observed at 1510 cm^{-1} is for C=N group The bands at 3300 cm^{-1} and 3700 cm^{-1} are due to the -NH and -OH groups respectively.

Synthesis of 4,4'-di-{2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamido} biphenyl (AO_{13}).

4,4'-Di-(3-thiosemicarbazide) biphenyl was prepared from 4,4'-diamino biphenyl according to method reported in literature.[62]

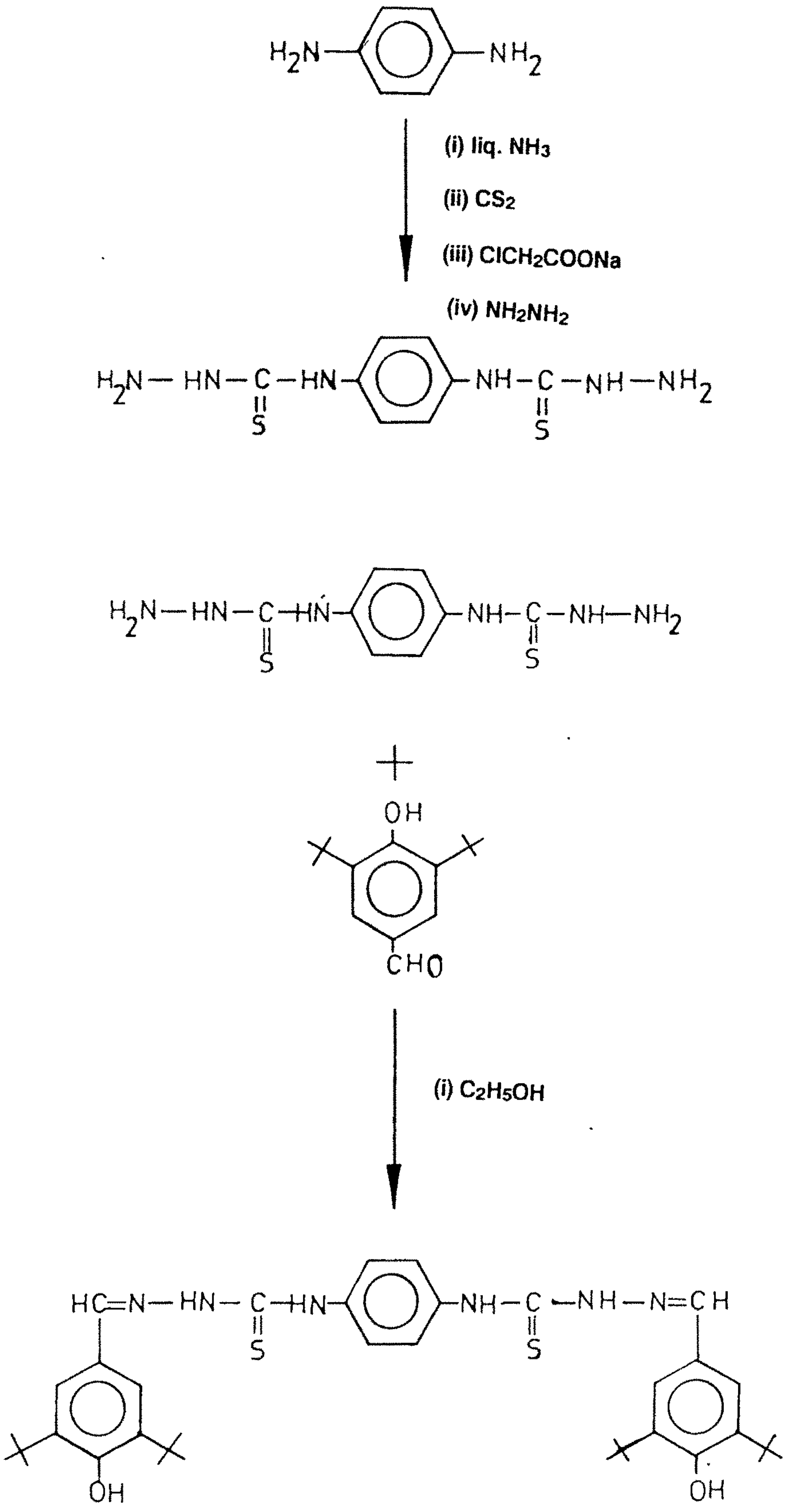
3,5-Di-tert-butyl-4-hydroxy benzaldehyde in ethanol when allowed to react with 4,4'-di-(3-thiosemicarbazide) biphenyl gave 4,4'-di- {2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamido} biphenyl (Scheme-12) The IR (KBr) spectra (Fig 2 21) showed a band at 1320 cm^{-1} for C=S group The band observed at 1500 cm^{-1} is due to C=N group The weak band at 3350 cm^{-1} is due to NH group. The band observed at 3500 cm^{-1} is for -OH group

Synthesis of 4,4'-di-{2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamido} biphenyl methane (AO_{14}).

4,4'-di-(3-thiosemicarbazide) biphenyl methane was prepared from 4,4'-diamino biphenyl methane according to the method reported by Nair and coworkers[64]

3,5-Di-tert-butyl-4-hydroxy benzaldehyde on condensation with 4,4'-di-(3-thiosemicarbazide) biphenyl methane in ethyl alcohol gave 4,4'-di-{2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamido} biphenyl methane (Scheme-13) The ^{1}HNMR spectra (Fig.2.22) was taken in $CDCl_3$ + 5 drops of DMSO showed a singlet at δ 1 30 for 36 protons of four tert-butyl groups of two aromatic rings of AO_{14}. Singlet at δ 3 80 indicated the presence of methylene protons Multiplet between δ 6.90 to δ 7.45 showed presence of twelve aromatic protons. The signal observed at δ 7.8 indicated singlet due to two protons of two azomethine group (CH=N). Singlet at δ 9.1 for two protons of two -NH groups. The IR (KBr) spectra (Fig.2.23) showed a band at 1214 cm^{-1} for (C=S) group. The band observed at 1540 cm^{-1} for (C=N) group The band observed at 3296 cm^{-1} is due to the -NH group The band at 3650 cm^{-1} indicated the presence of -OH group

Scheme-11



AO$_{12}$

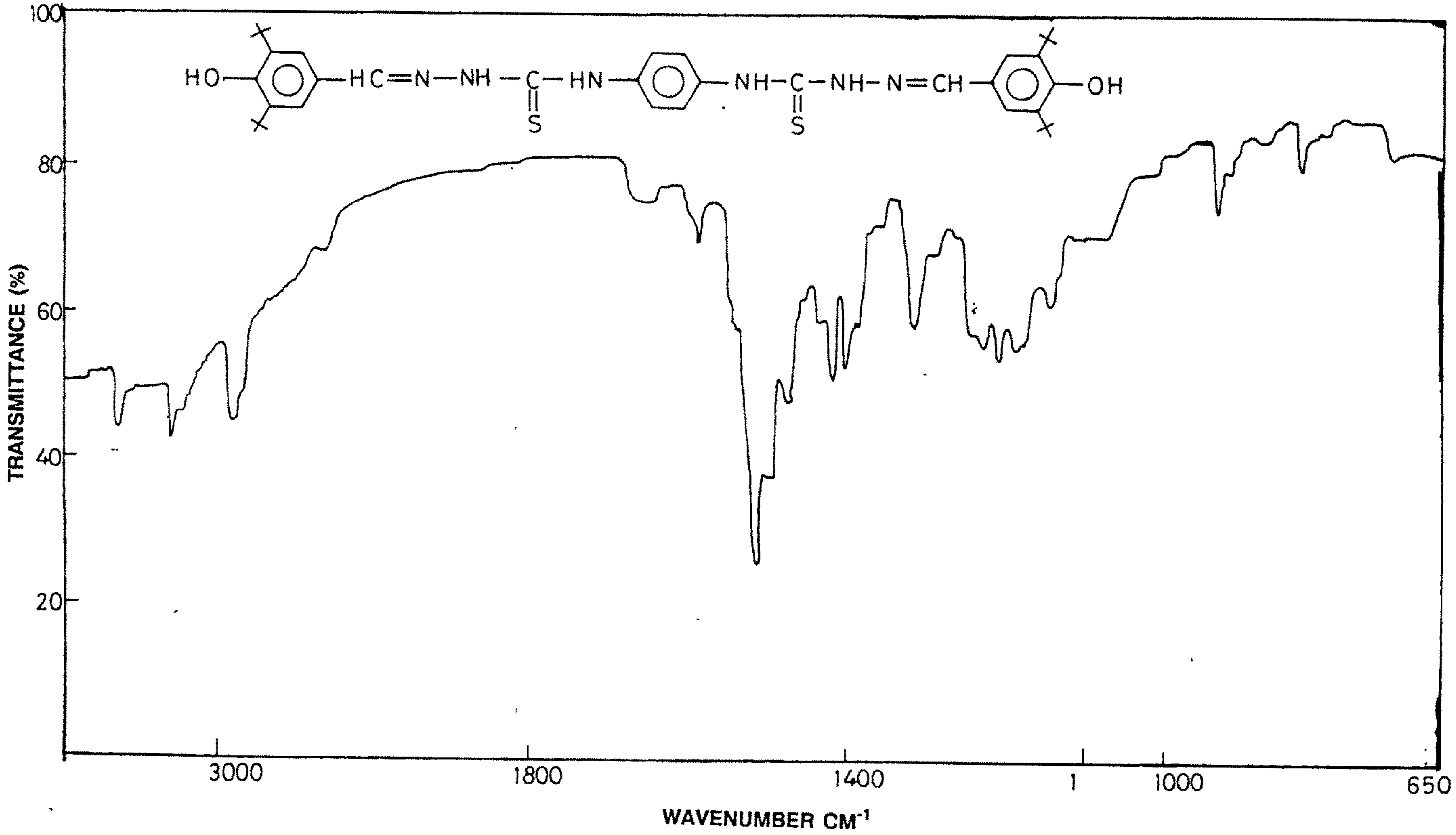
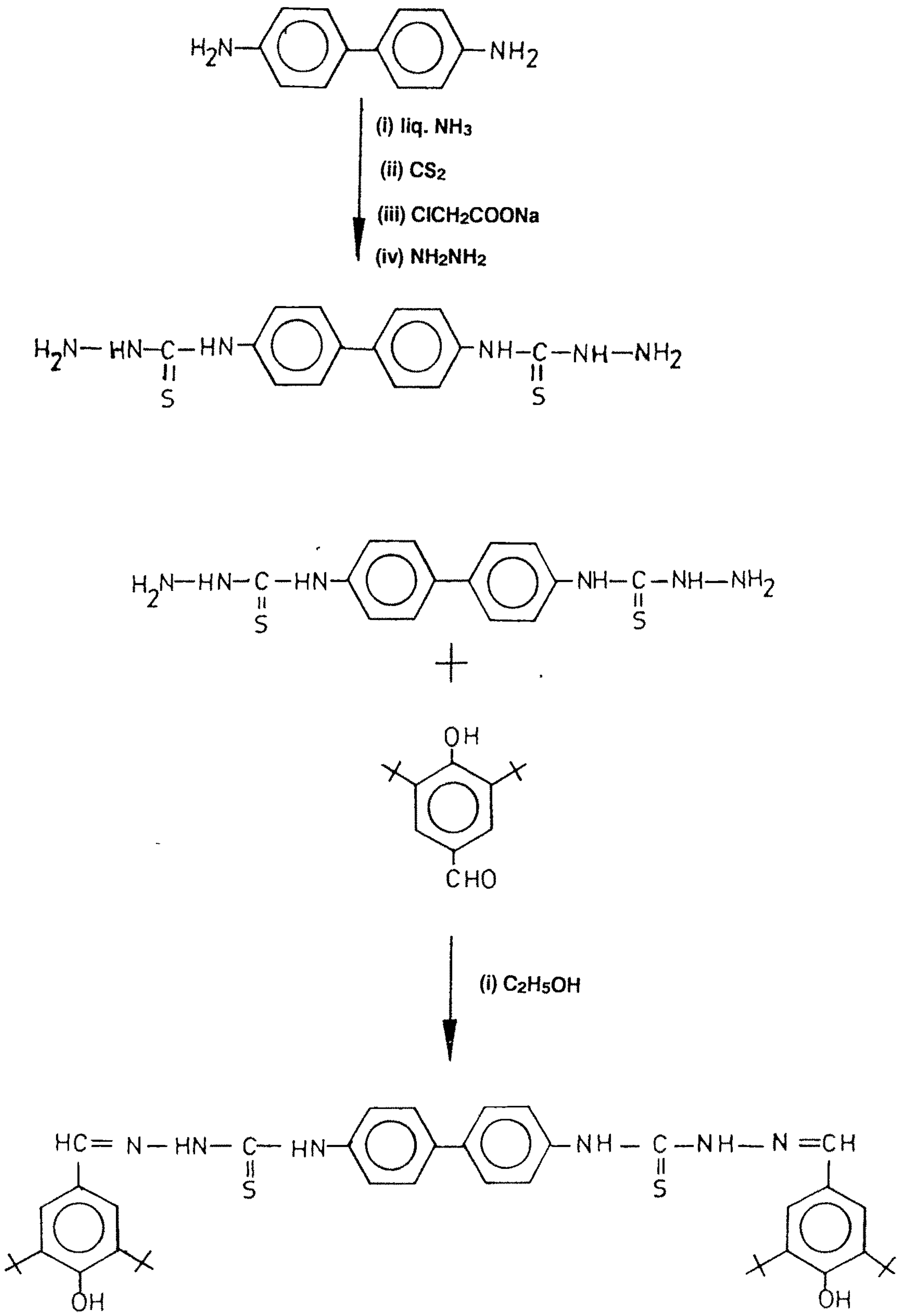


Fig. 2.20 IR spectra of Compound AO_{12}

Scheme-12



AO13

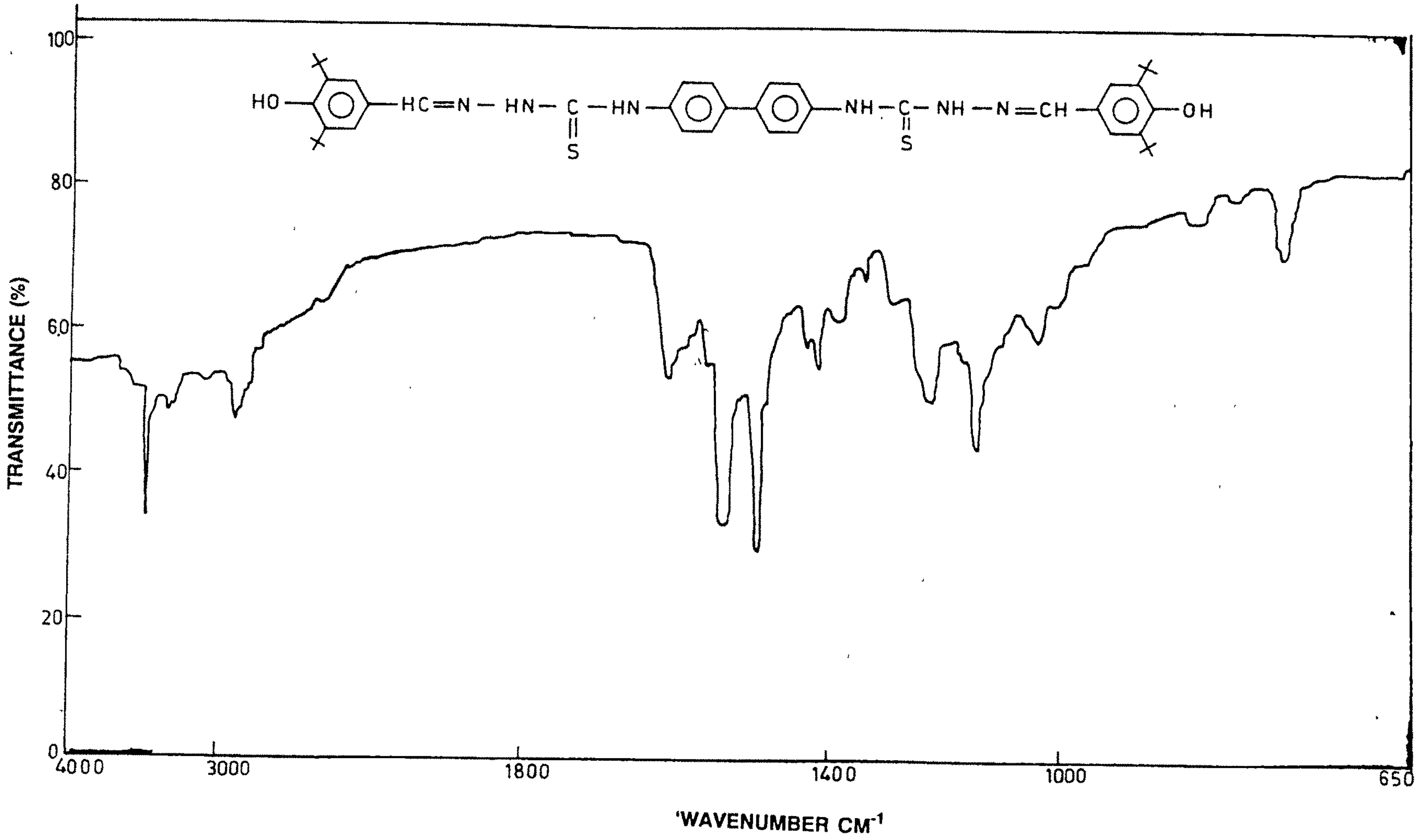
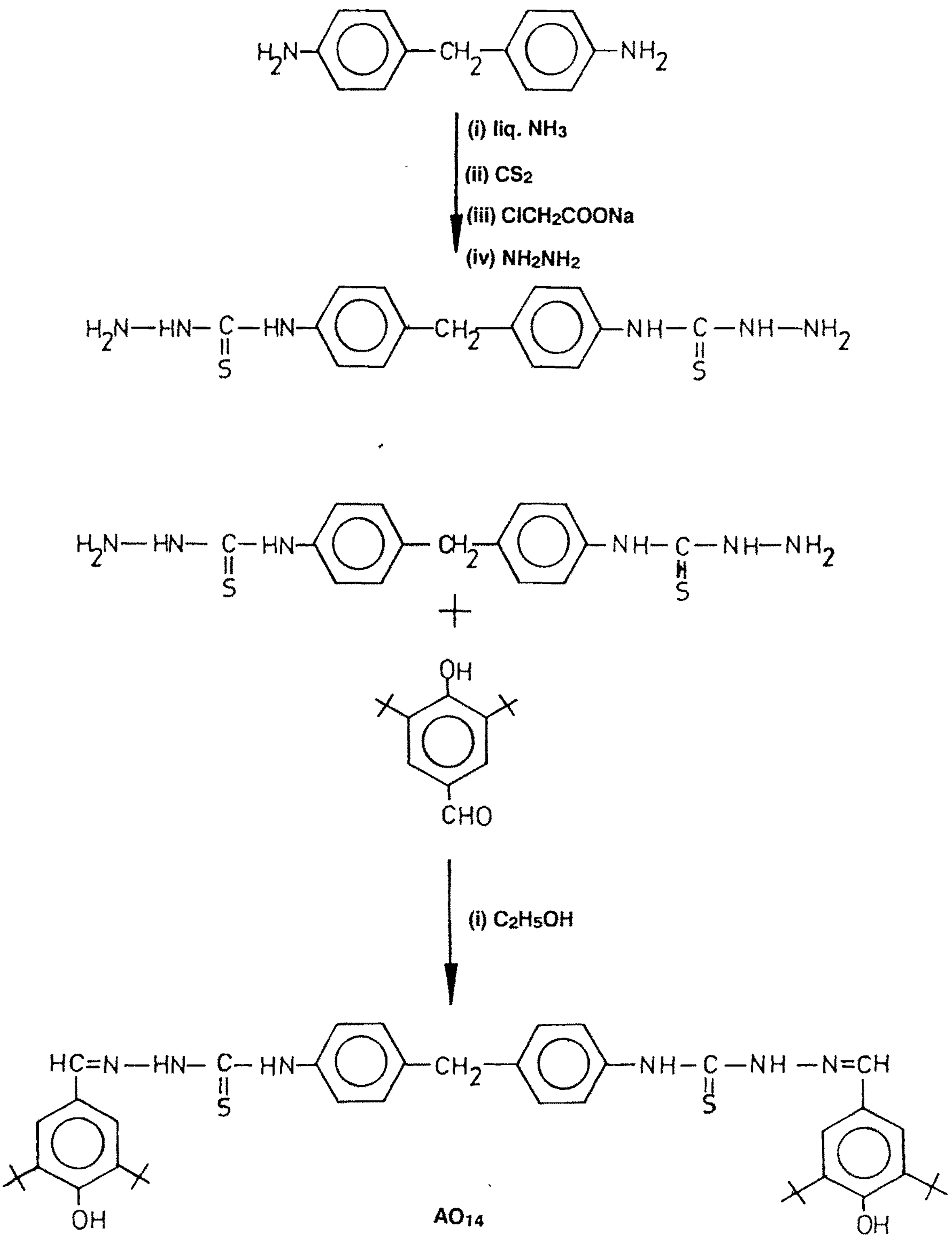


Fig. 2.21 IR spectra of Compound AO_{13}

Scheme-13



AO14

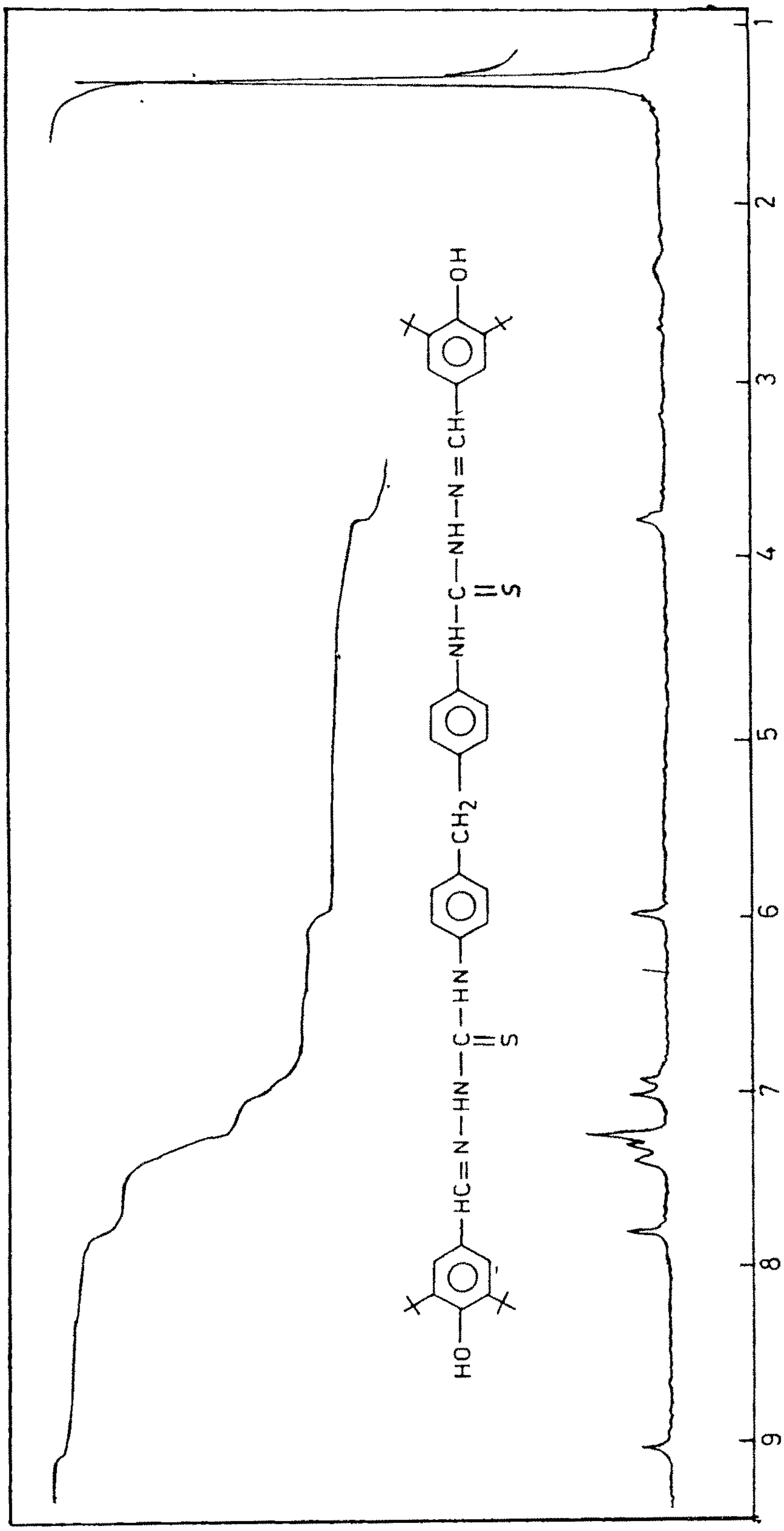


Fig. 2.22 ^{1}HNMR spectra of Compound AO_{14}

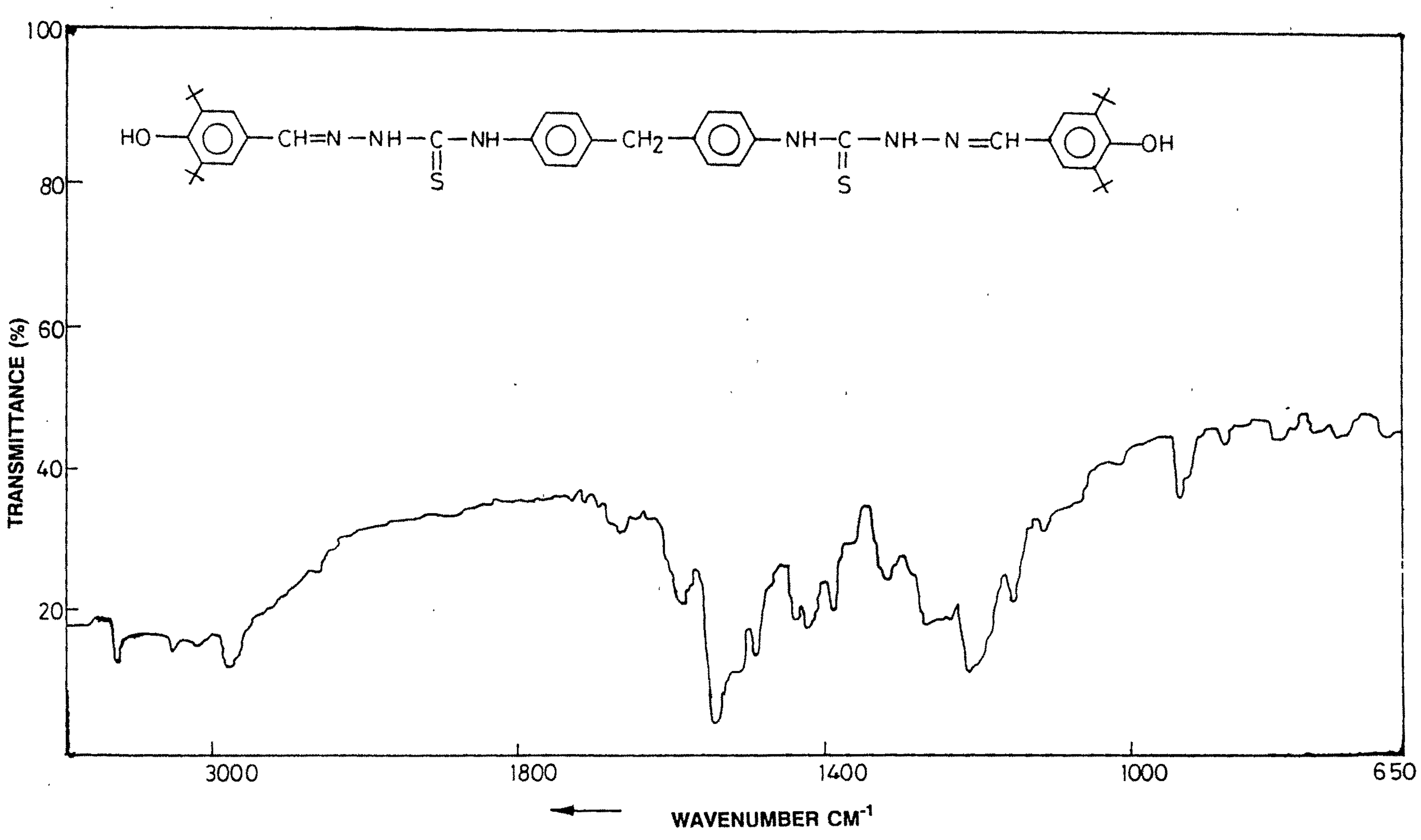


Fig. 2.23 IR spectra of Compound AO_{14}

Synthesis of 4,4'-di-{2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamido} biphenyl ether (AO_{15}).

4,4'-Di-(3-thiosemicarbazide) biphenyl ether was sythesised from 4,4'-di-amino-biphenyl ether according to the method reported in the literature.[64]

3,5-Di-tert-butyl-4-hydroxy benzaldehyde on refluexing in ethanol with 4,4'-di-(3-thiosemicarbazone) biphenyl ether gave 4,4'-di-{2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamido} biphenyl ether (Scheme-14) The ^{1}HNMR spectra (Fig.2.24) taken in $CDCl_3$ exhibited singlet at δ 1.45 for 36 protons of four tert-butyl groups of two aromatic rings. Singlet at δ 5.5 for two protons indicated the presence of two hydroxyl groups. Multiplet at δ 6.95 to δ 7.65 indicated fourteen aromatic protons Singlet at δ 7 75 indicated presence of CH=N group Singlet at δ 9.0 and δ 9.45 are due to the two protons of two -NH groups The IR (KBr) spectra (Fig.2.25) showed band at 1220 cm^{-1} is for C=S group. The band at 1540cm^{-1} is due to C=N group. The bands at 3300 cm^{-1} and at 3650 cm^{-1} are due to the -NH and -OH groups respectively.

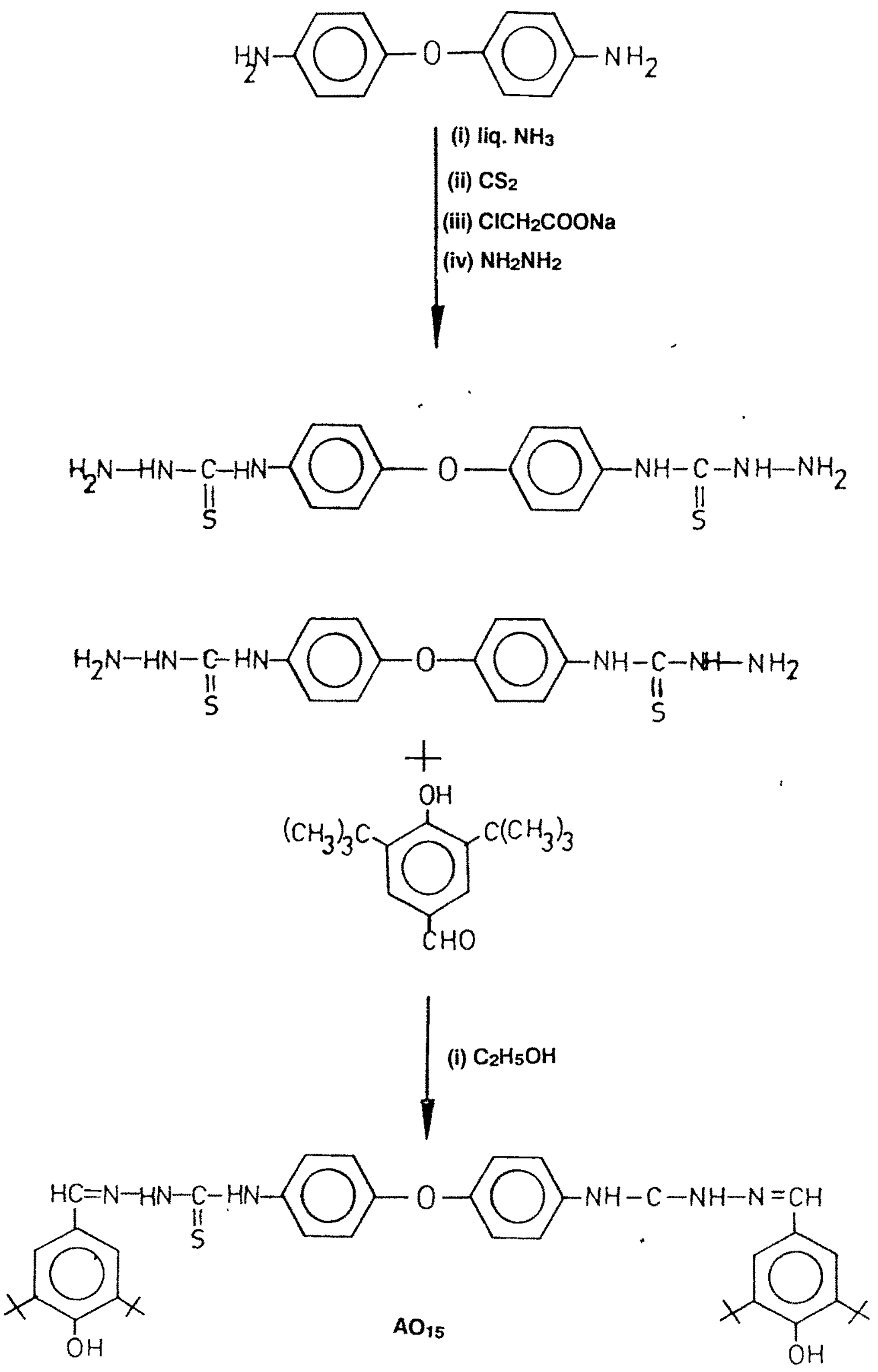
Synthesis of 3-(4-hydroxy phenyl)-5-(3,5-di-tert-butyl-4-hydroxy phenyl) 4,5-dihydro-1H-pyrazole (AO_{16}).

4,4'-Dihydroxy-3,5-di-tert-butyl chalcone from 3,5-di-tert-butyl- 4-hydroxy benzaldehyde was prepared according to the method reported in the literature[65].

4,4'-Dihydroxy-3,5-di-tert-butyl chalcone on reaction with hydrazine hydrate gave 3-(4-hydroxy phenyl)-5-(3,5-di-tert-butyl-4-hydroxy phenyl) 4,5-dihydro-1H-pyrazole (Scheme-15). The ^{1}HNMR spectra (Fig.2.26) was taken in $CDCl_3$ + 2 drops of DMSO showed a singlet at δ 1.4 for 18 protons of two tert-butyl groups of phenyl ring. Two proton H_A & H_B of pyrazole ring position are merged with DMSO and appeared as doublet at δ 3.3 Multiplet between δ 4.6 to δ 4 9 showed the presence of proton H_C of pyrazole ring. Singlet at δ 5.5 showed the presence of protons of -OH groups. Here it appears that part of the -OH proton is exchanged with deuterium. Two doublets located at δ 6.7 and δ 7.4 (J=9Hz) showed coupling of two aromatic protons of hydroxy phenyl ring. Singlet at δ 7 2 indicated two aromatic protons of phenyl ring The IR (KBr) spectra (Fig.2.27) showed band at 1510 cm^{-1} for C=N group The band observed at 3300 cm^{-1} and 3650 cm^{-1} are due to the -NH and -OH groups respectively

The ^{1}HNMR spectra of the compound AO_{11}, AO_{12} and AO_{13} could not be recorded due to the insolubility of these compounds

Scheme-14



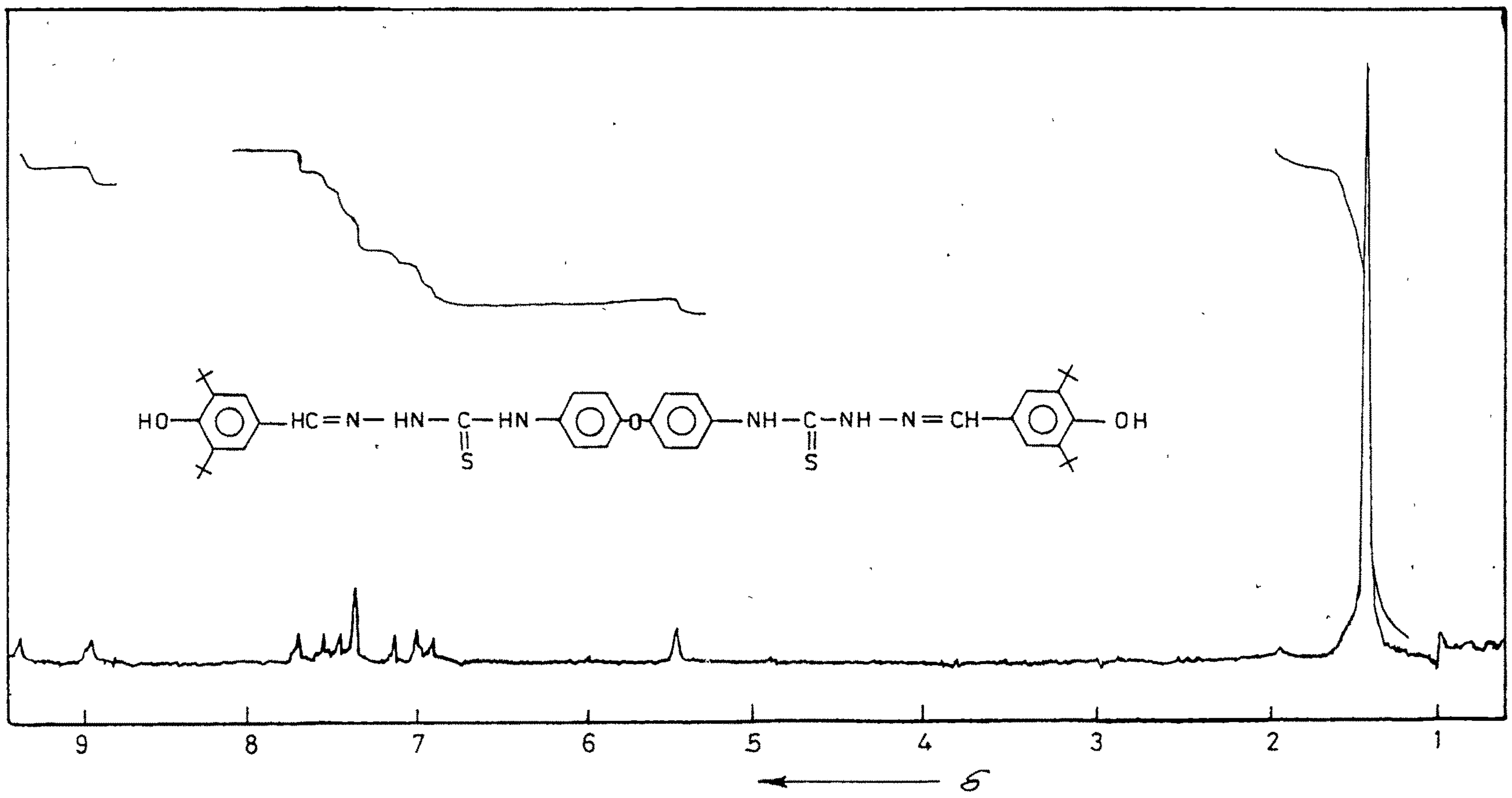


Fig. 2.24 ^{1}HNMR spectra of Compound AO$_{15}$

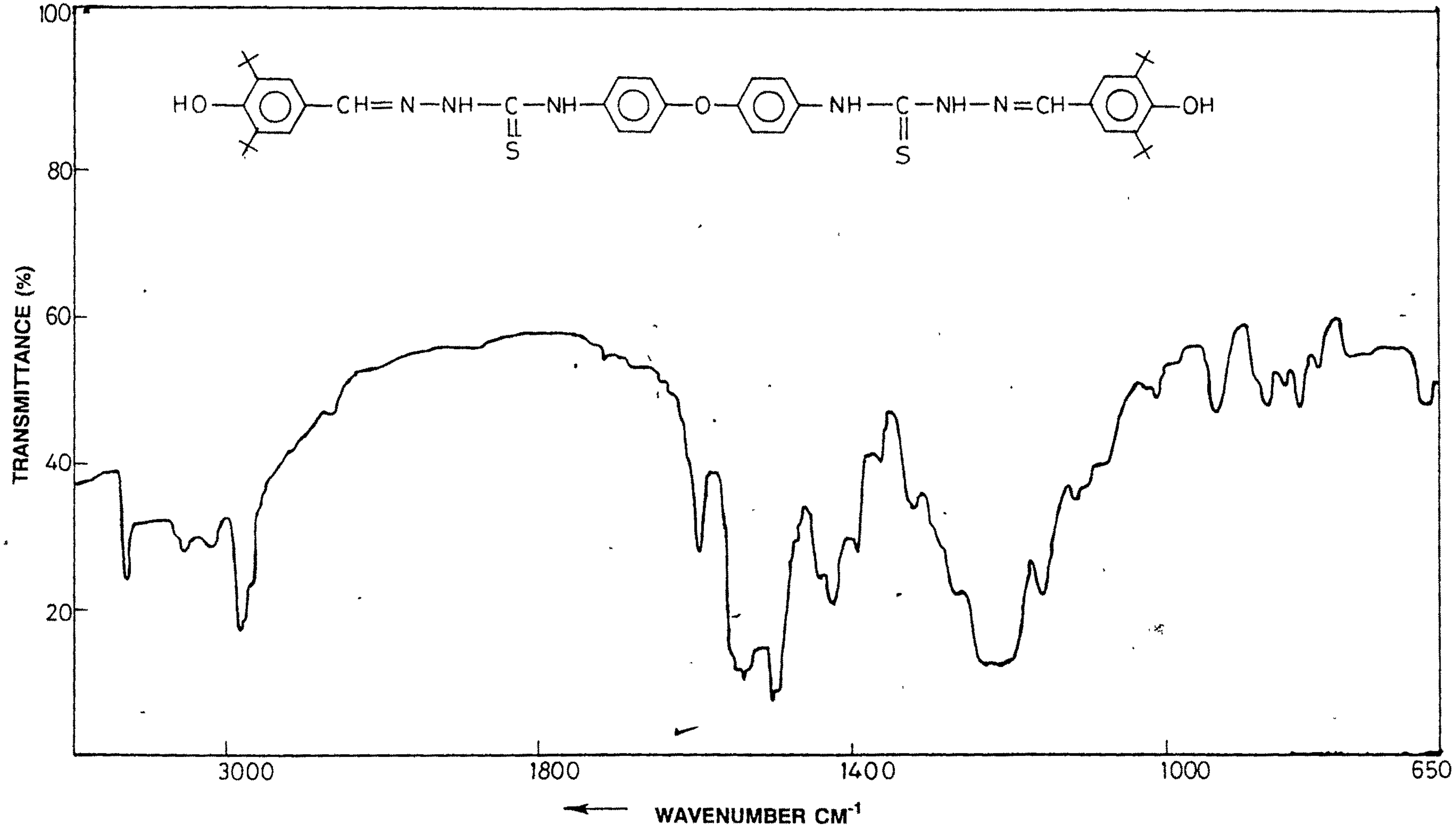
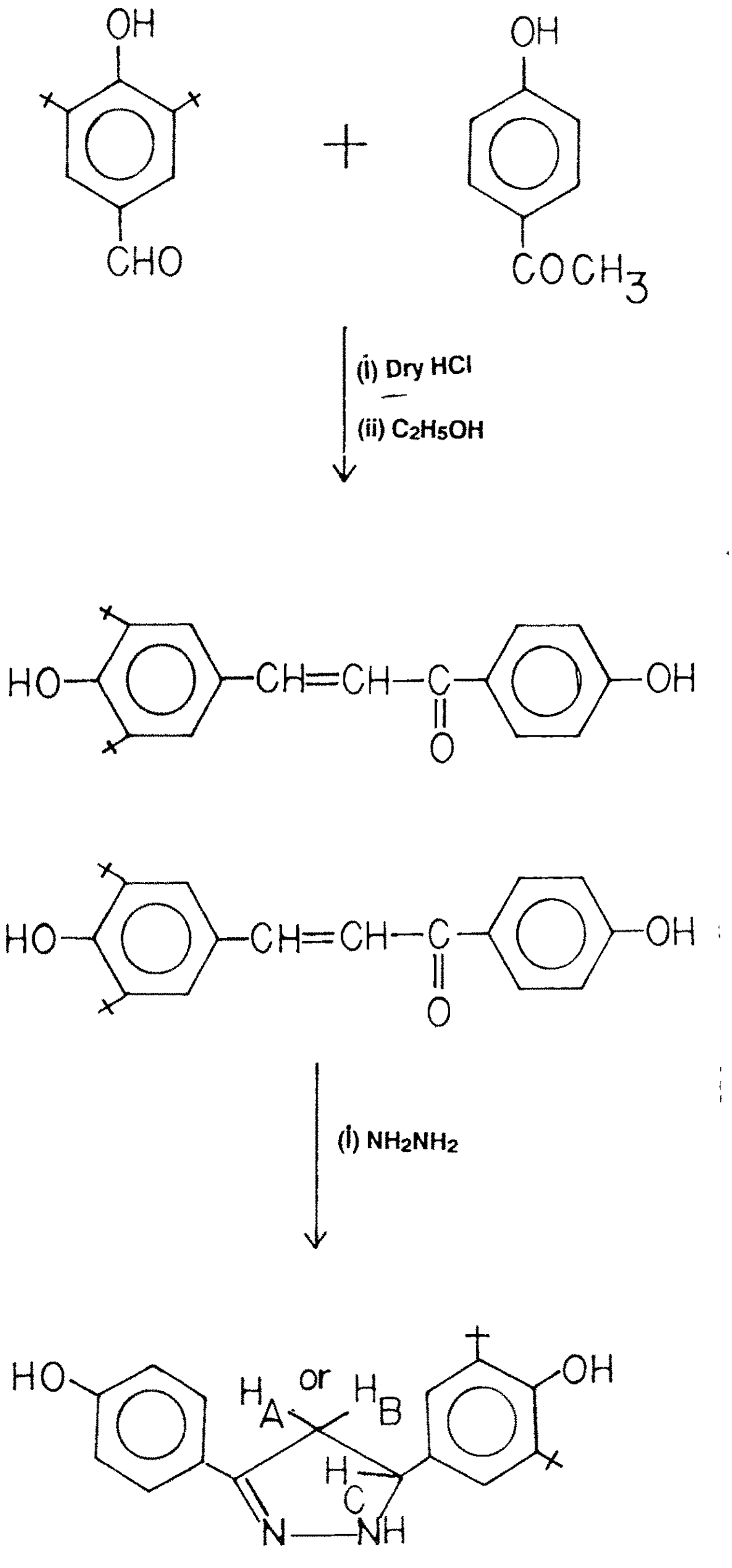


Fig. 2.25 IR spectra of Compound AO_{15}

Scheme-15



AO16

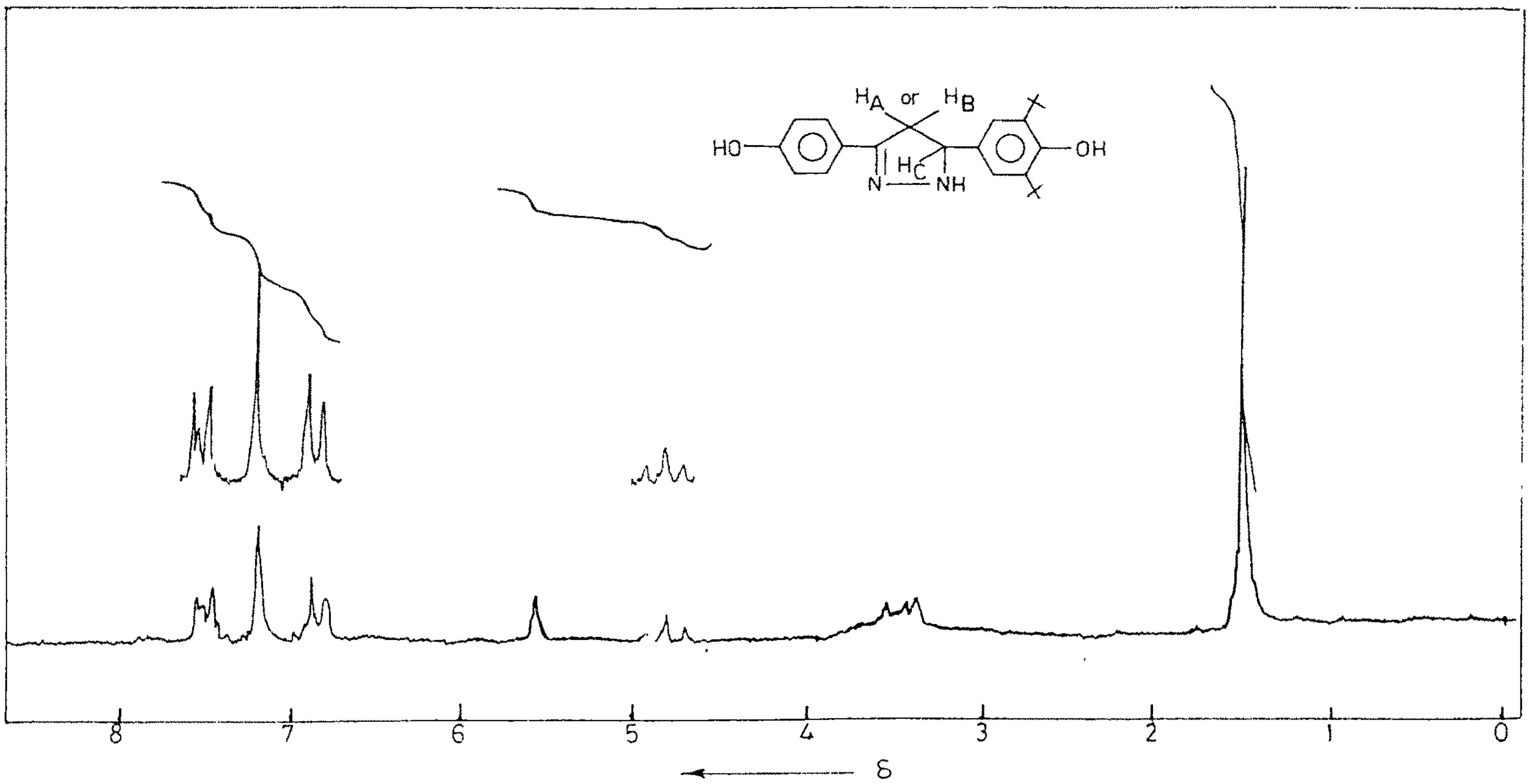


Fig. 2.26 ^{1}HNMR spectra of Compound AO_{16}

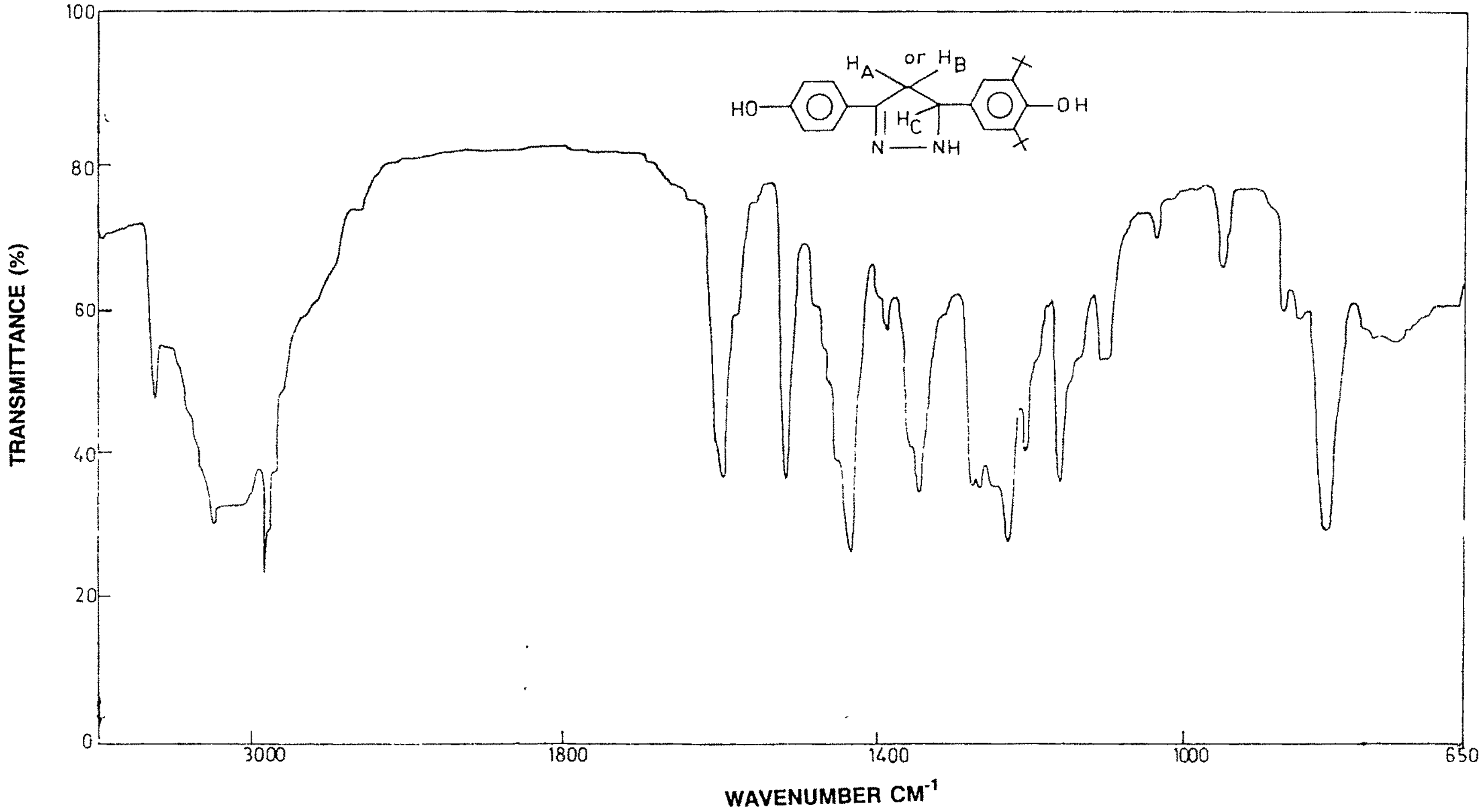


Fig. 2.27 IR spectra of Compound AO_{16}

Out of the antioxidants synthesised, AO_2, AO_3, AO_5, AO_8, AO_9 and AO_{15} were considered to check their stabilisation efficiency with Isotactic polypropylene (IPP) and they were synthesised in sufficient quantity

EXPERIMENTAL :

All melting points are uncorrected ^{1}HNMR spectra were recorded in Perkin-Elmer R-32 spectrophotometer (90 MHz) using TMS as internal standard. Silica gel used for column chromatography with mesh size 60-120 IR spectra recorded on Shimadzu spectrophotometer 408 using KBr pellet technique

3,5-Di-tert-butyl-4-hydroxy benzaldehyde was synthesised from 2,6-di-tert-butyl-4-methyl phenol (BHT, AO_1) according to the method reported by Coppinger and Campbell.[61]

N'-(3,5-Di-tert-butyl-4-hydroxyphenyl) methylene-4-hydroxy benzohydrazine (AO_2).

3,5-Di-tert-butyl-4-hydroxy benzaldehyde (0 01 mole) was dissolved in ethanol (50 ml), p-hydroxybenzohydrazide (0 01 mole) and two drops of acetic acid were added to it The mixture was refluxed for 12 hours. Excess of ethanol was distilled off and the product obtained was crystallised from ethanol M.p 273°C yield (82%).

Analysis :	Found :	C, 71.30%, H,8.01%; N,7.68%
$C_{22}H_{28}N_2O_3$.	Required :	C, 71 73%; H,7.60%; N,7.60%

N'-(3,5-Di-tert-butyl-4-hydroxy phenyl) methylene-4-pentyloxy benzohydrazine (AO_3).

A mixture of N'-(3,5-Di-tert-butyl-4-hydroxy phenyl) methylene-4- hydroxy benzohydrazine (0.01 mole), n-bromopentane (0.01 mole) and anhydrous potassium carbonate (10g), in dry acetone (30 ml) was refluxed for 28 hours. The excess of acetone was distilled off and the product poured into ice-cold water The solid obtained was crystallised from petroleum ether M.p. 189°C, yield (79%)

Analysis :	Found	C, 73 45%, H,8.21%; N,6.40%
$C_{27}H_{38}N_2O_3$:	Required :	C, 73 97%, H,8 67%; N,6.39%

N'-(3,5-Di-tert-butyl-4-hydroxy phenyl) methylene-4-octyloxy benzohydrazine (AO_4)

N'-(3,5-Di-tert-butyl-4-hydroxy phenyl) methylene-4-hydroxy benzohydrazine (0 01 mole) and n-octyl bromide (0.01 mole) in presence of anhydrous K_2CO_3 (10gm) in dry acetone (40 ml) was refluxed for 36 hours. Excess of acetone was distilled off. The product obtained on pouring the reaction mixture into ice-water, was purified by column chromatography using benzene- petroleum ether (50 : 50) as eluent. Crystallised from benzene gave M. p. 95°C, yiled (64%).

Analysis :	Found .	C, 74.69%; H,8.95%; N,5 54%
$C_{30}H_{44}N_2O_3$:	Required .	C, 75.00%; H,9.16%; N,5.83%

N'-(3,5-Di-tert-butyl-4-hydroxy phenyl) methylene-4-decyloxy benzohydrazine (AO_5).

A mixture of N'-(3,5-di-tert-butyl-4-hydroxy phenyl) methylene-4-hydroxy benzohydrazine (0.01 mole), n-bromo decane (0.01 mole) anhydrous potassium carbonate (10 gm) in dry acetone was refluxed for 28 hours. The product obtained on working up as above was purified by column chromatography by using petroleum ether as eluent and crystallised from petroleum ether, M.p. 80°C yield (58%).

Analysis :	Found :	C, 75 29%; H,9.26%, N,5 45%
$C_{32}H_{48}N_2O_3$:	Required ·	C, 75.59%; H,9.44%, N,5.51%

2-[(3,5-Di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carboxamide (AO_6)

To, 3,5-di-tert-butyl-4-hydroxy benzaldehyde (0.002 mole) in ethanol (30 ml), semicarbazide hydrochloride (0.004 mole) and sodium acetate (2 gm) were added and refluxed for 8 hours. The reaction mixture was allowed to cool, and poured into ice-cold water. The product obtained was crystallised from ethanol. M.p 229°C yield (78%).

Analysis ·	Found ·	C, 65.51%; H,8.26%; N,14 23%
$C_{16}H_{25}N_3O_2$ ·	Required	C, 65 97%, H,8.59%, N,14.43%

2-Amino-5-(3,5-di-tert-butyl-4-hydroxy phenyl) 1,3,4-oxadiazole (AO_7).

To a stirred mixture of 2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carboxamide (0.01 mole) and anhydrous sodium acetate (2 gm) in glacial acetic acid (10 5 ml), bromine (0.01 mole) in glacial acetic acid (5 ml) was added slowly. The reaction mixture became warm and colourless. After four hours, the reaction mixture was poured into ice cold water. The solid separated out was crystallised from petroleum ether. M.p. 183°C yield (64%).

Analysis : Found : C, 66.28%; H,8.12%; N,14.51%
$C_{16}H_{23}N_3O_2$: Required : C, 66.43%; H,7.95%; N,14.53%

2-[(3,5-Di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamide (AO_8).

A mixture of 3,5-di-tert-butyl-4-hydroxy benzaldehyde (0.01 mole) and thiosemicarbazide (0.01 mole) in ethanol (50 ml) was refluxed for 12 hours. The reaction mixture was allowed to cool. The product obtained when the reaction mixture was poured into ice cold water was crystallised from ethanol. M.p. 210°C yield (82%).

Analysis : Found . C, 61.94%; H,8.01%; N,13.88%
$C_{16}H_{25}N_3SO$: Required : C, 62.54%; H,8.14%; N,13.68%

2-[(3,5-Di-tert-butyl-4-hydroxy phenyl) methylene]-N-phenyl- hydrazine carbothioamide (AO_9).

A mixture of 3,5-di-tert-butyl-4-hydroxy benzaldehyde (0.01 mole) and 4-phenyl-3-thiosemicarbazide (0.01 mole) was refluxed in ethanol (40 ml), for 6 hours. It was then cooled and kept overnight The solid obtained was filtered and crystallised from benzene. M.p. 212°C yield (78%).

Analysis . Found · C, 68.93%; H,7.23%; N,10.60%
$C_{22}H_{29}N_3SO$ · Required : C, 68 92%; H,7.57%; N,10.96%

2-[(3,5-Di-tert-butyl-4-hydroxy phenyl) methylene] N-(4-methyl phenyl) hydrazine carbothioamide (AO_{10}).

To, 3,5-di-tert-butyl-4-hydroxy benzaldehyde (0.01 mole) in ethanol (50 ml), 4-(4-methyl phenyl) 3-thiosemicarbazide (0.01 mole) was added and refluxed for 5 hours. The product obtained was crystallised from benzene. M.p. 215°C yield (79%).

Analysis : Found : C, 69.10%; H,7.40%; N,10.81%
$C_{23}H_{31}N_3SO$: Required : C, 69.52%, H,7 81%, N,10 58%

1-2-Di {2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamido} ethane (AO_{11}).

3,5-Di-tert-butyl-4-hydroxy benzaldehyde (0.02 mole) was dissolved in ethanol (50 ml) To this 1-2-di(3-thiosemicarba-zide) ethane (0.01 mole) was added and refluxed for 4 hours. The reaction mixture was then allowed to cool and left overnight The solid seperated out was crystallised from benzene M.p 279°C yield (72%)

Analysis : Found : C, 64.04%, H,7.70%, N,12.77%

$C_{34}H_{52}N_6S_2O_2$: Required : C, 63.75%, H,8.12%; N,13.12%

1-4-Di{2-[(3,5-Di-tert-butyl-4-hydroxy phenyl)methylene] hydrazinecarbothioamido} benzene (AO_{12}).

To,3,5-di-tert-butyl-4-hydroxy benzaldehyde (0.02 mole) in ethanol (50 ml), 1,4-di-(3-thiosemicarbazide) benzene was added and refluxed for 5 hours The product obtained was crystallised from benzene M.p. 264°C, yield (75%)

Analysis : Found : C, 65.83%, H,7.07%; N,11.80%

$C_{38}H_{52}N_6S_2O_2$: Required : C, 66.27%, H,7.55%, N,12.20%

4,4'-Di{2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamido} biphenyl (AO_{13}).

A mixture of 3,5-di-tert-butyl-4-hydroxy benzaldehyde (0.04 mole) and 4,4'-di (3-thiosemicarbazide) biphenyl (0.02 mole) was refluxed in ethanol (50 ml) for 6 hours The product obtained on working up as above, crystallised from benzene-ethanol mixture M.p 248°C, yield (69%)

Analysis Found . C, 69.58%, H,7.12%; N,10.65%

$C_{44}H_{56}N_6S_2O_2$ Required . C, 69.10%, H,7.32%, N,10.99%

4,4'-Di{2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothiamido} biphenyl methane (AO_{14}).

A mixture of 3,5-di-tert-butyl-4-hydroxy benzaldehyde (0.004 mole) and 4,4'-di-3-thiosemicarbazide) biphenyl methane (0.002 mole) was refluxed in ethanol for 5 hours. The reaction mixture was cooled and kept overnight. The solid seperated was crystallised from DMF-water mixture M.p. 231°C, yield (65%)

Analysis ·	Found ·	C, 69.95%,	H,7 79%;	N,10.92%
$C_{45}H_{58}N_6S_2O_2$	Required .	C, 69.40%,	H,7.45%;	N,10 79%

4,4'-Di{2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamido} biphenyl ether (AO_{15}).

3,5-Di-tert-butyl-4-hydroxy benzaldehyde (0 004 mole) was dissolved in ethanol (50 ml) To this 4,4'-di-(3-thiosemicarbazide') biphenyl ether (0.002 mole) was added and refluxed for 4 hours. The reaction mixture was then allowed to cool and kept overnight. The solid seperated crystallised from benzene-ethanol mixture, M.p. 210°C, yield (68%).

Analysis .	Found	C, 67.23%;	H,6.92%,	N,10.28%
$C_{44}H_{56}N_6S_2O_3$.	Required :	C, 67.69%;	H,7.17%;	N,10.76%

3-(4-Hydroxy phenyl)-5 (3,5-di-tert-butyl-4-hydroxy phenyl) 4,5-dihydro-1H-pyrazole (AO_{16}).

To 4,4'-dihydroxy-3,5-di-tert-butyl chalcone (0.01 mole), hydrazine hydrate (0 01 mole, 50%) was added. The mixture was warmed gently on a boiling waterbath until complete dissolution of the solid and a discharge of yellow color was apparent The mixture was then left at room temperature overnight, and the crystalline precipitate was collected and recrystallised from benzene-ethanol, M.p. 148°C yield (79%).

Analysis :	Found :	C, 75.36%,	H,7 28%,	N, 7.47%
$C_{23}H_{28}N_2O_2$ ·	Required	C, 75.82%;	H,7.69%;	N, 7.69%

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