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**SUBSTITUTED CYCLOOLEFINS AND
PARTIALLY HYDROGENATED BIPHENYLS**

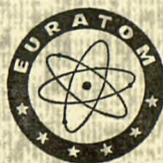
by

S. SANDRONI (*), C. BEAUDET (**), and G. JUPPE (*)

(*) Euratom

(**) SERAI

1969



Joint Nuclear Research Center
Ispra Establishment - Italy

Chemistry Department - Organic Chemistry

Euratom Contract No. 295-61-10 ORGC

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For a better understanding of the pyrolytic and radiolytic behaviour of partially hydrogenated polyphenyls larger amounts of high purity 1-phenylcyclohexene, 3-phenylcyclohexene, 4-phenylcyclohexene, 1-, 3- and 4-methylcyclohexene, 1-methylcyclopentene, 1-methylcycloheptene, 1,3- and 1,4-cyclohexadienes were synthesized and the compounds characterized by their ultraviolet, infrared, Raman and nuclear magnetic resonance absorptions.

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SUMMARY

For a better understanding of the pyrolytic and radiolytic behaviour of partially hydrogenated polyphenyls larger amounts of high purity 1-phenylcyclohexene, 3-phenylcyclohexene, 4-phenylcyclohexene, 1-, 3- and 4-methylcyclohexene, 1-methylcyclopentene, 1-methylcycloheptene, 1,3- and 1,4-cyclohexadienes were synthesized and the compounds characterized by their ultraviolet, infrared, Raman and nuclear magnetic resonance absorptions.

From spectral correlations a 2,5-phenylcyclohexadiene structure was assigned to the Birch reduction product of biphenyl with sodium.

KEYWORDS

PYROLYSIS
RADIOLYSIS
POLYPHENYLS
HYDROGENATION
CYCLOALKENES
PREPARATION
ULTRAVIOLET RADIATION

INFRARED RADIATION
NUCLEAR MAGNETIC RESONANCE
ABSORPTION
SPECTRA
MOLECULAR STRUCTURE
BIPHENYL

SUBSTITUTED CYCLOOLEFINS AND PARTIALLY HYDROGENATED BIPHENYLS

I. SYNTHESIS (*)

As precursor for the preparation of 1-phenylcyclohexene (I) readily dehydrated phenylcyclohexanol was chosen. The sample had been prepared by means of the Grignard reaction from phenylmagnesiumbromide and cyclohexanone by using sulfuric acid - acetic acid. The alcohol could be converted to the cycloolefin in a 50% yield. This method of preparation gave a higher yield and purity than when using iodine as ¹⁾ dehydrating agent .

3-Phenylcyclohexene (II) was prepared in a 68% yield by the Grignard reaction of phenylmagnesiumbromide with ²⁾ 3-bromocyclohexene . This method of synthesis gave better yields and a higher purity than the preparation from cis-2-³⁾ phenylcyclohexanol following the Chugaev procedure .

4-Phenylcyclohexene (III) was synthesized in a 35% yield by a modification of the method of Konigsberger and ⁴⁾ Salmon starting from styrene and butadiene. This preparation was found superior concerning yield and purity than the ³⁾ synthesis by the Chugaev method . The reaction of p-dibromobenzene with phenylmagnesiumbromide did not give the desired ⁵⁾ p-bromophenylcyclohexane as precursor of the olefin .

(*) Manuscript received on October 15, 1968.

1-Methylcyclohexene (IV), 1-methylcyclopentene (V) and 1-methylcycloheptene (VI) were synthesized from the corresponding ketones by the Grignard reaction with methylmagnesium iodide in 51%, 57% and 85% yield, respectively. The dehydration of the tertiary alcohols was effected by dimethylsulfoxide yielding (IV), by 15% acetic acid yielding (V) and by refluxing 1-methylcycloheptanol with iodine leading to the formation of (VI).

3-Methylcyclohexene (VII) was synthesized in 54% yield from 3-bromocyclohexene and methylmagnesium iodide⁶⁾.

4-Methylcyclohexene (VIII) was prepared in 74% yield by the dehydration of 4-methylcyclohexanol with concentrated sulfuric acid.

1,3-Cyclohexadiene (IX) and 1,4-cyclohexadiene (X) were obtained in 83% and 60% yield, respectively, by dehydrobromination of 3-bromocyclohexene and by Birch reduction of benzene⁷⁾⁸⁾.

The purity of the compounds was controlled by gas chromatography. The physical constants of the compounds synthesized are given in table 1.

II. ULTRAVIOLET SPECTRA

The ultraviolet spectra of the isomeric phenylcyclohexenes, and 2,5-phenylcyclohexadiene are compared with biphenyl in fig. 1. The absorption maxima and the extinction coefficients of these compounds, of cyclohexene, 1,3- and 1,4-cyclohexadiene and of two phenylcyclohexadienes described in literature are listed in table 2.

On examining these data, it may be seen that a conjugation between double bonds or between a phenyl ring and a double bond leads to one broad and very intense band without fine structure. In 1-phenylcyclohexene the conjugation between the double bond and the aromatic ring gives rise to a biphenyl type configuration. It also indicates a possible coplanarity of 10 out of 12 carbon atoms: The UV spectrum shows a structureless band identical in its position to biphenyl, while the ϵ -value is 0.6 times lower. Also the bathochromic shift in relation to 3- and 4-phenylcyclohexene is in agreement with a resonance between double bond and phenyl ring. Our data agree closely with the UV absorption data given by Egorov et al.⁹⁾ for (I) and (II) and by Cope et al.¹⁰⁾ for (II). The suggestion of Egorov et al.⁹⁾ of a 1,4 position for the double bonds in the phenylcyclohexadiene obtained by Birch

reduction of biphenyl could not be confirmed by us. The shape of the spectrum, the absorption maxima and the extinction compared to phenylcyclohexenes are not in agreement with a resonance between phenyl ring and double bond. Also a comparison with the UV spectra obtained for the cyclohexadienes excludes any resonance between the double bonds.

In analogy to benzene, where the Birch reduction leads to the formation of the unconjugated 1,4-cyclohexadiene, Hückel¹¹⁾ suggested also for the Birch reduction product of biphenyl a 1,4,1',4'- or 1,4,2',5'-dicyclohexadienyl structure. The spectral evidence does not confirm these structures: The infrared spectrum shows the characteristic strong bands of the phenyl ring at 695 and 755 cm^{-1} . In analogy to 1,4-cyclohexadiene we would also expect an absorption at lower wavelength than actually observed.

The spectra can be best explained on the assumption of a 2,5-phenylcyclohexadiene structure.

III. INFRARED AND RAMAN SPECTRA

The infrared absorption spectra in the region between 3500-400 cm^{-1} of the phenylcyclohexenes and 2,5-phenylcyclohexadiene are shown in fig. 2 to 3, of the methylcycloolefins in fig. 4 and 5. The Raman spectra of the methylsubstituted cycloolefins (IV) to (VIII) are shown in fig. 6 and 7.

The absorptions between 3200 and 2800 cm^{-1} include the aromatic and olefinic CH (3100-2980 cm^{-1}) and alicyclic CH₂ and CH₃ stretching vibrations. The IR intensities of aromatic CH are lower by a factor of appr. 0.6 than those of asymmetrical and symmetrical (~ 2930 resp. ~ 2850 cm^{-1}) CH₂ stretching bands.

The ethylenic double bond ν (C=C) appears in the region between 1700 and 1600 cm^{-1} . The olefinic absorption of (I) in the IR (1676 cm^{-1}) appears at a higher frequency than for the corresponding isomers (II) and (III) (1657 and 1658 cm^{-1}), indicating a resonance contribution between double bond and phenyl ring in α -position. The position of ν (C=C) in (XI) (1638 cm^{-1}) is nearly identical with that of (X) (1640 cm^{-1}) demonstrating the analogy between these molecules. Also in the Raman spectra ν (C=C) is higher in 1-substituted cycloolefins (1670 cm^{-1} (IV) and 1640 cm^{-1} (VII)), respectively)

By varying the ring size no difference is found between cyclohexene and cycloheptene for ν (C=C) (1670 cm^{-1} while a shift to a lower frequency is observed when passing to cyclopentene (1658 cm^{-1} for (V)).

The spectra of (I), (II), (III) and (XI) show the characteristic bands of aromatic systems at 1600 ± 5 , 1495 ± 2 and 1452 cm^{-1} . This excludes a dicyclohexadienyl structure for (XI). The absorption in the IR at 1435 cm^{-1} can be assigned to a cyclohexane CH_2 in-plane bending motion (β).

The region between 1350 and 1000 cm^{-1} includes α (CC) and β (CH) in-plane bending motions. The absorption at 1140 cm^{-1} can be related to olefinic β (CH) while for the bands between 1075 and 1000 cm^{-1} no unambiguous assignments can be given.

The absorptions between 1000 and 400 cm^{-1} indicate almost out-of-plane γ (CH) and Γ (CC) deformation vibrations. The characteristic vibrations for monosubstituted benzenes appearing at 900 (δ), 755 (γ), 700 (Γ), 530 (Γ , mass sensitive) and 460 (Γ) cm^{-1} can be confirmed. The absorption appearing at 890 cm^{-1} can be assigned to a cyclohexene ring deformation.

The band at $720 \pm 3 \text{ cm}^{-1}$ is not observed in 1,2 substituted cyclohexene and, therefore, assigned to the $\gamma(\text{CH}=\text{CH})$ cis configuration. Typical absorptions for monosubstituted $\Delta 3,4$ -enes and monosubstituted $\Delta 2,3$ -enes appear at 658 and 678 cm^{-1} , respectively. Characteristic absorptions for the 1-substituted cyclohexene can be observed at 920 (m-s), 803 (m-s) and 765 (s) cm^{-1} , for the 3-substituted cyclohexene at 890 (s) and 730 (s) cm^{-1} .

IV. NUCLEAR MAGNETIC RESONANCE SPECTRA *)

The spectra of the three isomeric methylcyclohexenes (fig. 8) are assigned in table 3.

The methyl signal in 1-methylcyclohexene is broadened due to the coupling with C(2)-H, C(3)-H and the C(6)-H-atoms. The vinyl absorption is strongly broadened due to the additional coupling with the C(1)-methyl group. The broad resonance of C(3)-H in 3-methylcyclohexene indicates an equatorial configuration of the methyl group. The C(3)-H is coupled with the C(4)-H-atoms by 11 Hz and 6 Hz. The resonance is additionally broadened by the allylic coupling of app. 3 Hz and 1 Hz resulting in a line breadth of app. 21 Hz (observed 24 Hz).

*)

with cooperation of Dr. Dieffenbacher, Varian AG, Zürich

The AB-system of the vinyl protons in 4-methylcyclohexene is not solvable. Due to the allylic coupling a complicated spectrum results which only seems to have the features of a doublet. The couplings could be positive or negative.

The spectra of the three isomeric phenylcyclohexenes listed in fig. 9 are interpreted in table 4.

The heptet observed in the spectrum of 1-phenylcyclohexene can be explained on the following basis: the coupling of 4.0 Hz of C(2)-H with both C(3)-H-atoms leads to a triplet being further split by the small coupling of 1.7 Hz of C(2)-H with the two C(6)-H-atoms.

The assignment of the vinyl signals in 3-phenylcyclohexene was made by estimating the relative chemical shift due to the phenyl ring with Dreiding models; a chair configuration of cyclohexene was assumed. Emsley, Feeney and Sutcliffe¹⁴⁾ calculated a $\Delta\delta$ -value of 0.7 ppm for the equatorial and 0.2 ppm for the axial conformation; for the latter case it is assumed that the phenyl ring is positioned vertically to the cyclohexene ring. A further indication for an axial conformation of the phenyl substituent is obtained from the line breadth of appr. 14 Hz for C(3)-H due to the coupling with the two C(4)-H-atoms (5 Hz each) and the two vinyl protons (4 Hz and 1.5 Hz). The sum of these coupling constants (2 times 5 Hz, 4 Hz, 1.5 Hz) is nearly precisely observed in the 14 Hz breadth of the multiplet.

An axial conformation of the phenyl ring can also be deduced from the breadth of the multiplet of C(4)-H in 4-phenylcyclohexene being coupled with the four protons of C(3)-H and C(5)-H. Both the C(4)-H resonance in this molecule and the C(3)-H resonance in 3-phenylcyclohexene are found shifted to lower fields than the corresponding absorptions of the methyl analogues. The H-atoms lie in the plane of the phenyl ring and, therefore, the resonance is shifted to lower fields due to a ring current effect of the benzene ring.

The spectra of 1-methylcyclopentene and 1-methylcycloheptene listed in fig. 10 are interpreted in table 5.

In both cases and in analogy with the observations from 1-methylcyclohexene the methyl absorptions are broadened due to the coupling with the C(2)-H, C(3)-H and C(6)-H-atoms. Also the vinyl absorption is strongly broadened due to the additional coupling with the C(1)-methyl group. An octet structure should be expected. The AB-system in 1-methylcyclopentene could not be solved.

The spectra of the two isomeric cyclohexadienes listed in fig. 11 are interpreted in table 6.

The 1,4-cyclohexadiene molecule is not planar. It can be assumed that both possible configurations are quickly alternating at room temperature. An averaged conformation results leading to a high symmetry. For this reason no coupling constants can be observed.

Due to the asymmetry of 1,3-cyclohexadiene a spectrum of higher order of the type $A_2A'_2, X_2X'_2$ is to be expected. The molecule does not exist in a planar conformation.

V. EXPERIMENTAL

V.1 Syntheses

1-Methylcyclopentene: A 2 liter three necked round bottomed flask was fitted with a mechanical stirrer, a dropping funnel, a thermometer, an efficient reflux condenser and a gas inlet tube and the apparatus swept with dry nitrogen. To a Grignard solution prepared from 380 g methyl iodide, 64.2 g magnesium and 400 ml absolute ether and cooled to 0°C were added dropwise 180 g of cyclopentanone in 250 ml ether. The reaction mixture was heated under reflux for 30 minutes and the com-

plex then decomposed at 0°C by adding 1000 ml of 15% aqueous acetic acid. The ether layer was washed with aqueous sodium bicarbonate and dried over magnesium sulphate.

After removal of the ether by distillation crude methylcyclopentene was distilled through a short Vigreux column. Fractionating distillation gave 100 g 1-methylcyclopentene (b.p. 76°C).

1-Methylcyclohexene: To a Grignard solution prepared from 170 g methyl iodide, 28.8 g magnesium and 200 ml absolute ether and cooled to 0°C were added dropwise 98 g cyclohexanone in 100 ml ether. The reaction mixture was heated under reflux for one hour and the reaction product then decomposed by addition of 400 ml of 15% aqueous acetic acid at 0°C. The ether layer was separated and the aqueous solution washed several times with ether. The combined ether solutions were washed with sodium bisulphite and then with water and dried over magnesium sulphate. After evaporation of the ether solvent a crude distillation through a short Vigreux column yielded a mixture of 1-methylcyclohexene and methylcyclohexane. The distillate was heated under reflux with 350 g of dimethylsulfoxide for nine hours and then distilled. The fraction boiling between 110.5 and 111.5°C contained 1-methylcyclohexene and smaller amounts of methylene cyclohexane. Repeated fractionating distillation yielded 49 g of pure 1-methylcyclohexene (b.p. 111.5°C).

3-Methylcyclohexene: To a Grignard solution prepared from 204 g methyl iodide, 35.46 g magnesium and 250 ml absolute ether and cooled to 0°C were added dropwise 180 g 3-bromocyclohexene in 150 ml ether. The reaction mixture was maintained at 50°C for one hour and the reaction product then decomposed by adding 1300 ml of water at 20°C. The ether layer was separated, washed with sodium bisulphite and dried over magnesium sulphate. After removal of the solvent the residue was fractionated. 60.2 g of 3-methylcyclohexene were collected boiling at 103.5°C.

4-Methylcyclohexene: A mixture of 114 g of 4-methylcyclohexanol and 2 g of concentrated sulphuric acid is distilled. The fraction boiling between 90°C and 96°C was washed with water and dried over magnesium sulphate. Fractionating distillation yielded 71.3 g of 4-methylcyclohexene (b.p. 103°C/750 mm Hg).

1-Methylcycloheptanol: 100.8 g of cycloheptanone dissolved in 100 ml ether were added at 5°C to a Grignard solution of 153.4 g methyl iodide and 26 g magnesium in 100 ml absolute ether. The mixture was heated under reflux for 90 minutes and the reaction product hydrolyzed at 0°C with 1000 ml of 3 N hydrochloric acid. The ether layer was separated and the aqueous solution washed with ether. The combined ether

solutions were washed with sodium bisulphite and with water and dried over magnesium sulphate. 1-methylcycloheptanol was obtained by fractionating distillation (bp. 71°C-72°C/10 mm Hg).

1-Methylcycloheptene: 20 g of 1-methylcycloheptanol were slowly distilled over 0.2 g of iodine. Fractionating distillation of the distillate yielded 84.7 g of 1-methylcycloheptene (b.p. 139°C).

1-Phenylcyclohexene: To a Grignard solution prepared from 17 g bromobenzene, 2.7 g magnesium and 50 ml absolute ether and cooled to 5°C were added dropwise 9.8 g of cyclohexanone in 2- ml ether. The reaction mixture was heated under reflux for 1/2 hour and then hydrolyzed at 0°C by a saturated aqueous solution of ammonium chloride. The upper layer was separated, the aqueous solution washed several times with ether and the combined ether solutions dried over magnesium sulphate. The solvent was distilled and to the residue added a mixture of 4 ml sulphuric acid in 16 ml acetic acid. After 1/2 hour of stirring at room temperature 100 ml of water were added. The 1-phenylcyclohexene formed was extracted with ether. Fractionating distillation yielded 7.9 g of material (b.p. 120°C/10 mm Hg). The alkene was further purified by column chromatography using aluminium oxide as stationary phase and hexane as eluent.

3-Phenylcyclohexene: To a Grignard solution prepared from 62.8 g of bromobenzene, 9.6 g of magnesium and 150 ml absolute ether and cooled to -10°C were added dropwise 64.4 g of 3-bromocyclohexene in 200 ml ether. The mixture was left at room temperature for several hours and then hydrolyzed at 0°C by adding 100 ml of water. The ether layer was separated and dried over magnesium sulphate. After removal of the solvent the residue was purified by column chromatography using aluminium oxide as stationary phase and n-hexane as mobile phase. Fractionated distillation yielded 43.1 g of 3-phenylcyclohexene (b.p. $100^{\circ}\text{C}/12$ mm Hg).

4-Phenylcyclohexene: 312 g of styrene, 500 g butadiene and 0.2 g of 2-phenylnaphthylamine were heated at 120°C for 100 hours in a glass pressure bottle..100 ml of boiling benzene and after cooling 100 ml of methyl alcohol were added in order to precipitate the polystyrene formed. Fractionating distillation of the benzene solution yielded 166 g of 4-phenylcyclohexene (b.p. $108^{\circ}\text{C}/10$ mm).

1,3-Cyclohexadiene: A one liter three necked round bottom flask was fitted with a dropping funnel, a reflux condenser and a mechanical stirrer. To 450 g of distilled quinoline heated under reflux were added dropwise 170 g of 3-bromocyclohexene. The mixture was distilled and the fraction

boiling between 77°C and 81°C treated with 78 g silver nitrate in 39 ml water. The yellow precipitate formed was filtered with suction, washed twice with a small amount of ether and dissolved in 140 ml of water. To the cooled solution 48 g of ammonia and 100 g of sodium nitrate were added. The upper layer of 1,3-cyclohexadiene was collected, washed with water, dried and fractionately distilled under nitrogen yielding 70.5 g of pure diene (b.p. 77-77.5°C).

1.2.4.6-Tetrabromocyclohexane: To 380 ml liquid ammonia cooled to -60°C in an open neck flask fitted with thermometer, stirrer and dropping funnel was under vigorous stirring added 50 ml of water free benzene and then 20 g of metallic sodium in small portions. The mixture was kept at -65°C for an additional 1/2 hour. 75 ml of absolute ethanol were added dropwise, the ammonia evaporated and the excess of sodium destroyed by addition of methylalcohol. The reaction mixture was then poured on 200 g of crushed ice, the upper layer separated and the aqueous solution extracted with chloroform. The organic extracts were washed with water and then dried over calcium chloride. The solution was cooled to 0°C and 51 g of bromine in 80 ml chloroform added dropwise. 1.2.4.6-tetrabromocyclohexane precipitated on addition of 125 ml methyl alcohol to the cooled solution. (m.p. 187.4-188.6°C).

1.4-Cyclohexadiene: A 250 ml three necked flask was fitted ^{with} a dropping funnel, reflux condenser and mechanical stirrer. 43 g tetrabromocyclohexane in 49 ml of acetic acid were added dropwise under vigorous stirring to 43 g of zinc powder in 49 ml of glacial acetic acid. The mixture was distilled until the temperature in the bath reached 118°C. The upper layer of the condensate was separated, washed with a concentrated aqueous solution of potassium hydroxide and water and dried over calcium chloride. Fractionating distillation of the crude product yielded 5.1 g of 1.4-cyclohexadiene (b.p. 89.5-90°C).

V.2 Gas chromatographic Analysis

Chemical and isomeric impurity content in the samples was lower than 2%. Gas chromatographic analyses were made with a F&M 810 gas chromatograph with programmed temperature (100-250°C) and a flame ionization detector: the columns were of Versamide - 10% Diatoport and polyphenylether - 10% Diatoport 1.8 mt. long.

V.3 Recording of Spectra

Ultraviolet spectra were recorded by a Cary model 14 spectrophotometer in cyclohexane solution.

Infrared spectra were recorded by a Beckman IR-7 spectrophotometer (prism-grating) equipped with NaCl and CsI optics. Samples were measured as 0.02 mm thick films in a NaCl cell for the region between 3500 to 600 cm^{-1} and in a KRS-5 cell for the region between 700 to 400 cm^{-1} .

Raman spectra were recorded by a Cary model 81 Raman spectrophotometer in a 2 mm diameter cell.

Nuclear magnetic resonance spectra were recorded by a Varian NMR spectrometer using chloroform (1-phenylcyclohexene, 1-methylcyclohexene) or monodeuterated chloroform (all other compounds) as solvents.

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TABLE I

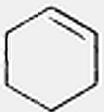
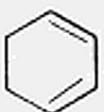
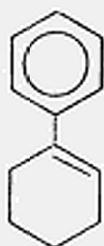
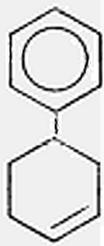
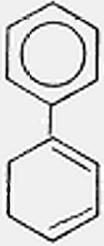
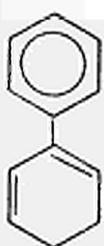
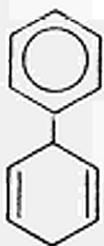
Physical Constants

	Compound	B.P. (°C, 760 mm)	d ^d (g/ml, 25°C)	n _D ⁿ (25°C)
I	1-phenylcyclohexene	82 (1 mm)	1.5675 (23°C)	0.9938 (23°C)
II	3-phenylcyclohexene	100 (8 mm)	1.5441 (21°C)	0.9682 (21°C)
III	4-phenylcyclohexene	108(10 mm)	1.5415	0.9679
IV	1-methylcyclohexene	111.5	0.802	1.4486
V	1-methylcyclopentene	76	1.4300	0.7775
VI	1-methylcycloheptene	139	0.820	1.4568
VII	3-methylcyclohexene	103.5	0.974	1.4419
VIII	4-methylcyclohexene	103.4	0.799 (23°C)	1.4394 (23°C)
IX	1,3-cyclohexadiene	77.5	0.837 (22°C)	1.4732 (22°C)
X	1,4-cyclohexadiene	89.5-90	0.8543(22°C)	1.4712 (22°C)
XI	2,5-phenylcyclohexadiene	(*)		

(*)

We are indebted to Dr. B. Zimmerli, Ecole Polytechnique, Lausanne, for supplying us with a sample of the Birch reduction product from biphenyl with Na.

TABLE II

 1820 (3.88)	 2580 (3.90)	 (< 2000)
 2470 (4.05)	 2480 (2.30) 2530 (2.41) 2550 (2.41) 2590 (2.41) 2620 (2.42) 2640 (2.20) 2680 (2.30)	 2475 (2.30) 2530 (2.42) 2590 (2.45) 2620 (2.45) 2640 (2.30) 2680 (2.30)
 2480 (3.95) (12)	 2500 (4.25) (9)	 2150 (4.0) 2565 (2.57) 2625 (2.67) 2690 (2.58)

UV-ABSORPTIONS : λ_{max} in Å; extinction as $\log \epsilon$

TABLE III

Assignment of the NMR-Spectra of
Methylcyclohexenes

Compound	δ -Value (ppm)	Relative Intensity	Assignment
1-Methylcyclohexene (IV) (15)	1.65 (M)	4	CH ₃
			C(4)-H
			C(5)-H
3-Methylcyclohexene (VII)	1.9 (M)		C(3)-H
			C(6)-H
	5.3 (M)		C(2)-H
	0.9 (D)		J_{CH_3} , $3 \approx 6.5$ Hz
	1.0-1.9 (br)		ringprotons C(3)-CH ₃
4-Methylcyclohexene (VIII)	2.1 (S, br)		C(3)-H
	5.55 AB-Q		C(1)-H
			C(2)-H
	0.9 (D)		C(4)-CH ₃
	1.2 (M, br) ¹⁴⁾		C(4)-H
	1.65 (M, br)		C(3)-H
4-Methylcyclohexene (VIII)			C(5)-H
			C(6)-H
	2.0 (M, br) ¹⁴⁾		C(1)-H
	5.6 AB-Q		C(2)-H

S = singlet
D = doublet
T = triplet
M = multiplet
br = broad

TABLE IV

Assignment of the NMR-Spectra of
Phenylcyclohexenes

Compound	δ -Value (ppm)	Relative Intensity	Assignment
1-Phenylcyclohexene (I)	1.65 (M)	4	C(4)-H C(5)-H ¹⁴⁾
	2.1 (M)	2	C(3)-H ¹⁴⁾
	2.3 (M)	2	C(6)-H
	6.0 (M)	1	C(2)-H
	7.2 (M)	5	Phenyl protons $J_{2,3} \approx 4.0$ $J_{2,6} \approx 1.7$
3-Phenylcyclohexene (II)	1.25 (br)		
	2.1 (M,br)		C(6)-H
	3.35 (S)		fine structure
	5.75 AB-Q		$\delta_1 = 5.70$ C(1)-H $\delta_2 = 5.85$ C(2)-H $J_{1,2} = 11$ Hz $J_{1,3} = J_{2,6} \approx 1.5$ $J_{1,6} = J_{2,3} \approx 3$
	7.2 (S)		Phenyl protons
4-Phenylcyclohexene (III)	1.8 (M,br)	2	C(6)-H
	2.1 (M,br)	4	C(3)-H C(5)-H
	2.7 (M,br)	1	C(4)-H
	5.7 AB-Q	2	C(1)-H C(2)-H
	7.1 (S)		Phenyl protons

TABLE V

Assignment of the NMR-Spectra of
1-Methylcycloheptene and -Pentene

Compound	δ -Value (ppm)	Relative Intensity	Assignment
1-Methylcyclopentene (V)	1.75 AB-Q		C(1)-CH ₃
	2.2 (M)	4	
	5.25 (S,br)	1	C(2)-H
1-Methylcycloheptene (VI)	1.5 (M,br)	4	CH ₂
	1.7 (S,br)	4	CH ₃
	2.05 (M,br)	5	CH ₂
	5.5 (T)		C(2)-H fine structure

TABLE VI

Assignment of the NMR-Spectra of
Cyclohexadienes

Compound	δ -Value (ppm)	Assignment
1,4-Cyclohexadiene (X)	2.64 (S)	C(3)-H fine structure
		C(6)-H
	5.65 (S,br)	C(1)-H fine structure
		C(2)-H
		C(4)-H
1,3-Cyclohexadiene (IX)	2.25 (S)	C(5)-H
		C(6)-H
	5.8 (M,br)	C(1)-H
		C(2)-H
		C(3)-H
	C(4)-H	

FIG. 1 ULTRAVIOLET SPECTRA OF BIPHENYL AND PARTIALLY HYDROGENATED BIPHENYLS

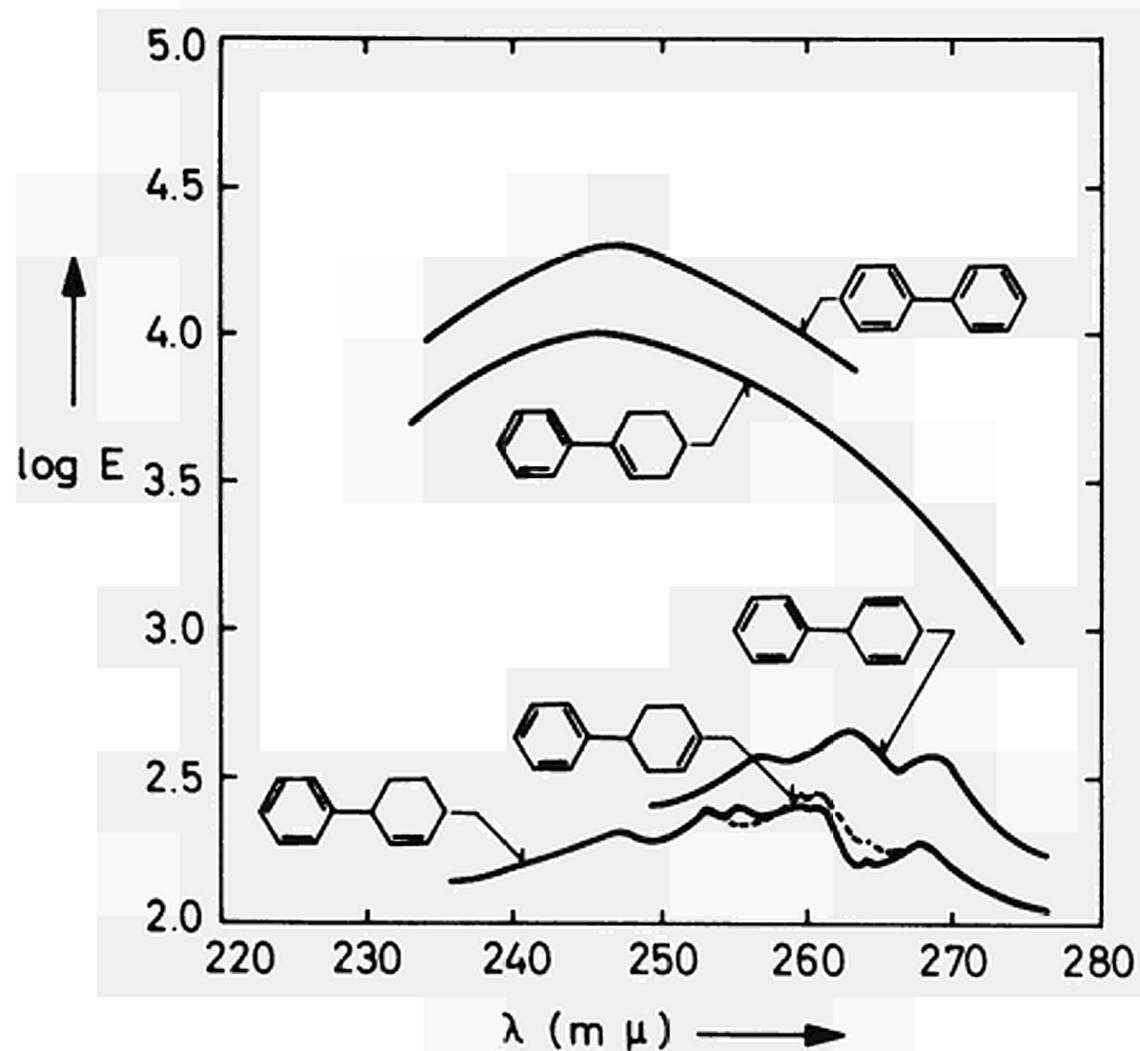
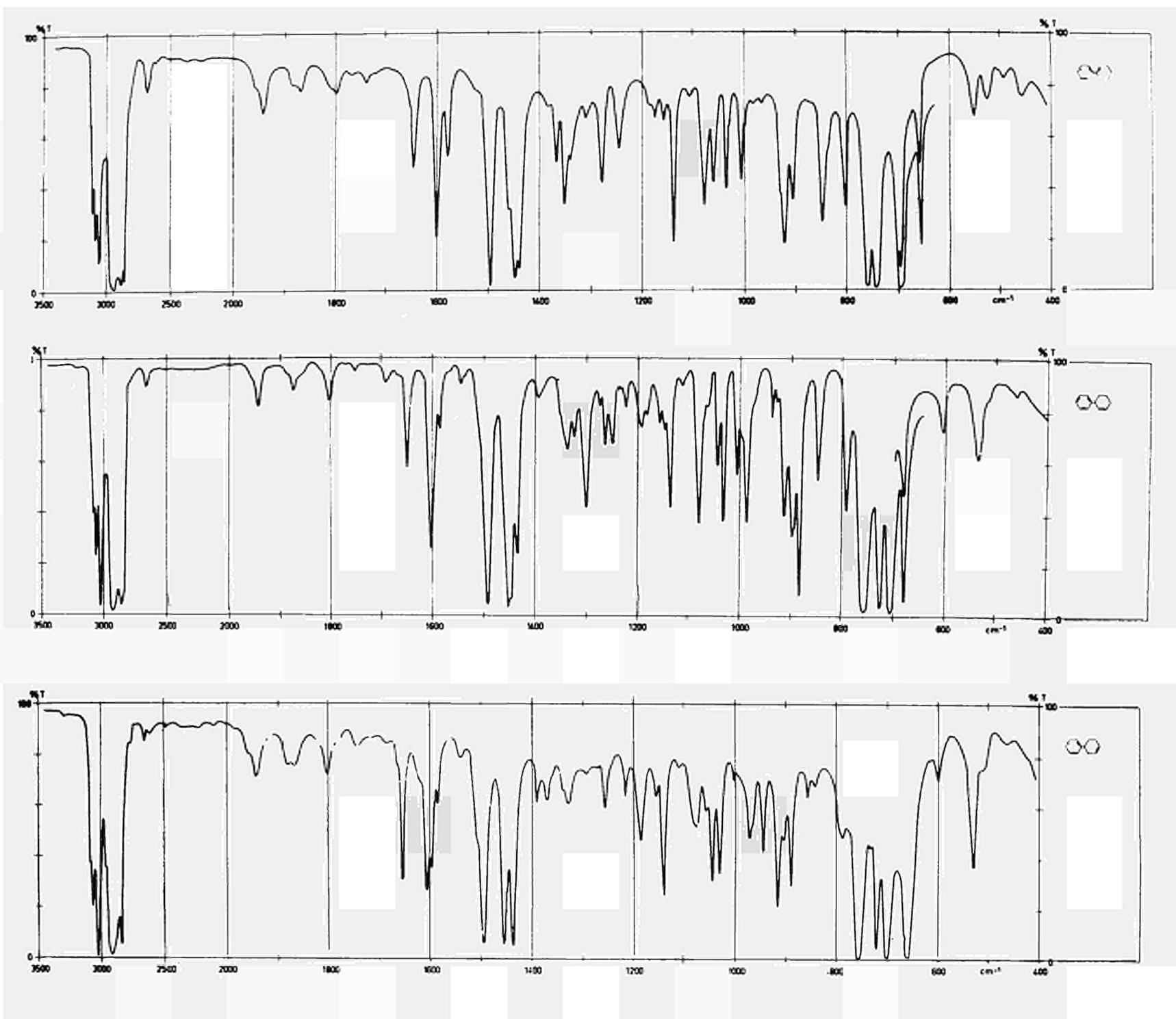


Fig.2 -IR spectra of isomeric phenylcyclohexenes



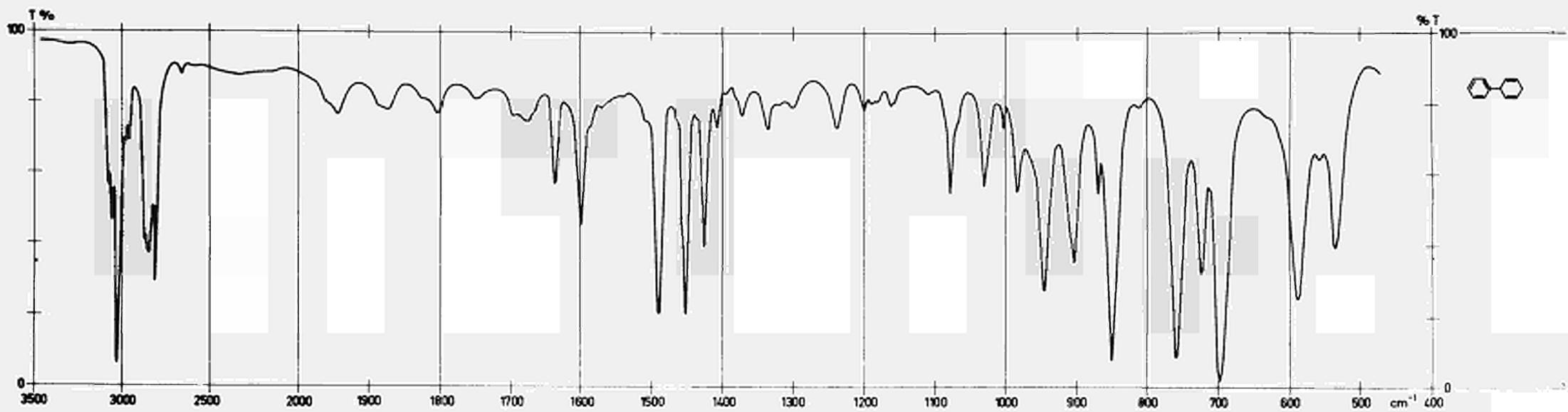
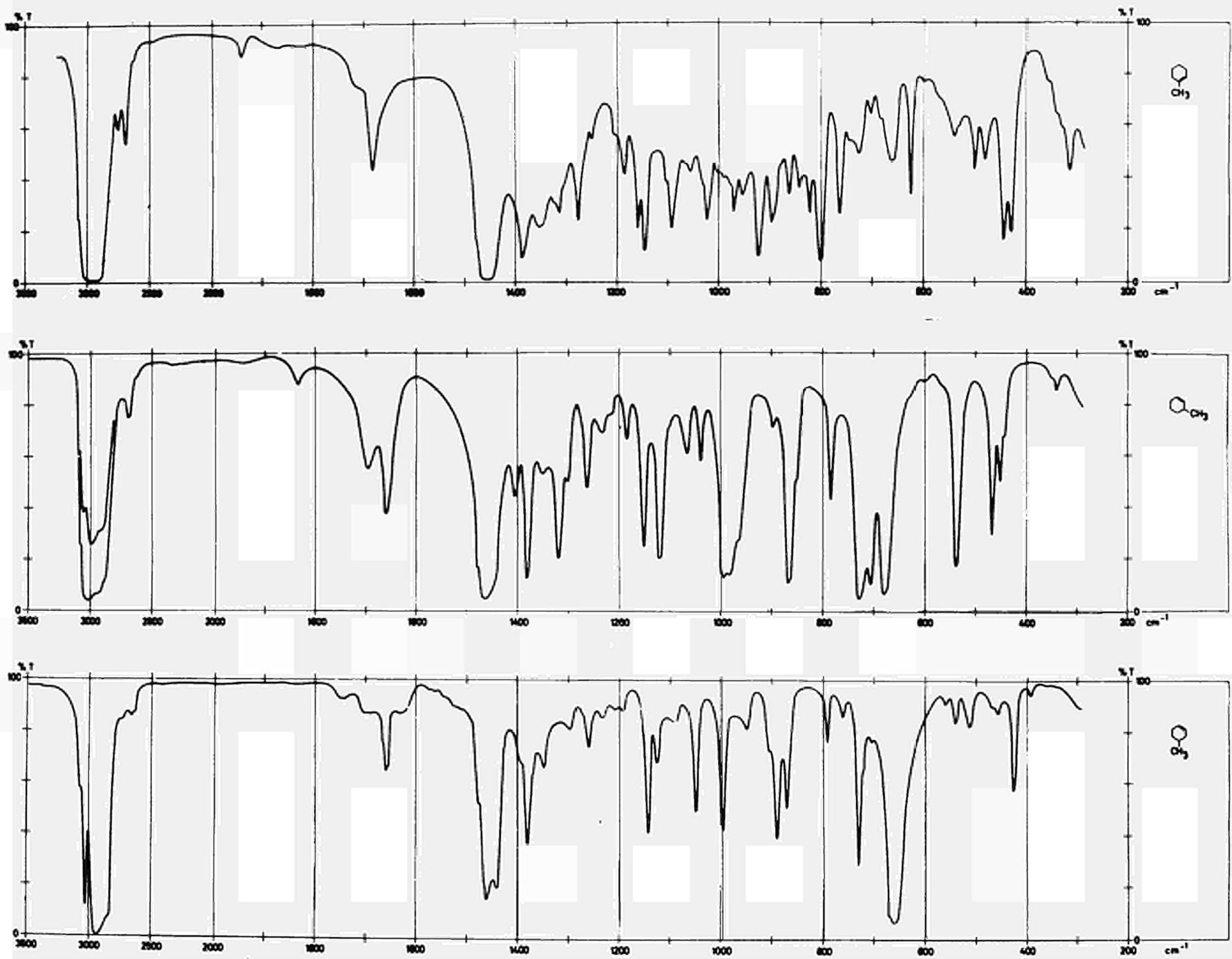


Fig. 3 - IR spectrum of 2,5-phenylcyclohexadiene

Fig. 4 - IR spectra of methylcyclohexenes



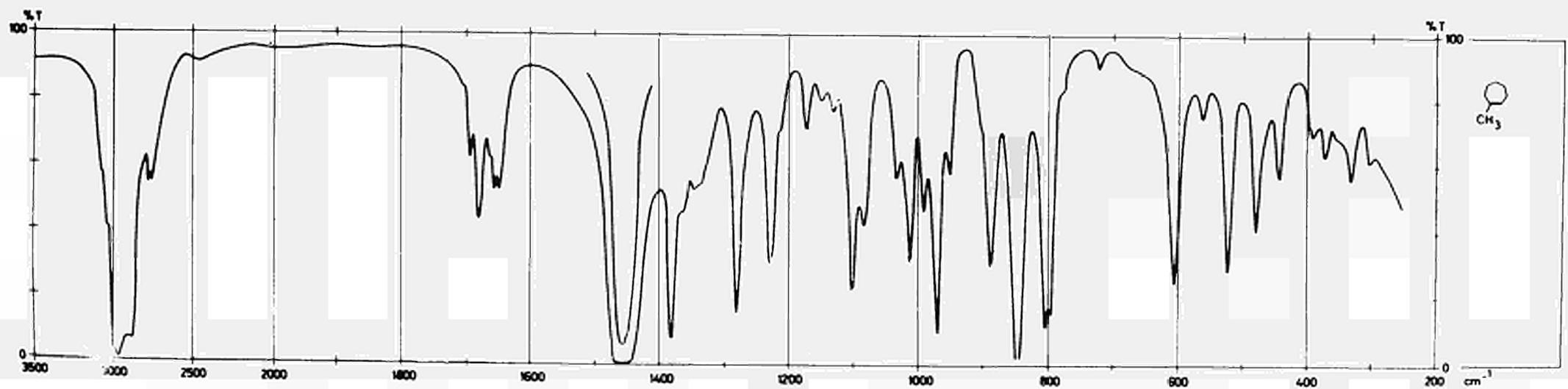
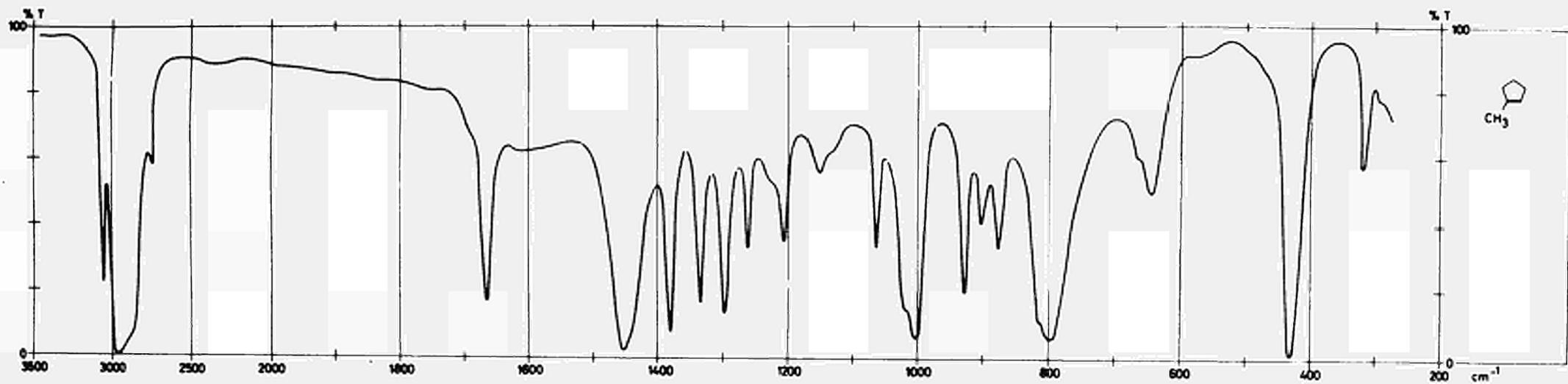
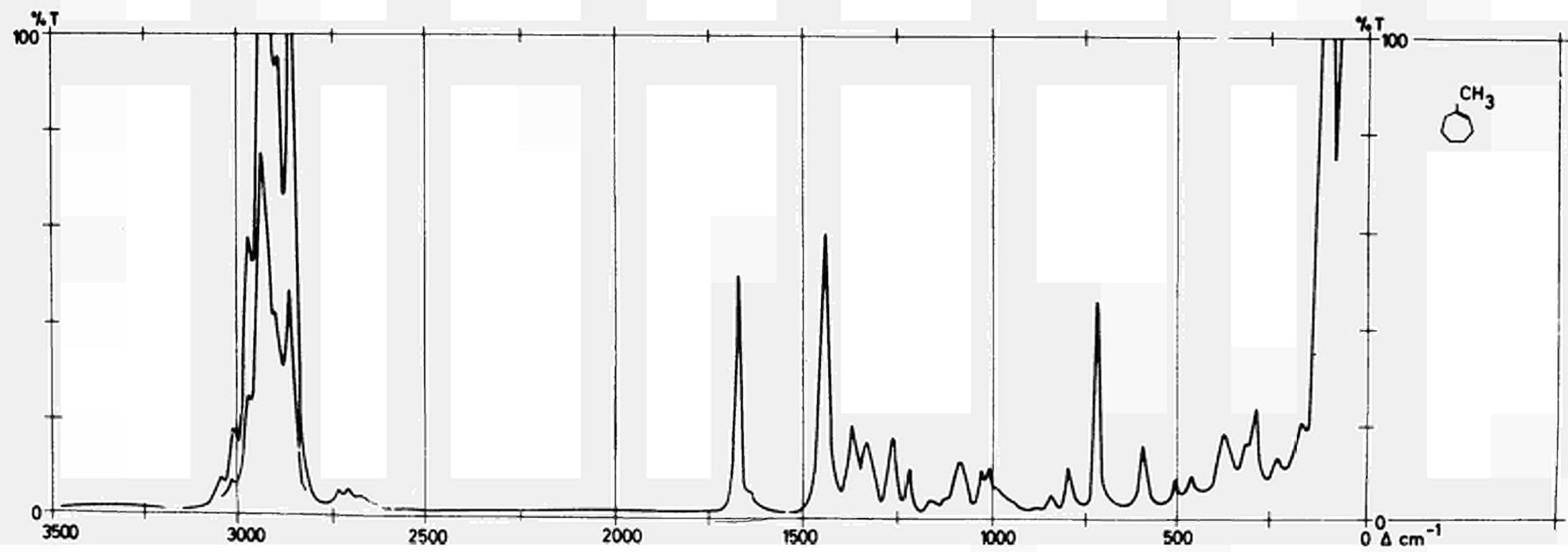
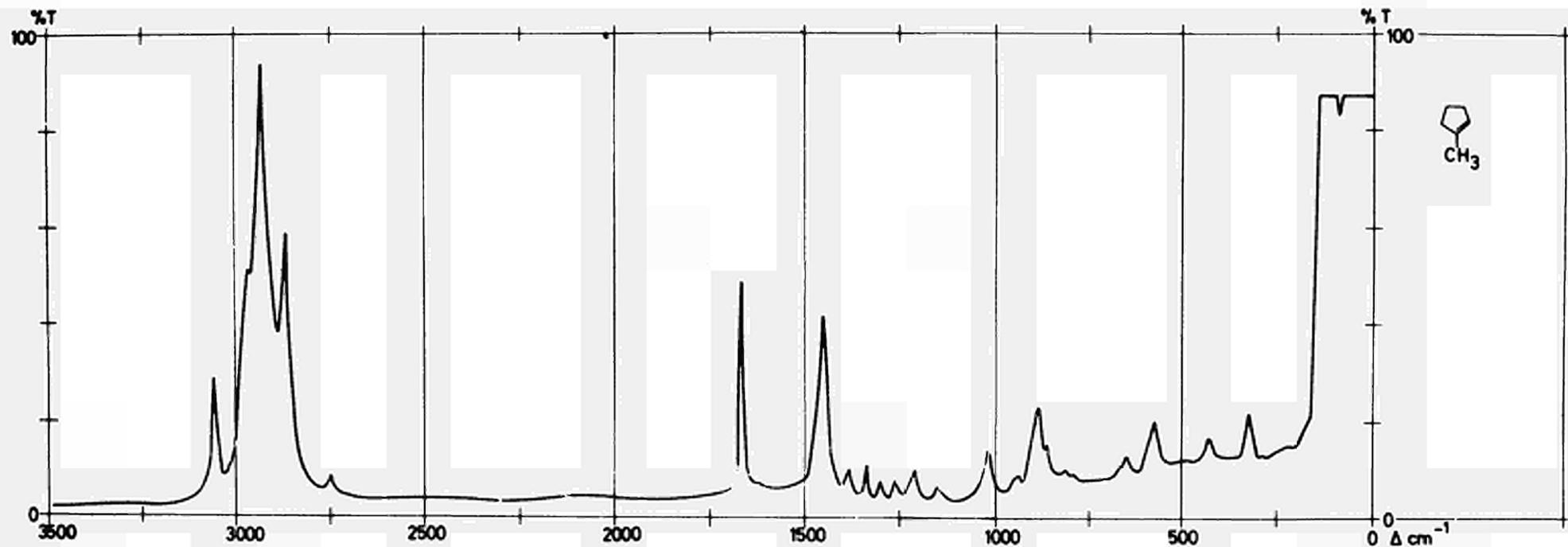


Fig. 5 - IR spectra of 1-methylcyclopentene and 1-methylcycloheptene

Fig. 7 - Raman spectra of 1-methylcyclopentene and 1-methylcycloheptene



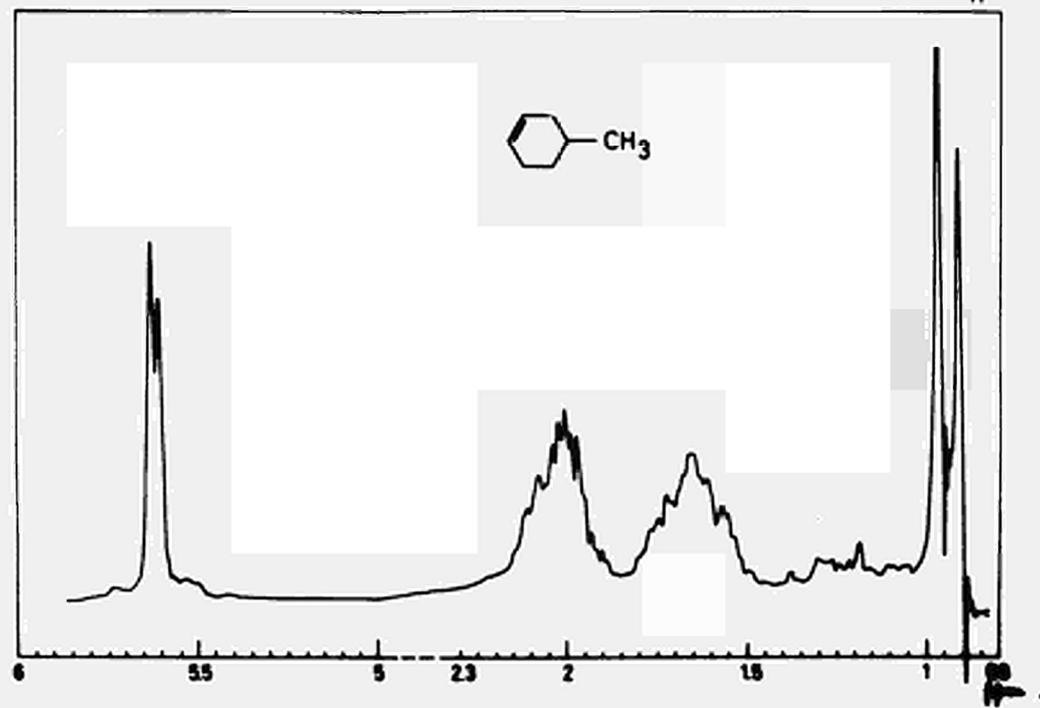
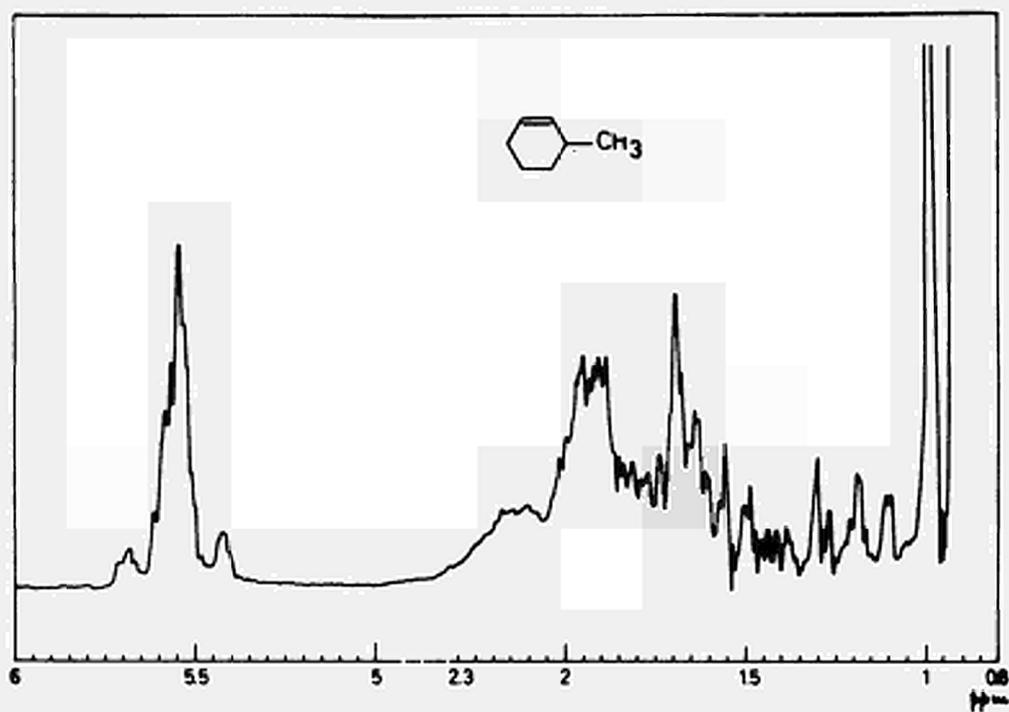
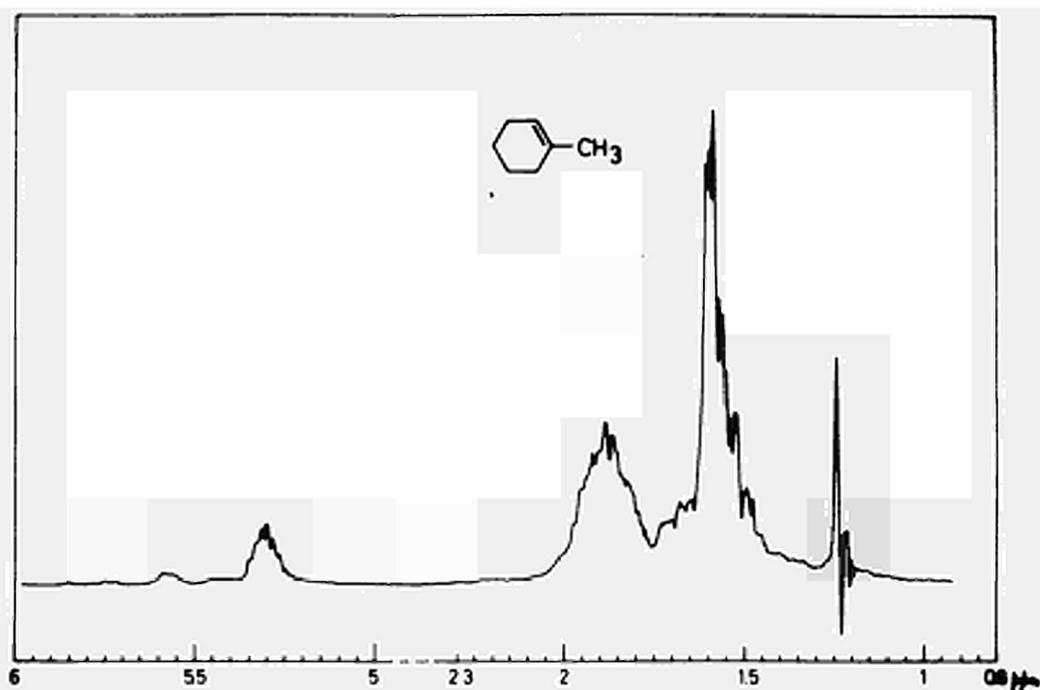


Fig. 8 - NMR spectra of methylcyclohexenes

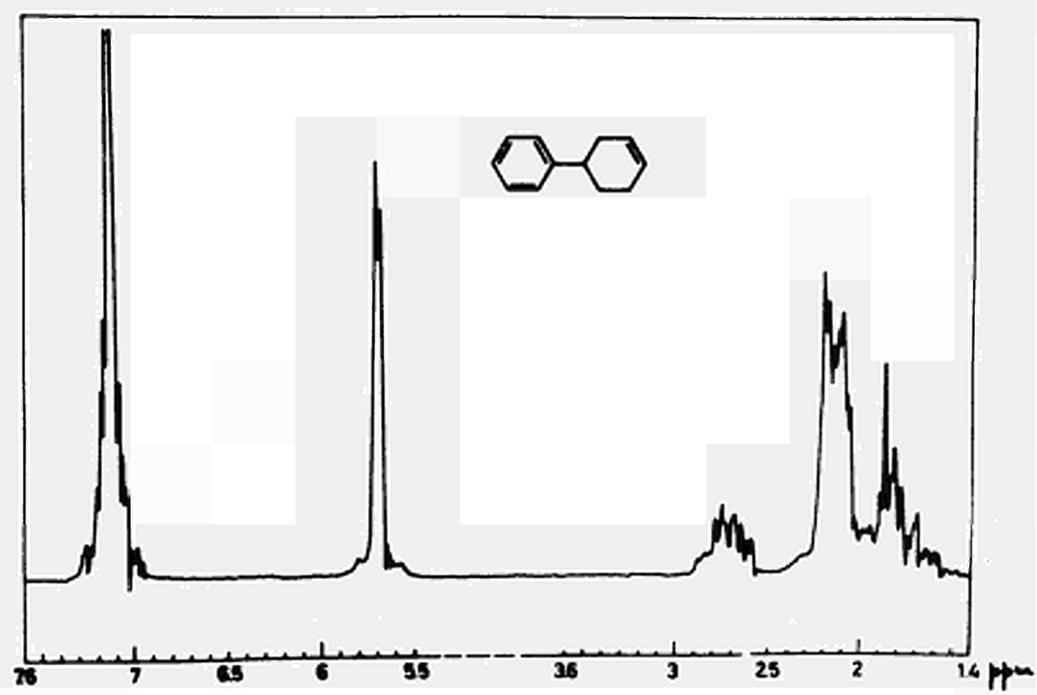
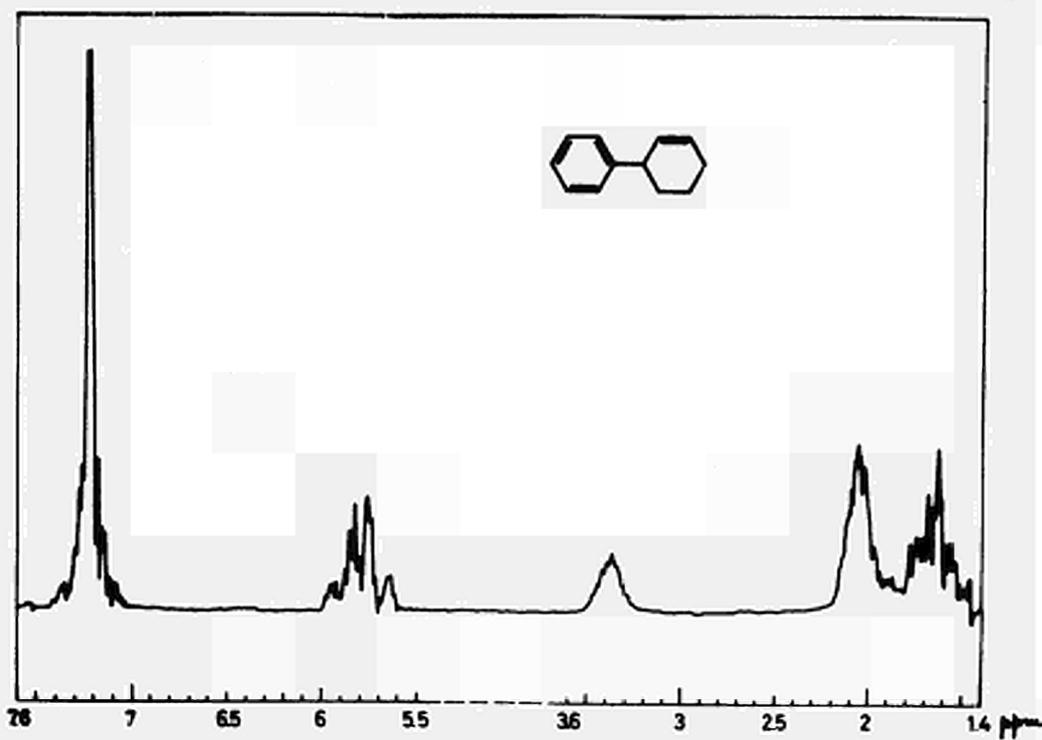
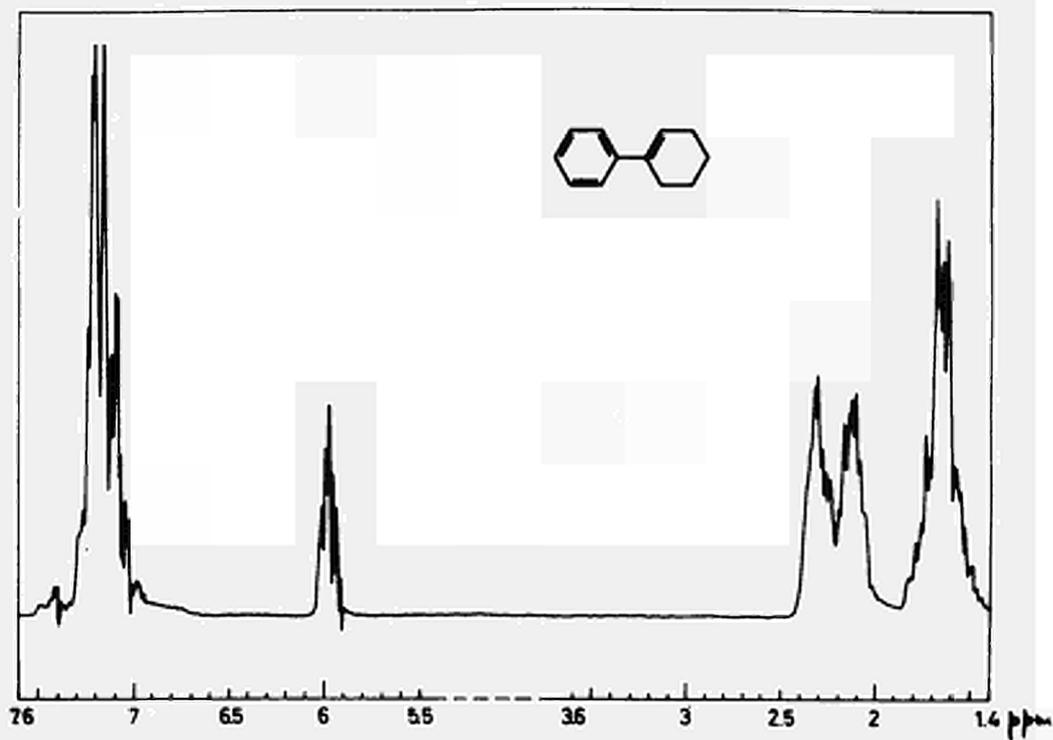


Fig. 9 - NMR spectra of phenylcyclohexenes

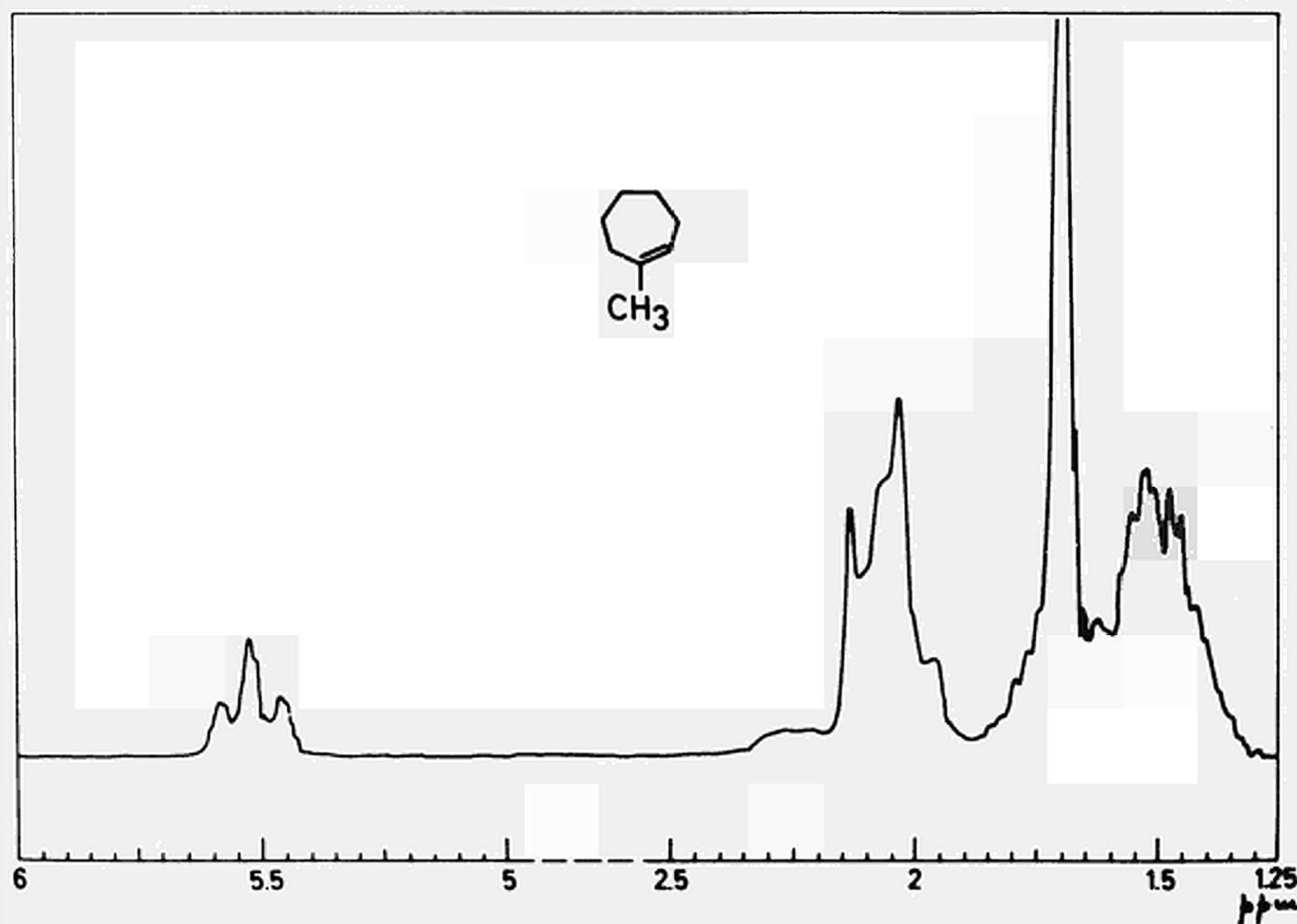
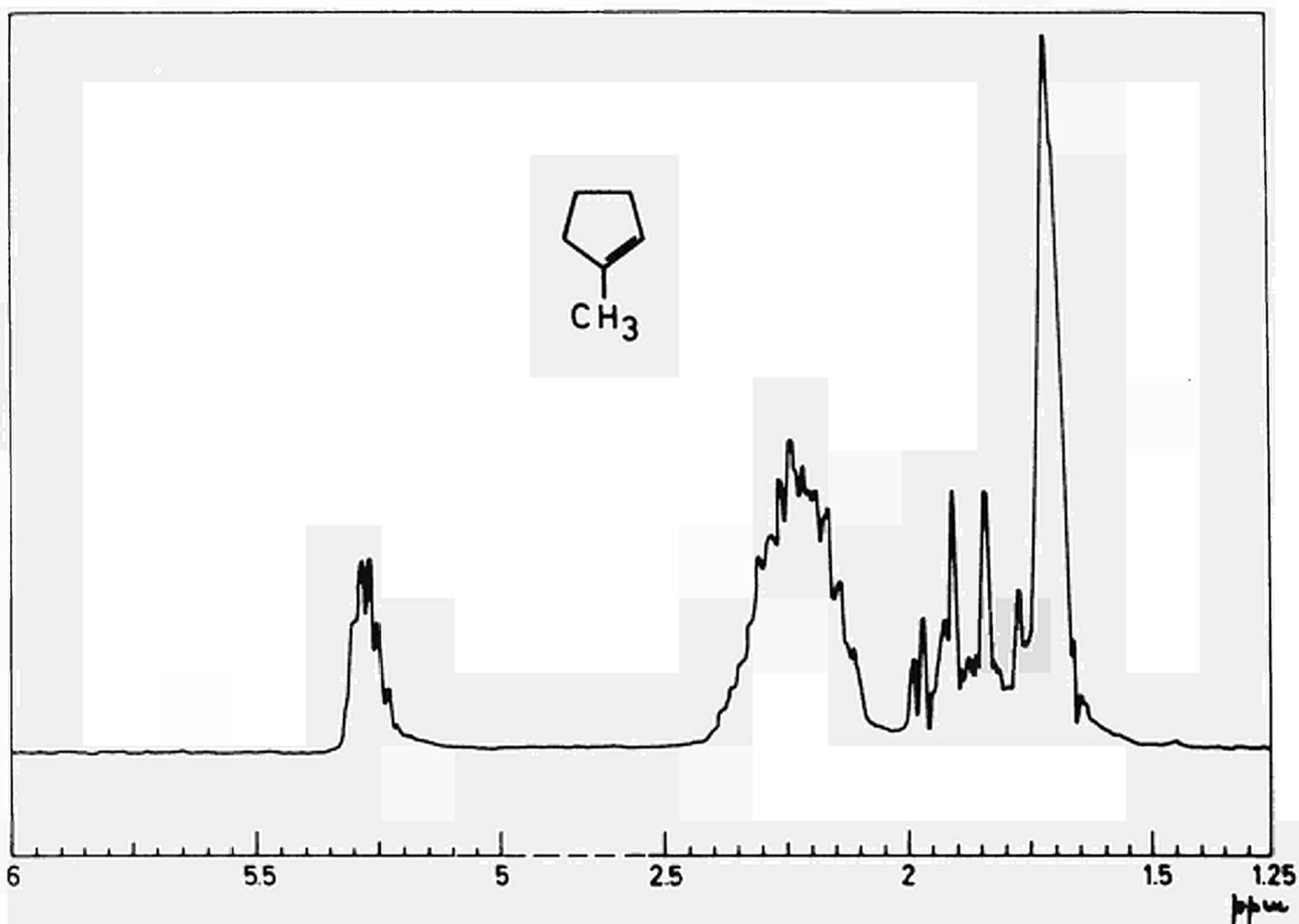


Fig. 10 - NMR spectra of 1-methylcyclopentene and 1-methylcycloheptene

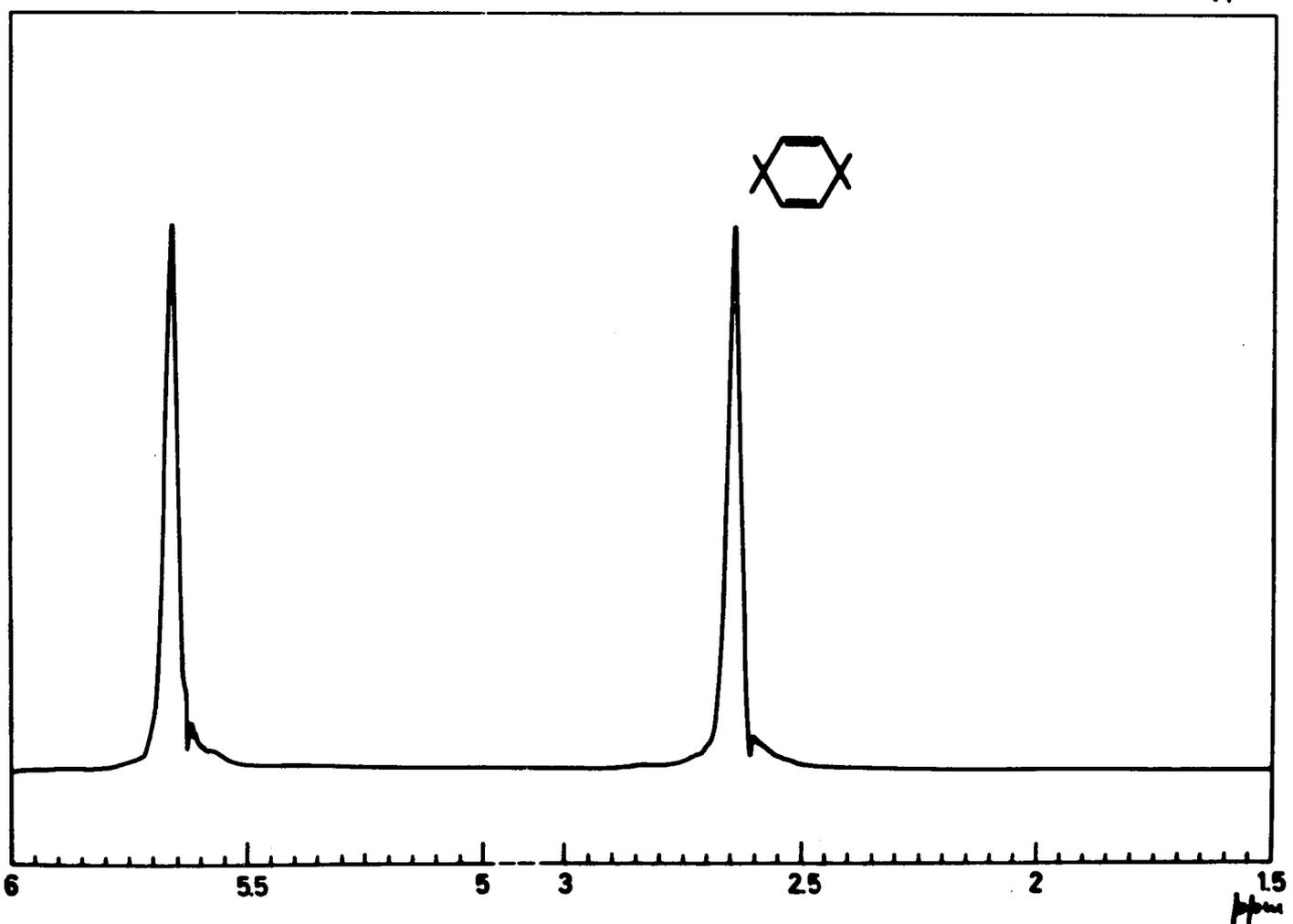
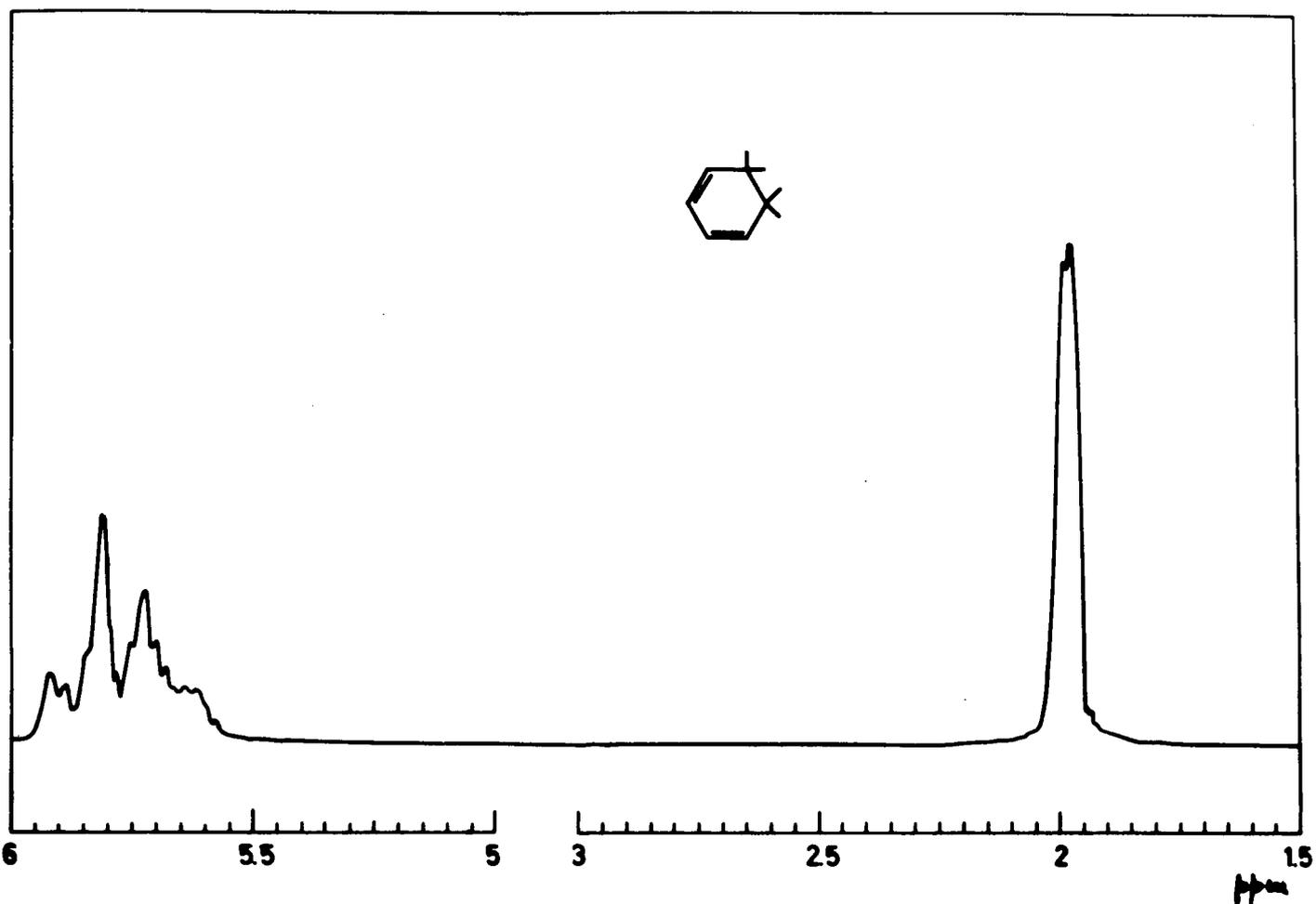


Fig. 11 - NMR spectra of 1,3- and 1,4-cyclohexadiene

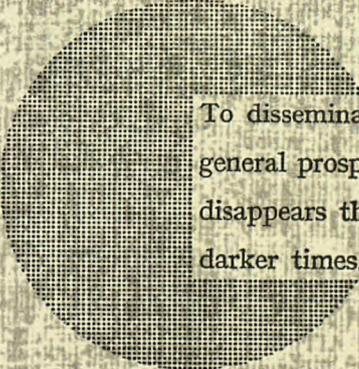
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Alfred Nobel

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