CHAPTER 4
UV/VIS SPECTROSCOPY

4.1 INTRODUCTION

UV/VIS Spectroscopy was another analytical technique used in the solid state mainly to prove the formation of the complexes. Any shifting of the bands would also be an indication of hydrogen bonding with in the complexes. An added use of this technique was to identify if charge transfer reactions were taking place, this is discussed later.

Before any details as to the theory behind UV and the results and discussion of the analysed complexes, it is important to note that in this study the results of UV are of relatively little importance if not combined with the results of infrared spectroscopy and NMR (Nuclear Magnetic Resonance) Spectroscopy. However, when combined, valid structural proposals can be made [1]. Hence the reason why the other chapters focus on both IR and NMR along with other useful structural determination techniques.

The principles of UV centre on the fact that molecules have the ability to absorb ultraviolet or visible light. This absorption corresponds to the excitation of outer electrons in the molecules concerned. It is these transitions of electrons which are important to understand.

When a molecule absorbs energy an electron is promoted from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO).

It must be noted that occupied molecular orbitals with the lowest energy are the σ orbitals, then at a slightly higher energy are the π orbitals and non-bonding orbitals (those with unshared pairs of electrons) at still a higher energy. The highest energy orbitals belong to π^* and σ^*, i.e. the unoccupied or as otherwise known as, the antibonding orbitals [1].

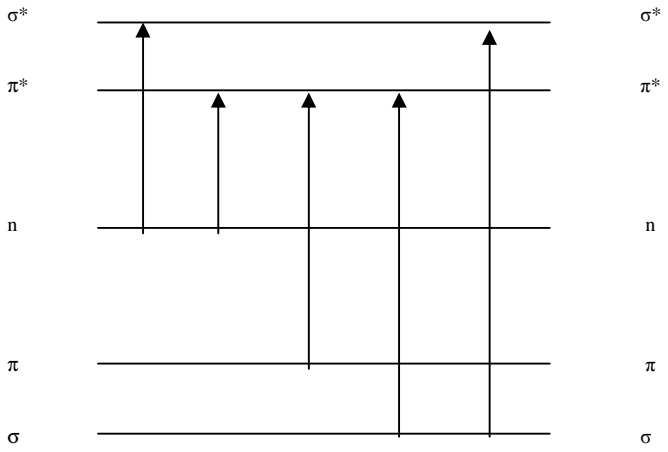

Fig. 4.1 Electronic energy levels and transitions [1]

4.2 INSTRUMENTATION

The actual instrument used to determine the ultra violet spectra of the complexes was the Milton Roy Spectronic GENESYS 5.

As with any UV/VIS spectrophotometer, three of the main elements are a UV-light source, a monochromator and a detector. The monochromator works as a diffraction grating to dispense the beam of light into the various wavelengths. The detectors role is to record the intensity of the light which has been transmitted [1].

Before the samples are run, a reference must first be taken. This calibrates the spectra to screen out ant spectral interference. In the case of liquid samples the solvent which has been used to dissolve the sample is used. However, there are certain criteria that solvents must pass before they can be deemed as suitable solvents. The main criterion is that the solvent should not absorb ultraviolet radiation in the same region as the sample being analysed [1].

In the case of solid-state UV/VIS spectroscopy the reference is normally KBr as the KBr does not absorb radiation in the same region as most complexes.

4.3 PREPARATION OF SAMPLE

The complexes that were analysed were in the solid state. A KBr reference pellet was first made by grinding up pure KBr in a pestle and mortar until a fine powder remained. This was then placed in a high pressure press and left for approximately 5 minutes at approximately 8 tons, until a thin, clear pellet was formed. The complexes were also pressed into pellets. A mixture of KBr and each complex were ground then pressed to form pellets.

4.4 CHARGE TRANSFER

As with Infrared and Raman spectroscopy, the absence of bands can at times provide as much, if not more information than the presence of bands.

Of particular relevance to the UV spectra of the synthesized complexes is the fact that only the expected bands are visible, i.e. there are no extra bands. An extra band would indicate a charge transfer state [2]. This takes place when n electrons are able to be excited to π^* orbitals. The aromatic ring gains an electron while the atom or molecule from which the n electron was removed loses an electron – becomes electron deficient [1].

4.5 UV OF AROMATIC COMPOUNDS

The electronic energy levels involved in aromatic compounds are of the type, $\pi \longrightarrow \pi^*$. Due to electron – electron repulsions and symmetry operations, three electronic transitions take place to these excited states. In the liquid state, bands at 184 nm and 202 nm are known as primary bands while a band at 253 nm is known as a secondary band [1]. Benzene exhibits two intense absorption bands at 180 nm and 200 nm and a weak absorption band at 260 nm, all of which are linked with the π-system of the benzene ring.

The bands at 180 nm and 200 nm can be ascribed to transitions to dipolar excited states, while the band at 260 nm is ascribed as the forbidden transition to a homonuclear excited state.

Different nomenclatures are used to describe these three bands, i.e. the 180 nm band is also known as $A_{1g} \longrightarrow E_{1u}$, while the 200 nm band as $A_{1g} \longrightarrow B_{1u}$ an the 260 nm band as $A_{1g} \longrightarrow B_{2u}$.

However, the 180 nm band is beyond the range of most instruments and therefore for the remainder of this chapter the words primary and secondary will be used to describe the bands at 200 nm and 260 nm respectively [3].

The 184 nm band as it is beyond the range of most instruments and so what is generally seen are the primary and secondary bands at 202 nm and 253 nm respectively.

When substituents are added to the ring system other possible energy level transitions must be considered. These are of the type $n \longrightarrow \pi^*$, however, these particular bands are hidden by the secondary benzene band at 253 nm. Another feature of adding substituents to benzene is that the bands shift to larger wavelengths depending on the nature of the substituents, i.e. their electron donating or withdrawing nature [1].

An example of this is when COOH (electron withdrawing group) is added to a benzene ring to form benzoic acid. A noticeable bathochromic or red shift of both the primary and secondary bands is clearly seen [1, 3, 4].

SPECTRA OF BENZENE AND BENZOIC ACID

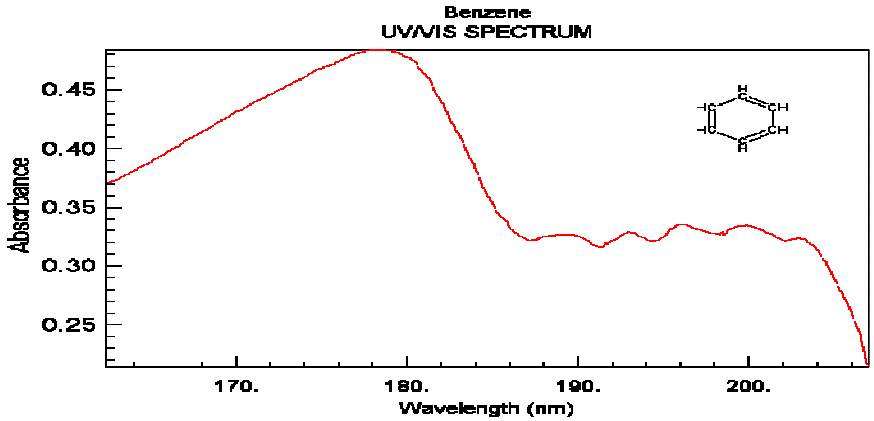

Fig. 4.2 UV Spectrum of benzene [5]

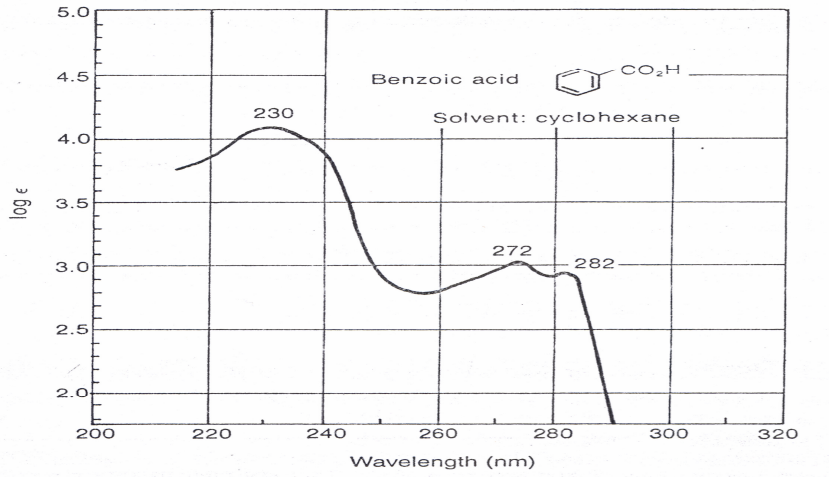

Fig. 4.3 UV Spectrum of benzoic acid [1]

Also of particular interest to the complexes that were synthesized are the literature values for the shifts present in chloro, nitro, amino and hydroxy benzoic acids. All show marked shifts of the primary and secondary bands relative to benzoic acid which are shown in Table 4.1.

SUBSTITUENT ON BENZOIC ACID	**PARA-DERIVATIVES**	**META-DERIVATIVES**		**ORTHO-DERIVATIVES**	
	WAVELENGTHS ABSORBED (nm)				
		200 nm	**260 nm**	**200 nm**	**260 nm**
Cl	241	231.5	283	229	280
NO_2	264.5	_	_	_	_
NH_2	284	250	310	248	327
OH	255	236.5	296	237	302

Table 4.1 [3] Literature values for wavelengths absorbed, indicating the shifting of the primary and secondary bands

The values listed in Table 4.1 refer to data obtained for the wavelengths absorbed for the benzoic acids (non-complexed) in solution. These values differ from

the results obtained in this study, mainly due to the fact that the data for these complexes was obtained in the solid state.

4.6 SOLVENT EFFECTS

The shifting of peaks that is caused by the effects of particular solvents is most prominent when in the case of benzene, the added substituents are polar, e.g. OH group. Notable shifting can also take place due to solute – solvent hydrogen bonding[1].

Although the complexes that were synthesized were analysed in the solid state and hence no solvents effects were involved, the general shifts and trends are similar to those that occur in the liquid state. Yet it is important to remember that solid and liquid state values will most certainly be different in terms of the specific amounts of shifting that complexes undergo due to the added substituent.

4.7 DISUBSTITUTED BENZENE DERIVATIVES

Depending on the electronic nature of the substituents and their positioning relative to each other on the benzene ring, the degree of shifting differs. i.e. in multi-substituted benzene derivatives the position of the electronic transitions depends on the relative position of the substituents on the ring [4].

If both the substituted groups are electron withdrawing in nature and are para to each other (4-nitro complex), the primary band will shift to an approximate value of 268 nm while the secondary band will remain unshifted.

If both substituents are para to each other but one group is electron withdrawing while the other is donating (all the other para complexes), then the shift of the primary band is greater than the sum of the shift brought about by the individual groups.

The final permutation which incorporates the remainder of the complexes is if both groups are ortho or meta to each other. In this case the shift of the primary band is equal to the sum of the shifts of the individual groups [1].

4.8 UV SPECTRA OBTAINED FROM COMPLEXES

All the complexes show a bathochromic or red shift of the two expected bands – the primary and secondary bands and are shown in Figs. 4.4 – 4.22.

The primary band has shifted to with in the range of 223 nm - 253 nm and the secondary band has shifted to with in the range of 274 nm - 307 nm . The shifts that are seen in the solid state are slightly different to those quoted in the literature for the liquid state.

All complexes analysed were found to be closely related in terms of the degree of shifting. This is further proof of the isostructural nature of the complexes.

The absorbance values of the peaks in all the complexes are also relatively similar. However, the 3-nitro and 3-bromo complexes show a noticeable hyperchromic effect and the 2-chloro and benzoate complexes show a definite hypochromic effect relative to the other complexes.This is most likely due to the fact that absorbance unlike wavelength is related to the concentration of sample analysed.

4.9 CONCLUSION

Prominent shifting of the bands are observed in all the complexes synthesized, relative to the bands observed for uncomplexed benzoic acids. However, the shifting may also, in part, be due to the presence of hydrogen bonding which from the results of the other analytical techniques is known to exist with in the complexes. As there are no extra bands present in the spectra, one can rule out the possibility that charge transfer reactions are occurring.

Thus,

- Substitution was confirmed on the ortho, meta and para positions.
- No clear trend could be observed reflecting the electronic characteristics of substitution, i.e. electron donating or electron withdrawing properties.
- Complexation of benzoic acids shows clear bathochromic shifts for both primary and secondary bands, for all complexes in this study.

4.10 REFERENCES

CHAPTER 4

1. D. L. Pavia, G. M. Lampman, G. S. Kritz, Introduction to Spectroscopy, A guide for students of organic chemistry, 2nd ed., 267-293
2. C. N. R. Rao, Ultraviolet and Visible Spectroscopy, 2nd ed., Butterworths, London, 1967, Chapter 11
3. C. N. R. Rao, Ultraviolet and Visible Spectroscopy, 2nd ed., Butterworths, London, 1967, Chapter 5
4. Prof. Dr. H-H Perkampus, Benzene and Benzene Derivatives-Introduction Institute of Physical Chemistry, Dusseldorf University, pages 2-6
5. www.wooster.edu/chemistry/is/brubaker/uv/uv_spectrum

4.11 WAVELENGTH AND ABSORBANCE AS WELL AS SPECTRA OF ALL THE COMPLEXES

COMPLEX	WAVELENGTH (nm)		ABSORBANCE (log ε)	
2-amino	244	280	1.907	1.737
3-amino	238	277	2.128	1.945
4-amino	247	298	2.290	2.044
2-nitro	250	298	2.666	2.523
3-nitro	244	307	3.391	3.502
4-nitro	250	298	2.405	2.348
2-fluoro	250	298	2.430	2.226
3-fluoro	247	295	2.697	2.781
4-fluoro	250	298	2.084	1.962
2-bromo	247	277	2.140	1.874
3-bromo	244	301	3.389	3.499
4-bromo	250	298	2.750	2.710
2-chloro	223	298	1.725	1.270
3-chloro	250	298	2.841	2.834
4-chloro	247	295	2.436	2.102
2-methyl	250	295	2.776	2.560
3-methyl	247	298	2.654	2.596
4-methyl	247	298	2.403	2.445
4-methoxy	250	298	2.604	2.482
2-hydroxy	253	298	2.809	2.463
Benzoate	238	274	1.725	1.574

Table 4.2 Wavelength and absorbance value for the complexes

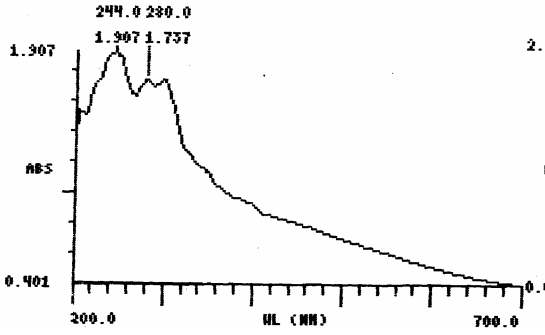

Fig. 4.4 UV spectrum of the 2-amino complex

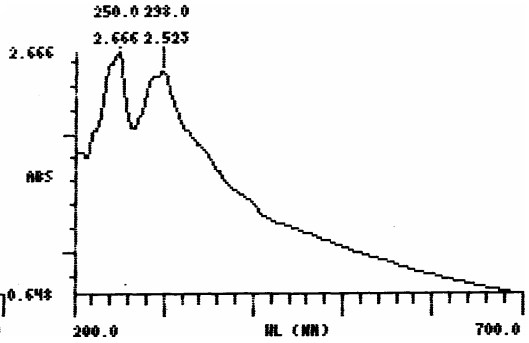

Fig. 4.7 UV spectrum of the 2-nitro complex

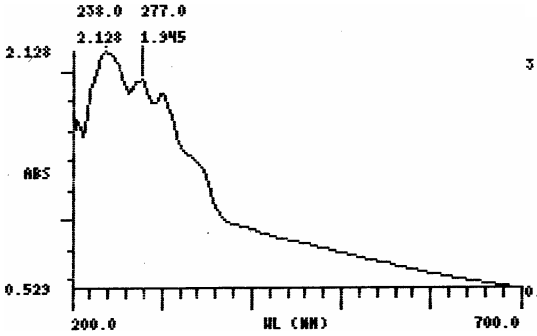

Fig. 4.5 UV spectrum of the 3-amino complex

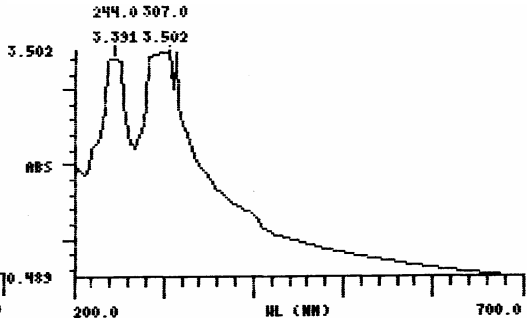

Fig. 4.8 UV spectrum of the 3-nitro complex

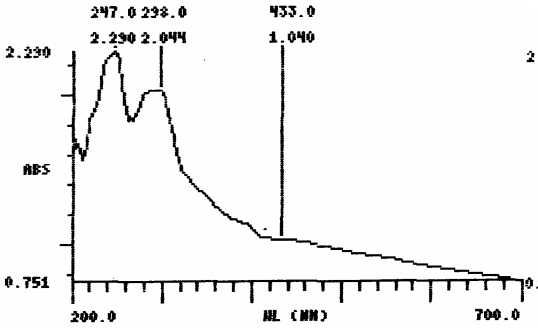

Fig. 4.6 UV spectum of the 4-amino complex

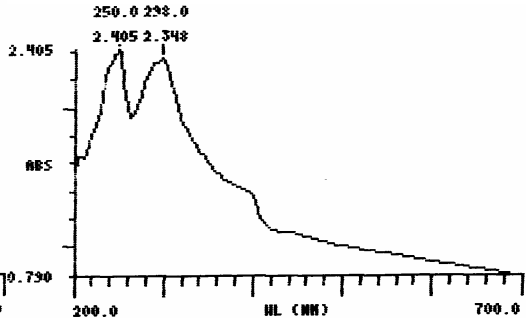

Fig. 4.9 UV spectrum of the 4-nitro complex

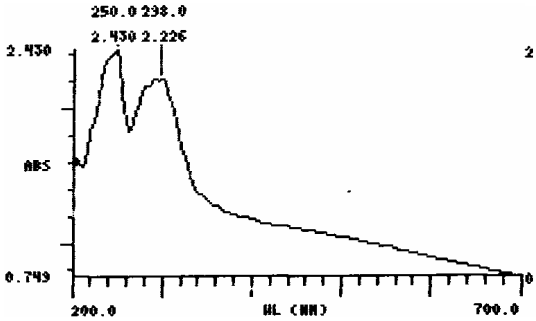

Fig. 4.10 UV spectrum of the 2-fluoro complex

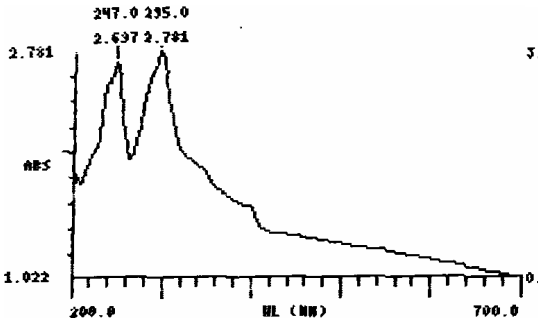

Fig. 4.11 UV spectrum of the 3-fluoro complex

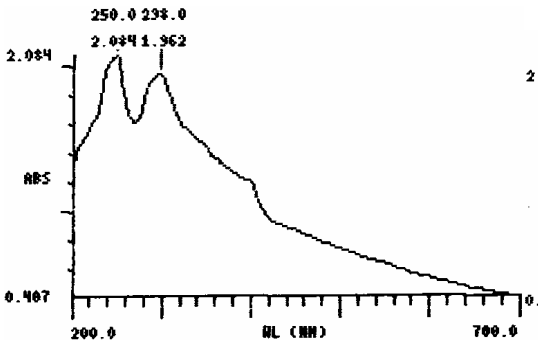

Fig. 4.12 UV spectrum of the 4-fluoro complex

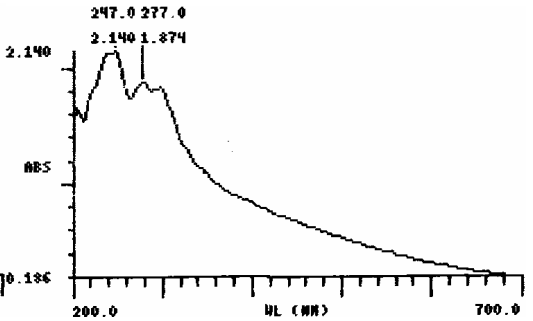

Fig. 4.13 UV spectrum of the 2-bromo complex

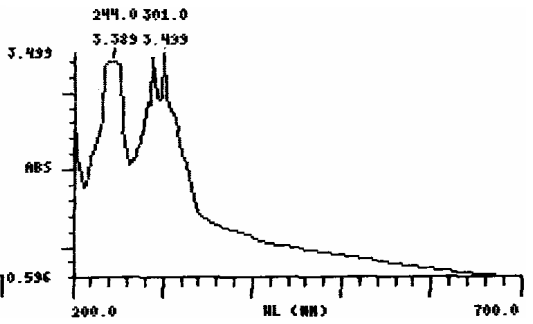

Fig. 4.14 UV spectrum of the 3-bromo complex

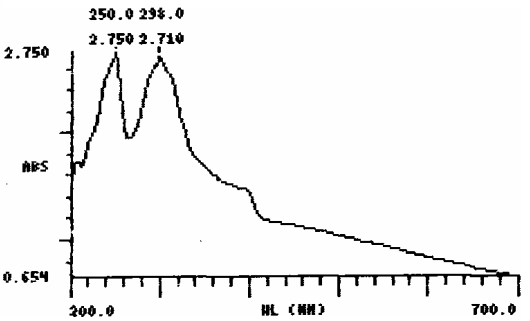

Fig. 4.15 UV spectrum of the 4-bromo complex

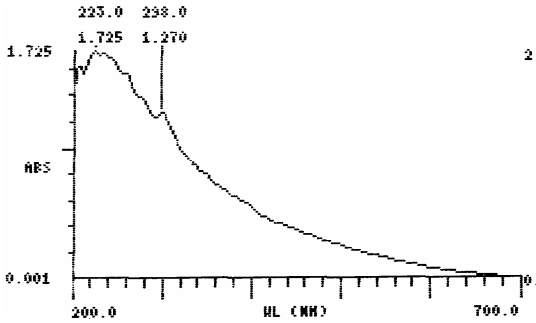

Fig. 4.16 UV spectrum of the 2-chloro complex

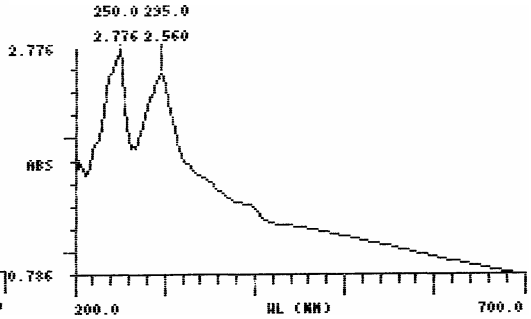

Fig. 4.19 UV spectrum of the 2-methyl complex

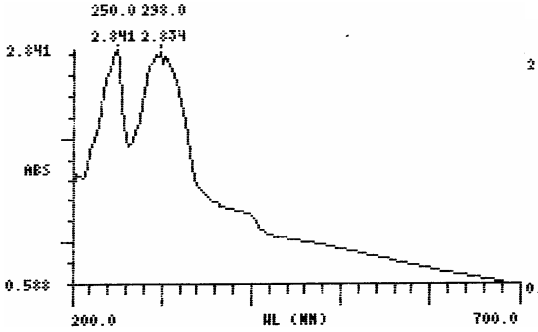

Fig. 4.17 UV spectrum of the 3-chloro complex

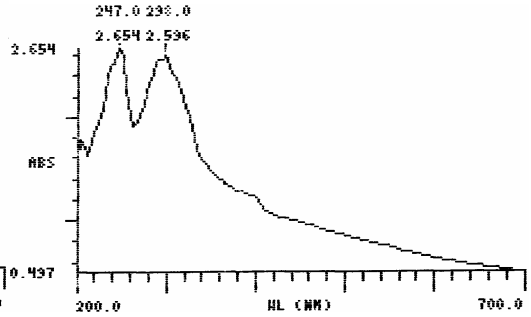

Fig. 4.20 UV spectrum of the 3-methyl complex

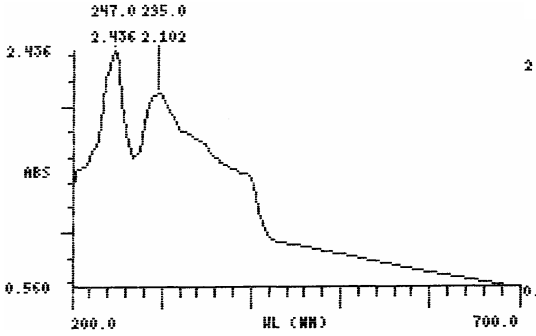

Fig. 4.18 UV spectrum of the 4-chloro complex

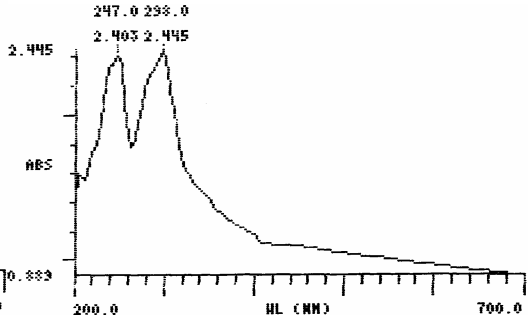

Fig. 4.21 UV spectrum of the 4-methyl complex

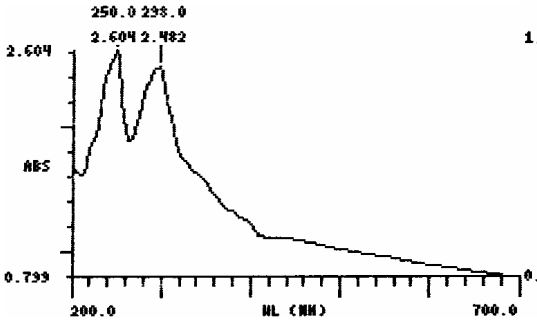

Fig. 4.22 UV spectrum of the 4-methoxy complex

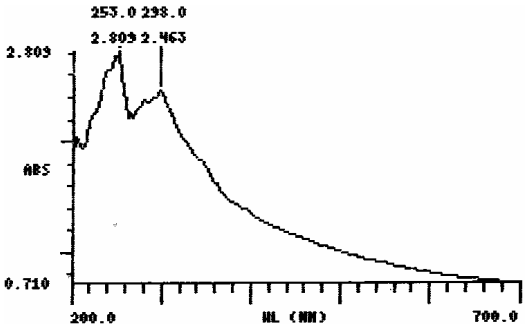

Fig. 4.23 UV spectrum of the 2-hydroxy complex

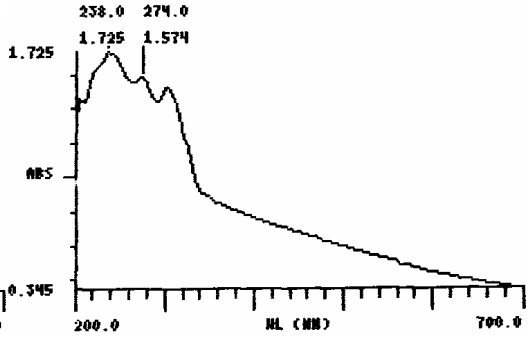

Fig. 4.24 UV spectrum of the benzoate complex