

## Preparation and Spectroscopic Study of Some Schiff – Bases Derived from 4-Amino phenazone and Some Aromatic Aldehydes.

Hassan A. Habeeb

*Dept. of Chemistry, College of Education  
University of Al-Qadisiya*

Falah H. Hussein\*

*Dept. of Chemistry, College of Science,  
University of Babylon*

and

Sami W. Radi

*Dept. of Chemistry, College of Science  
University of Kufa*

### Abstract

The work consists of preparation and study of some Schiff-bases derived from primary heterocyclic amine: 4-amino phenazone and the aromatic aldehydes: benzaldehyde, 3-aminobenzaldehyde, 4-N-N-dimethyl amino benzaldehyde and 3,4-dihydroxy benzaldehyde using refluxing method in absolute ethanol. The prepared bases have been characterized by FT-IR, electronic and fluorescence spectra. Some of spectral properties have been concluded. Some of physical and chemical properties have been measured. The purity of bases was checked using TLC.

### الخلاصة

يتضمن البحث تحضير ودراسة مجموعة من قواعد شيف المشتقة من الامين الاولي 4-امينوفينازون و 4,3-داي هيدروكسي بنزالدهيد بواسطة طريقة التصعيد في الايثانول المطلق. شخّصت قواعد شيف المحضرة بواسطة مطيافية FT-IR سجلت كذلك اطيافها الالكترونية واطياف الفلورة، وتم دراسة بعض الخواص الفيزيائية والكيميائية للمركبات المحضرة.

### Introduction

Schiff bases draw much attention through the last decade<sup>(1-6)</sup>, since these bases have the character of formation in huge variance of structural environment. So the use of Schiff bases is connected with organic source. In general, the important application of those bases concentrates in several fields: azomethine are use in catalysis of polymerization reactions<sup>(7)</sup>. Some of the bases, which are derived from salicyldehyde, have biological activity against bacteria and Fungi<sup>(8)</sup>. Some of complexes of azomethine with copper are use in inks and dyes industry<sup>(9)</sup>. Bases derived from benzyliden aniline (para sub.) characterize with photoconductivity<sup>(10)</sup>, polymers prepared from Schiff-bases have superconductivity<sup>(11)</sup>, and virtue of stopped pain, anti of light and oxidation<sup>(12,13)</sup>.

The condensation reaction of equimolar quantity of primary amine with appropriate aromatic aldehydes was the major method to prepare of the Schiff-bases<sup>(4,14-17)</sup>.

Schiff-bases have the ability of coordination with transition metal ions to prepare of stable-complexes of cobalt(II) with bi and tri-dentate Schiff-bases<sup>(3)</sup>, tin(IV) with bi-dentate Schiff-bases ligands<sup>(1,2)</sup>, and ferrous(III), chromium (III), cerium (III), nickel (II) and copper (II) with bi dentate Schiff-bases<sup>(18)</sup>.

\* Author to whom all correspondence should be addressed.

The aim of the present work is to prepare and investigate of some Schiff-bases by refluxing-condensation reaction of equimolar of primary amine: 4-amino phenazone with some of aromatic aldehydes.

### Experimental

All chemicals utilized in this work were reagent grade, and were used as received. Absolute ethanol, methanol and benzaldehyde were supplied from BDH, 3-amino benzaldehyde, 4-N, N-dimethyl benzaldehyde were supplied by Fluka AG, 3,4-dihydroxy benzaldehyde was obtained from Riedel de Hâen.

### Schiff-bases preparation

Schiff-bases were prepared according condensation reaction mentioned in literatures<sup>(6,15,19,20)</sup>, by mixing equimolar amount of 4-amino phenazone with appropriate aromatic aldehydes (0.03mol) in 30 ml of absolute ethanol and refluxing for 3 hours. The crystallized Schiff-base was separated by filtration from cold solution, then washed with petrolum ether for several times to remove the remained amine, then recrystallized from hot methanol and dried at 70°C for 2 hours.

### Spectral studies

FT-IR Spectra of bases were recorded using Perkin Elmer FT-IR spectrophotometer at a range of 500-4000  $\text{cm}^{-1}$  by using KBr disc. UV-visible absorption spectra have been recorded using Shemadzu-UV 160 spectrophotometer, and Fluorescence spectra were obtained by using Jewan model 6200 Fluorimeter. Rf values of bases were measured on silica gel plates by using thin layer chromatography. The eluent used was (benzene: methanol 8:2) v:v.

### Results and Discussion

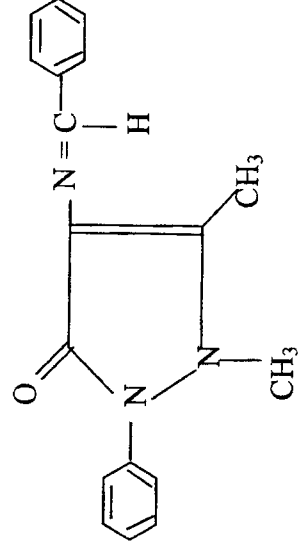
The refluxing method used in this work is considered as a sufficient and simple method to prepare Schiff-bases derivatives. Table(1) listed the physical and chemical properties of prepared bases. Scheme(1) shows the structural formula of derivatives:

**Table(1): Physical and chemical properties of Schiff-bases**

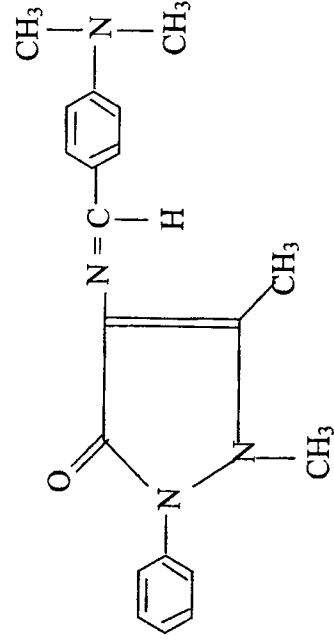
No.	Base	Molecular formula	M. Wt (gm. mol <sup>-1</sup> )	Color	Yield %	R <sub>f</sub>
1	BP	C <sub>18</sub> H <sub>17</sub> N <sub>3</sub> O	291	Brown	96.2	0.751
2	3.ABP	C <sub>18</sub> H <sub>18</sub> N <sub>4</sub> O	306	Yellow	98.5	0.824
3	4-N,N,DMBP	C <sub>20</sub> H <sub>22</sub> N <sub>4</sub> O	334	Yellow	96.5	0.781
4	3,4-DHBP	C <sub>18</sub> H <sub>19</sub> N <sub>5</sub> O	321	Yellow	96.8	0.713

**Table(2): Spectral Properties of bases**

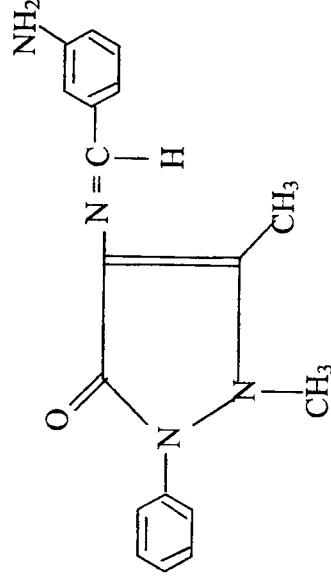
No.	Base	$\lambda_{\text{max}}$ , nm Absorption	$\lambda_{\text{max}}$ , nm Emission	E l.mol <sup>-1</sup> .Cm <sup>-1</sup> .	C=N Stretching Cm <sup>-1</sup>
1	BP	405	467	24440	1604
2	3.ABP	422	480	24520	1610
3	4-N,N,DMBP	394	400	23460	1609
4	3,4-DHBP	413	610	24510	1600



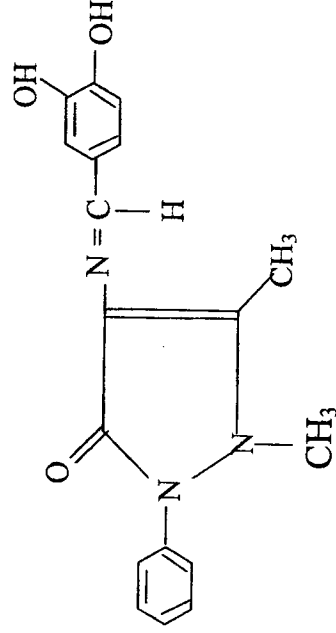
**benzaldene-Phenazone (BD)**



**4-N,N-dimethyl benzaldene-Phenazone (4-N,N-DMBP)**



**3-amino benzaldene-Phenazone (3-ABP)**

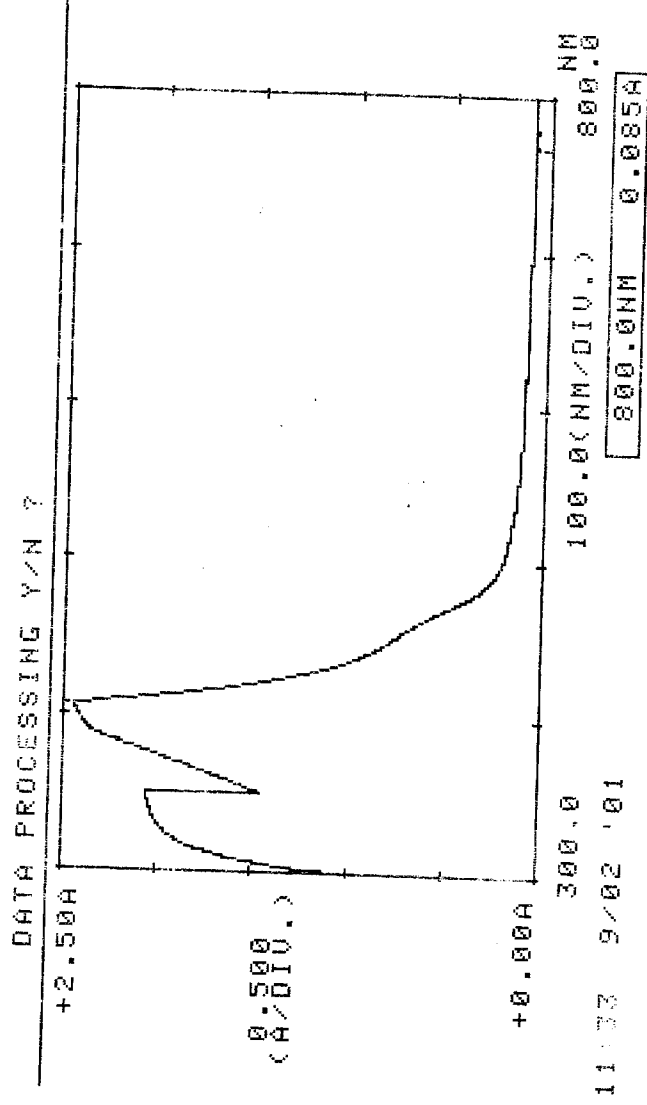


**3,4-dihydroxy benzaldene Phenazone. (3,4-DMBP)**

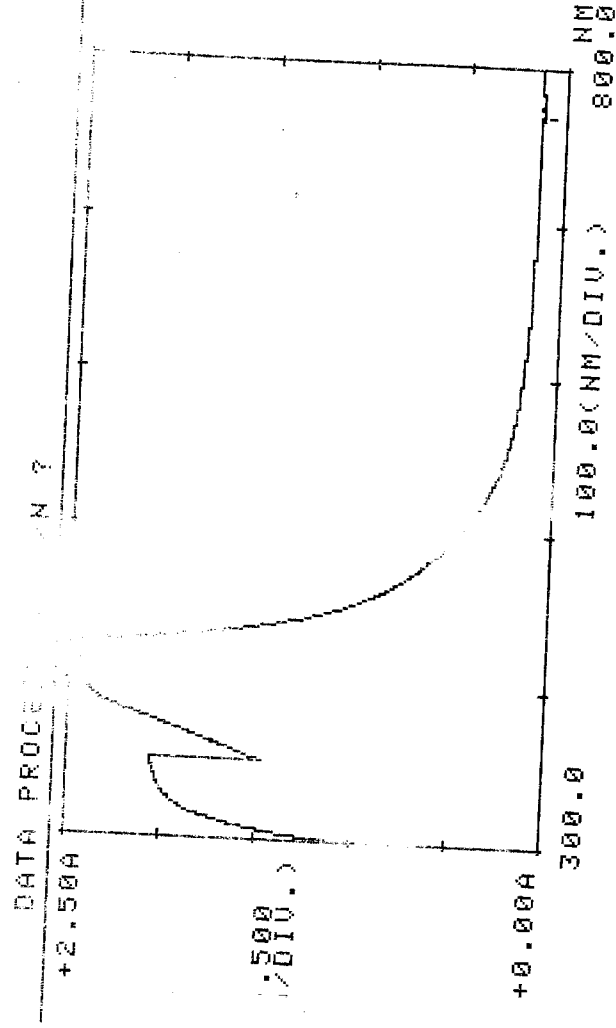
**Scheme (1)**  
*Structural formula of Schiff-bases.*

Figures(1), (2), (3) and (4) show the electronic spectra of the Schiff-bases. It is clear that the absorption spectra of these bases are similar to each other, but there is difference in values of  $\lambda_{\max}$  as a result of structural difference of bases. Absorption maximum ( $\lambda_{\max}$ ) of Schiff-bases in the range above 390 nm attributed to  $n-\pi^*$  electronic transition of imine group, but the other  $\lambda_{\max}$  is due to  $\pi-\pi^*$  transition in aromatic system and C=N group<sup>(1,2)</sup>. The high values of molar absorption coefficient indicate to good absorptivity of bases in UV-visible region.

FT-IR spectra of derivatives using KBr disc are showed in figures(5), (6), (7) and (8), the band appear in the region 1600-1610  $\text{cm}^{-1}$  is due to stretching of C=N group. The beak appear at 3444 in Fig(5) and 3308 in Fig(7) are due to shoulder of impurity of unreacted amine.



**Fig. (1): Electronic Spectrum of 3-ABP.**



**Fig. (2): Electronic Spectrum of BD.**

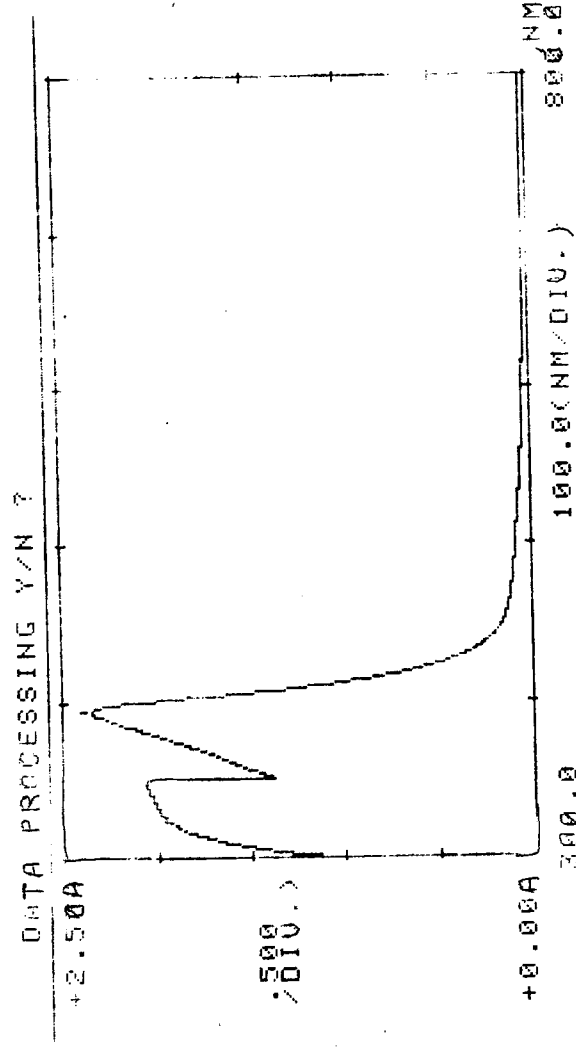


Fig. (3): Electronic Spectrum of 4-N,N-DMBP.

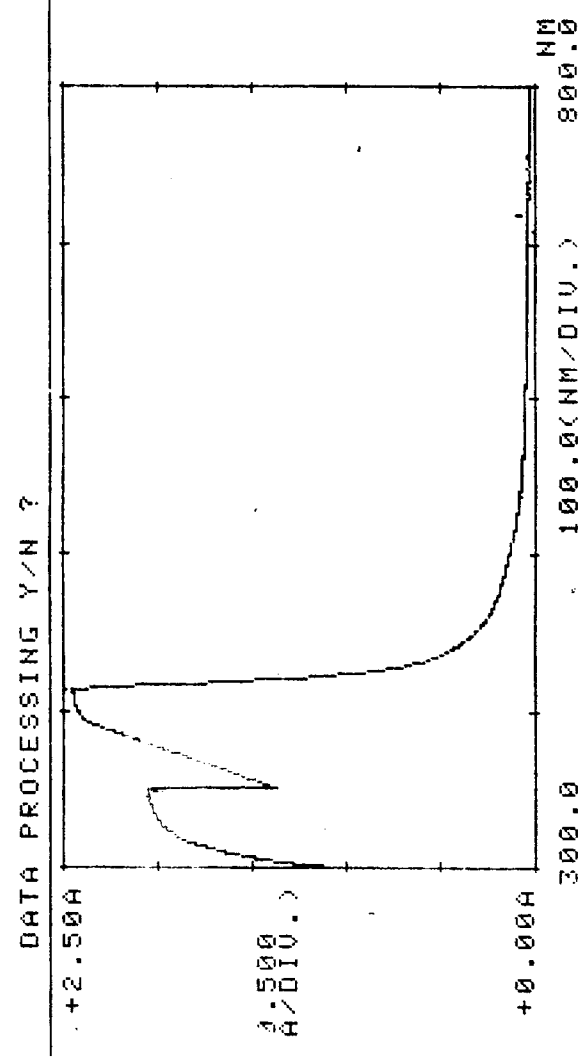


Fig. (4): Electronic Spectrum of 3,4-DMBP.

\*Thu Apr 20 12:48:16 2000,t61

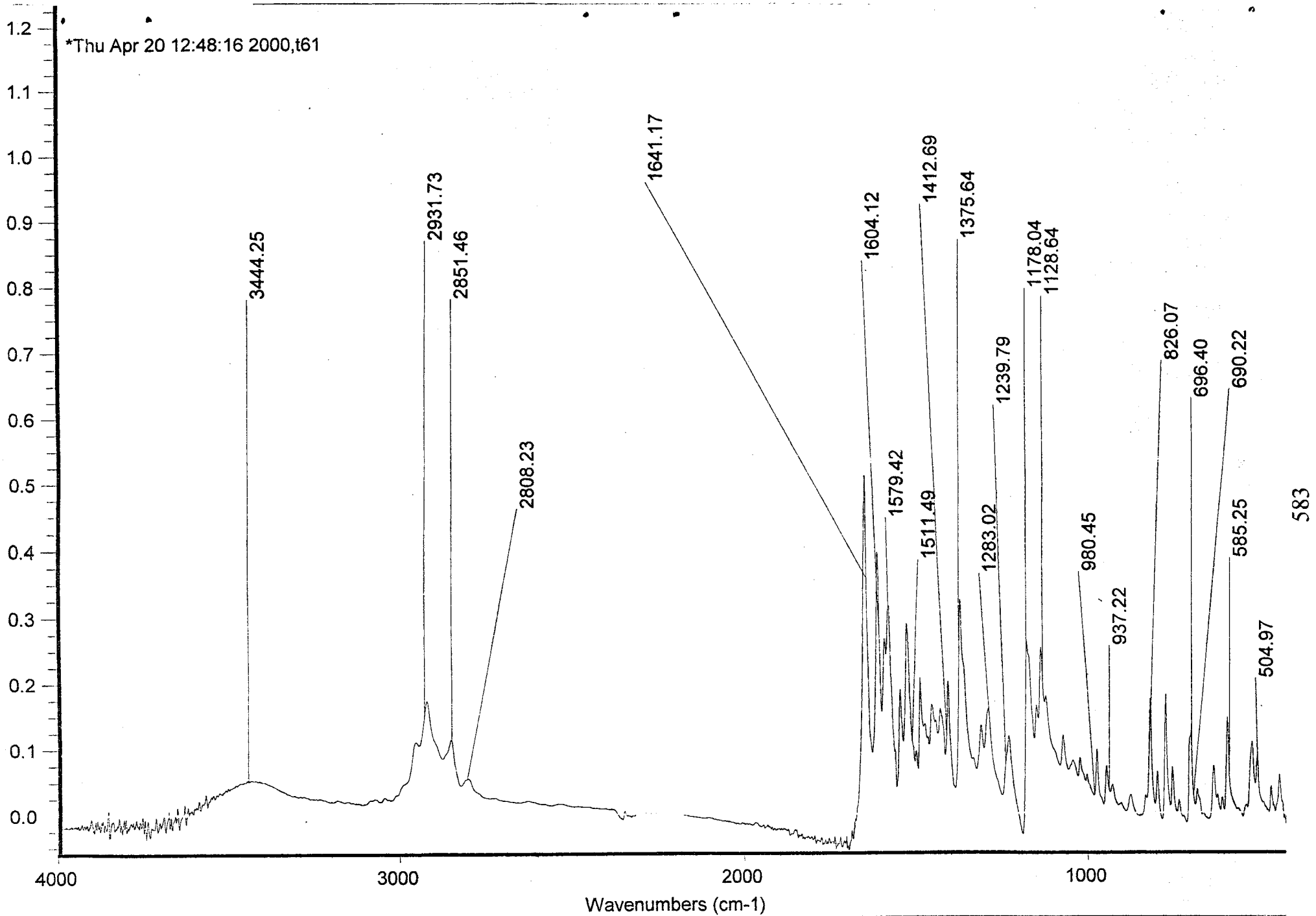


Fig.(5): FT-IR Spectrum of BP.

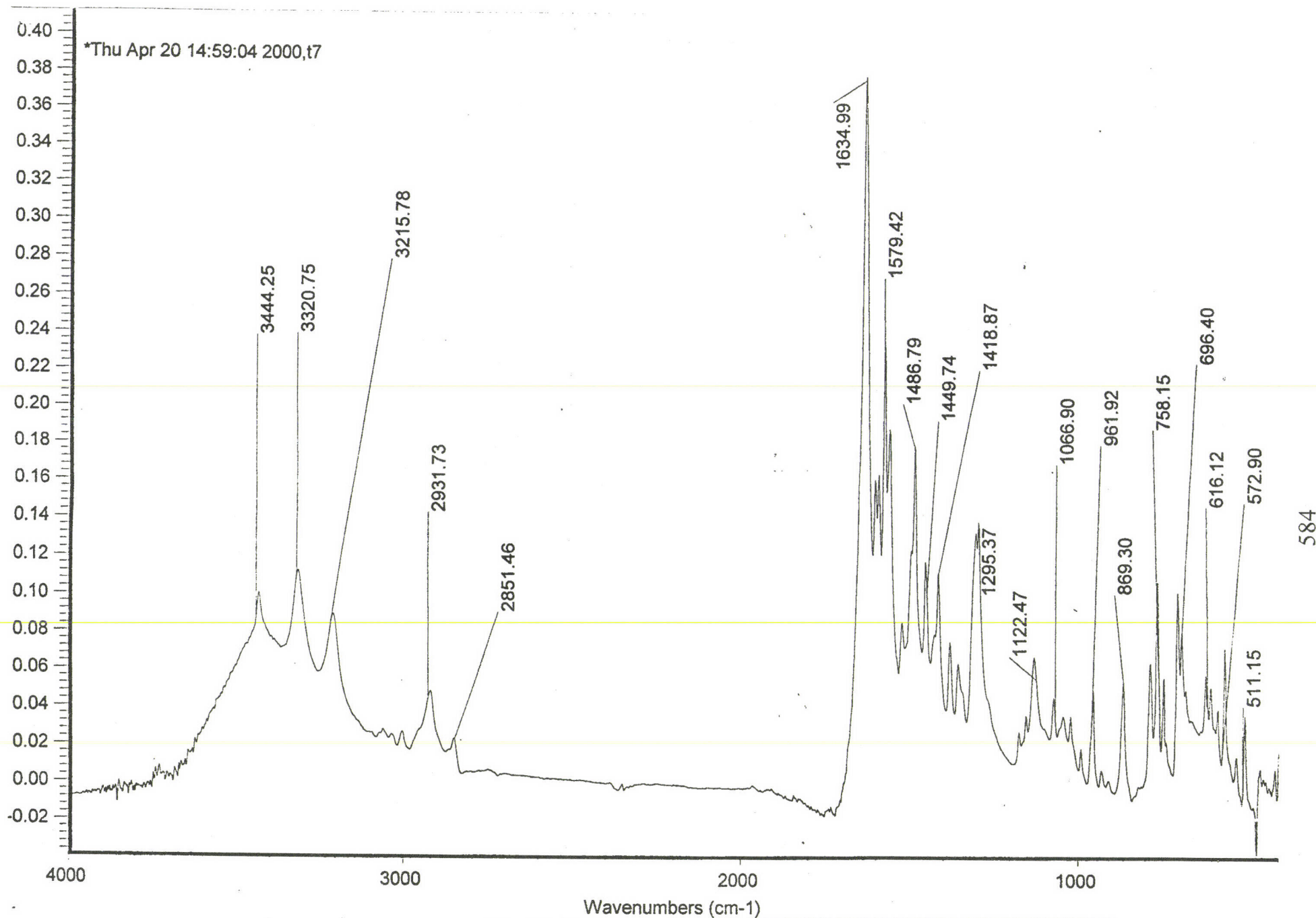


Fig.(6): FT-IR Spectrum of 3-ABP.



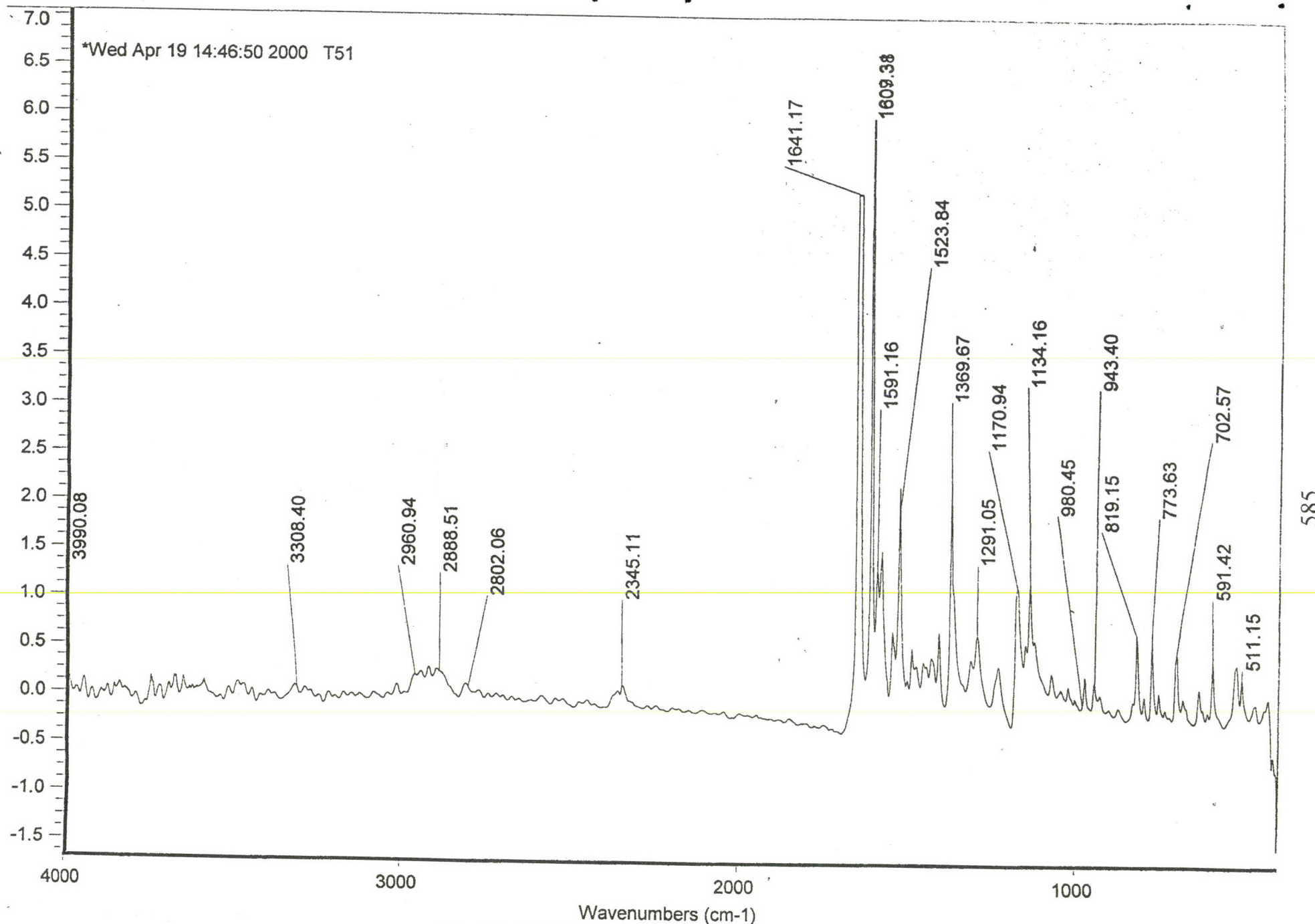


Fig.(7): FT-IR Spectrum of 4-N,N-DMBP.

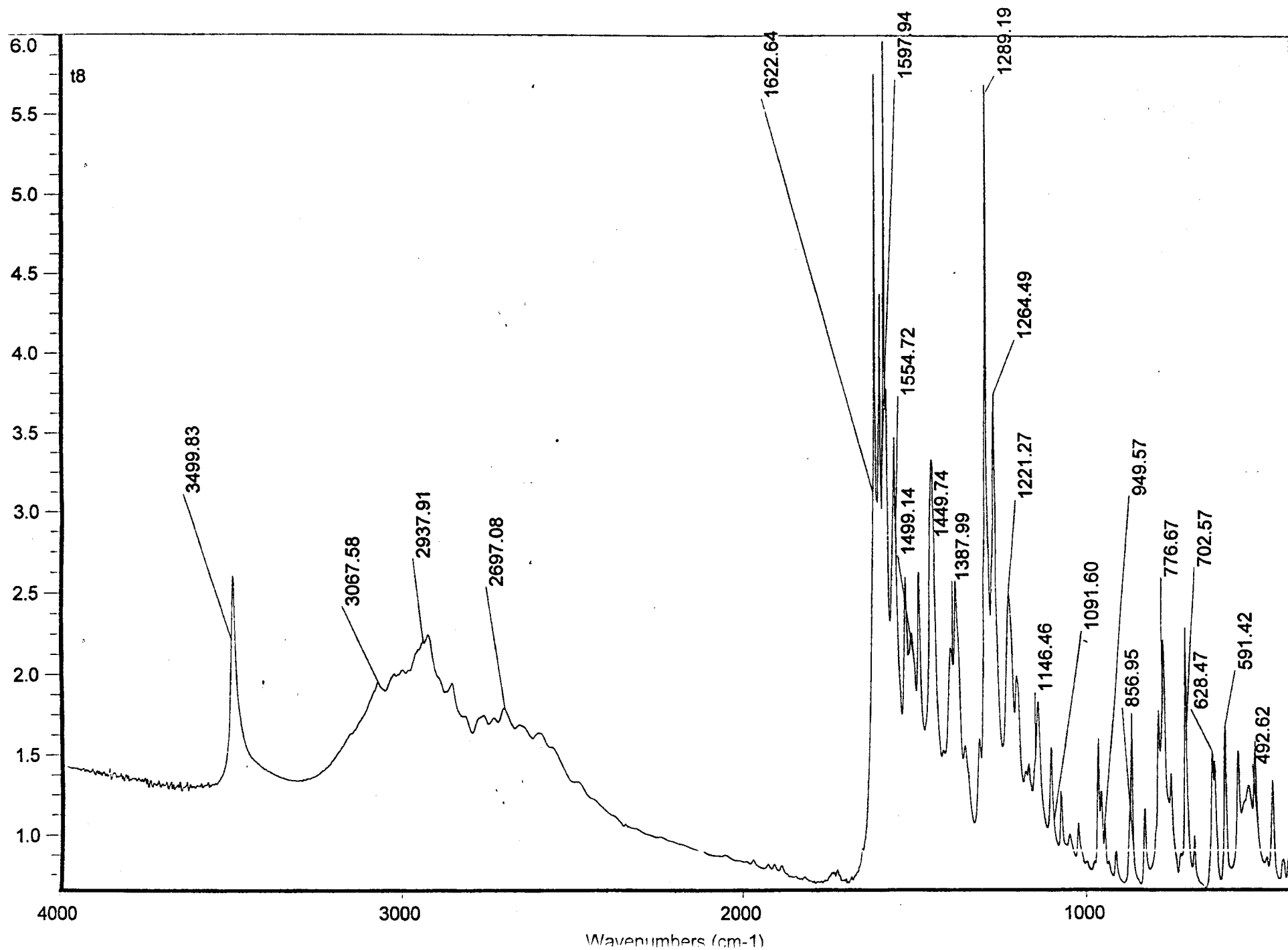


Fig.(8): FT-IR Spectrum of 3,4-DHBP.

## References

1. T. A. K. Al-Allaf, A. Z. M. Sheet and M. A. Al-Shama'a, Mu'tah, *Journal for Research and Studies*, 1997, **12**, 11.
2. T. A. K. Al-Allaf, and M. A. Al-Shama'a, Mutah, *Journal for Research and Studies*, 1996, **6**, 105.
3. L. K. Arsalan, A. I. Abdullah, and M. A. Abdullah, *Zanco*, 1990, **3**, 25.
4. A. A. Saeed, and F. H. Hussein, *Iraqi Journal of Chemistry*, 1989, **14**, 60.
5. A. A. Saeed, *Iraqi Journal of Chemistry*, 1991, **16**, 81.
6. A. A. Saeed, *Iraqi Journal of Chemistry*, 1991, **16**, 93.
7. E. Muller, C. Wiegand and G. Braun, *Ger. Pat. (1958)*; *C. A.*, 1960, **54**, 14778.
8. A. Varshney, and J. P. Tandon, Proc. *Indian Acad. Sci. Chem.*, 1986, **97**, 141.
9. H. Baumann and K. Grychtol, *Ger. Offen, 1977*; *C. A.*, 1978, **88**, 51943.
10. T. Port. And S. Skulska, *Rozen Chem.*, 1970, **44**, 1121.
11. T. Hang, A. Schmitter, 1975; *C. A.* 1975, **83**, 194518.
12. E. A. Kalemnikov, S. V. Markevich, *USSR. Pat; 1976, C. A.*, 1977, **86**, 107476.
13. I. Ishii, Y. Nomuta, *Top. Pat; 1975, C. A.*, 1976, **67**, 60505.
14. T. Gunduz and C. Dikmen, *Berichte*, 1956, **89**, 1956.
15. T. A. K. Al-Allaf, and A. Z. M. Sheet, *Polyhydron*, 1995, **14**, 239.
16. T. A. K. Al-Allaf, M. A. Al-Shama'a, and L. J. *Rashan Appl. Organometal. Chem.*, 1996, **10**, 545.
17. S. Pati "The Chemistry of the Carbon-Nitrogen Double Bond", *John Wiley and Sons*, 1979, **68**.
18. A. A. Saeed, and S. M. A. Ritha, *Iraqi Journal of Chemistry*, 1991, **16**, 73.
19. A. R. J. Al-Azzawy, Thesis, University of Al-Mustansiryah, Baghdad, 1989.
20. A. A. Saeed, and M. J. A. Habib, *Iraqi Journal of Chemistry*, 1987, **12**, 271.