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# The infrared and Raman spectra of propranolol hydrochloride

J Marshell
Department of Physics, Loyola College, Madras-600 034, India
and
S Gunasekaran
Department of Physics, Pachaiyappa's College, Madras-600 030, India

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**Abstract** : The propranolol hydrochloride molecule comprises of two parts ; one part being substituted napthalene while the other is an aliphatic chain of 2 propanol-1-1-(1-methyl ethyl amino) group. The assignment of the observed frequencies for the molecule is based on this partitioned structure. The molecule has $C_s$ point group of symmetry.

**Keywords** : Infrared and Raman spectra, propranolol hydrochloride molecule assignment

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## 1. Introduction

Blood pressure is the pressure exerted on the walls of the vessels by the circulating blood and this depends upon the activity of the vasoconstrictor and vasodilator nerves and several other factors. The two main factors are the cardiac output and peripheral resistance. The cardiac output is responsible for the systolic pressure while the peripheral resistance is reflected in the diastolic pressure. Both the cardiac output and the peripheral resistance are under the control of the nervous system, chiefly the vagus and vasomotor centres so that the brain can always adjust the blood pressure as may be necessary. These two centres are regulated by reflexes from Carotid sinus and Aortic arch. They are also influenced by drugs called the antihypertensives which act through the autonomic nervous system (peripherally). The antihypertensives come under two categories, the Ganglion blockers and the Receptor blockers commonly called Beta blockers like propranolol. These drugs cause vasodilation and are used in the treatment of hypertension. Propranolol is one of the recent drugs which is currently recieving a lot of attention in the treatment and management of essential hypertension. The structure of propranolol hydrochloride is given in Figure 1. The vibrations of the molecule can be viewed as separately comprising of a substituted

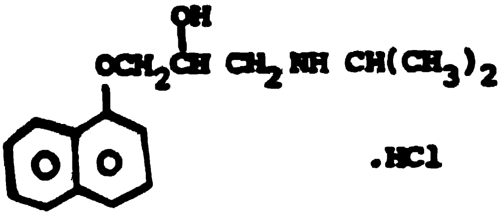

**Figure 1.** Structure of propranolol hydrochloride.

napthalene group and a chain aliphatic structure of 2 propanol-1-(1-methyl ethyl amino) group.

## 2. Experimental

The infrared spectrum was recorded on a Perkin Elmer 640 spectrometer in the range 4000 – 625 cm$^{-1}$ is presented in Figure 2. The Raman spectrum was recorded on a DILOR Z24 spectrometer in the range 4000 – 10 cm$^{-1}$ is presented in Figure 3. The sampling technique was KBr pellet in both cases. The probable assignments for the molecule is given in Table 1.

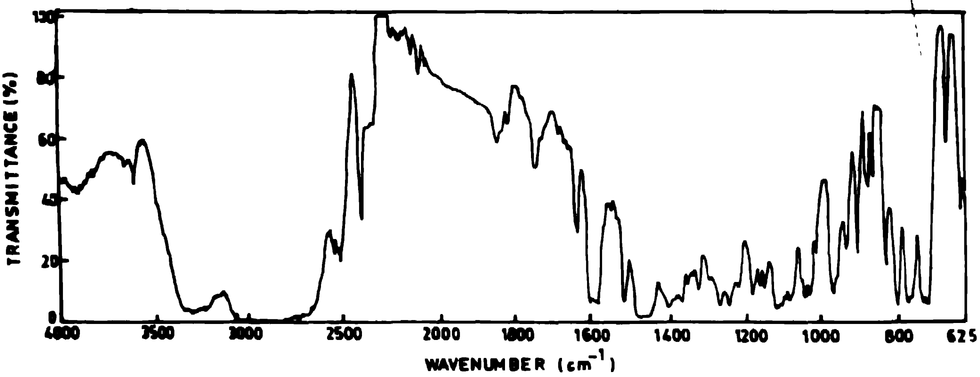

**Figure 2.** IR spectrum of propranolol hydrochloride.

## 3. Result and discussion

### *3.1. Skeleton vibrations :*

The assignment of various modes of vibration for the mono-subsitiuted napthalene part of the molecule is based on the previous works undertaken in this field [1–8]. The C–C ring stretching vibration occurs in the range 1266 – 1615 cm$^{-1}$. The C–C ring stretches for the napthalene molecule are the $b_{3g}$ (1624 cm$^{-1}$), $b_{1u}$ (1601 cm$^{-1}$), $a_g$ (1579 cm$^{-1}$), $b_{2u}$ (1508 cm$^{-1}$), the $b_{1u}$(1268 cm$^{-1}$). All of these modes have been identified for the present molecule to occur at 1630, 1590, 1532, 1512 and 1270 cm$^{-1}$ in the infrared spectrum while the $a_g$ (1579 cm$^{-1}$) mode is found to occur at 1583 cm$^{-1}$ in the Raman spectrum. All C–C ring stretching vibrations belong to $a'$ species in $C_s$ symmetry. In napthalene the out-of-plane skeletal deformations are the $b_{3u}$ (780 cm$^{-1}$) and the $a_u$ (740 cm$^{-1}$) modes. The frequencies

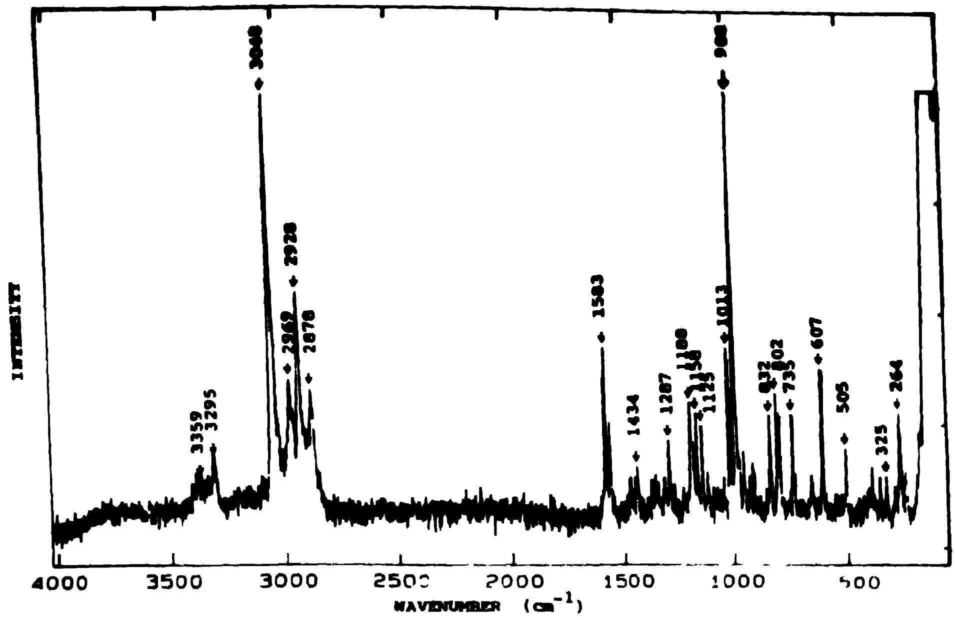

**Figure 3.** Raman spectrum of propranolol hydrochloride.

at 775 cm$^{-1}$ and the doublet at about 732 cm$^{-1}$ in infrared spectrum and at 735 cm$^{-1}$ in Raman spectrum are assigned to these modes of vibration. The in-plane skeletal deformations, the $b_{3g}$ (506 cm$^{-1}$) and the $b_{2u}$ (618 cm$^{-1}$) modes in napthalene occur without much shifting in the spectrum at 505 cm$^{-1}$ and 607 cm$^{-1}$ respectively. The skeletal out-of-plane deformation vibrations belong to the $a''$ species while the in-plane deformation vibrations belong to $a'$ species of symmetry of the molecule.

The C–H in-plane bending modes of napthalene are $b_{1u}$(810 cm$^{-1}$), $b_{2u}$(1010 cm$^{-1}$), $a_g$(1025 cm$^{-1}$), $b_{3g}$(1099 cm$^{-1}$), $a_g$(1144 cm$^{-1}$) and $b_{2u}$(1144 cm$^{-1}$) and the $b_{3g}$(1240 cm$^{-1}$). Though substitutions may cause small modifications in frequencies, all of these modes have been identified in IR spectrum at 830 cm$^{-1}$, 1010 cm$^{-1}$, 1023 cm$^{-1}$, 1038 cm$^{-1}$, 1100 cm$^{-1}$, 1150 cm$^{-1}$ and 1245 cm$^{-1}$ respectively. Raman frequencies at 832 cm$^{-1}$, 988 cm$^{-1}$, 1013 cm$^{-1}$ and 1125 cm$^{-1}$, have been assigned to the C–H in-plane bending modes. The C–H out-of-plane bending vibrations are the 868 cm$^{-1}$, 878 cm$^{-1}$, 936 cm$^{-1}$ and 965 cm$^{-1}$ corresponding to the $a_u$(860 cm$^{-1}$), $b_{2g}$(875 cm$^{-1}$), $b_{3g}$(937 cm$^{-1}$) and $a_u$(965 cm$^{-1}$) modes of napthalene respectively. No out-of-plane bending vibrations occur in the Raman spectrum of the compound. All in-plane bending modes belong to $a'$ species and the out-of-plane bending modes to $a''$ species of the $C_s$ point group of symmetry of the molecule. The symmetrical ring breathing mode in napthalene occurs at 760 cm$^{-1}$ [1], but it has been assigned to the frequency at 805 cm$^{-1}$ in IR and 802 cm$^{-1}$ in Raman spectra of the molecule. However, it has been observed that the ring breathing mode in benzene is strongly affected by substitution. The shift in frequency is attributed to its interaction with the C–C–C in-plane bending mode, both modes belong to the same species in $C_s$ symmetry [9,10]. The aromatic C–H stretching occur in the range 3100–3000 cm$^{-1}$ [11]. In napthalene there are two C–H stretching modes corresponding to $a_g$ (3004 cm$^{-1}$) and (3055 cm$^{-1}$) of which a very strong absorption at 3048 cm$^{-1}$ corresponding to C–H mode, is seen in the Raman spectra of the molecule.

**Table 1.** Vibrational assignment of propranolol hydrochloride.

| Raman frequency (cm$^{-1}$) | Infrared frequency (cm$^{-1}$) | Assignment |
|---|---|---|
| 264 (M) | | C–CH$_3$ bending o p |
| 325 (W) | | C–CH$_3$ bending i.p. |
| 505 (M) | | Skeletal deformation i.p. |
| 607 (S) | | Skeletal deformation i p |
| | 640 (M) | 1470–830 |
| | 675 (W) | 1512–830 |
| | 728 (VS) | Skeletal deformation o p. |
| 735 (M) | 738 (VS) | Skeletal deformation o p |
| | 775 (VS) | Skeletal deformation o p |
| 802 (M) | 805 (VS) | C–C Ring breathing |
| 832 (M) | 830 (S) | C–H bending i p |
| | 868 (M) | C–H bending o p |
| | 878 (M) | C–H bending o p |
| | 908 (S) | CH$_3$ Wagging |
| | 936 (S) | C–H bending o.p. |
| | 965 (VS) | C–H bending o.p. |
| 988 (VS) | | C–H bending i.p |
| 1013 (S) | 1010 (S) | C–H bending i.p. |
| | 1023 (VS) | C–H bending i.p. |
| | 1038 (VS) | C–H bending i.p. |
| | 1080 (VS) | CH$_3$ rocking |
| | 1100 (VS) | C–H bending i.p. |
| 1125 (M) | 1150 (VS) | C–H bending i.p. |
| 1158 (M) | 1161 (S) | C–O Stretching |
| 1188 (M) | 1184 (VS) | C–N Stretching |
| | 1220 (S) | CH$_2$ rocking |
| | 1245 (VS) | C–H bending i.p. |
| | 1270 (VS) | C–C ring stretch |

**Table 1.** *(Cont'd.).*

| Raman frequency ($cm^{-1}$) | Infrared frequency ($cm^{-1}$) | Assignment |
|---|---|---|
| 1287 (W) | | $CH_2$ twisting |
| | 1300 (S) | 2 × 1150–1010 |
| | 1329 (S) | 2 × 1150–965 |
| | 1344 (S) | 2 × 1184–1023 |
| | 1359 (S) | $CH_2$ Wagging |
| | 1370 (VS) | $CH_3$ Symmetric bending |
| | 1405 (VS) | $CH_2$ Symmetric bending |
| 1434 (W) | | $CH_3$ asymmetric bending |
| | 1470 (VS) | $CH_3$ and $CH_2$ Asymmetric bending |
| | 1512 (VS) | C–C ring stretch |
| | 1532 (M) | C–C ring stretch |
| 1583 (S) | 1590 (VS) | C–C ring stretch |
| | 1630 (S) | C–C ring stretch |
| | 1650 (W) | 775 + 878 |
| | 1680 (W) | 738 + 936 |
| | 1741 (M) | 2 × 868 |
| | 1818 (W) | 805 + 1023 |
| | 1850 (W) | 830 + 1023 |
| | 2080 (VW) | 805 + 1270 |
| | 2115 (VW) | 965 + 1150 |
| | 2145 (VW) | 738 + 1405 |
| | 2402 (S) | 936 + 1470 |
| | 2505 (S) | 1038 + 1470 |
| | 2540 (S) | 936 + 1590 |
| 2878 (M) | | $CH_3$ Symmetric C–H stretch |
| | 2900 (VS) | C–H Stretchings |
| 2928 (S) | | $CH_2$ Asymmetric C–H stretch |
| 2969 (M) | | $CH_3$ Asymmetric C–H stretch |
| 3048 (VS) | | Aromatic C–H stretching |
| 3295 (W) | 3300 (VS) | O–H Stretching |
| 3359 (W) | | N–H Stretching |

VS–Very Strong, S–Strong; M–Medium; W-Weak; VW–Very Weak, i p.–in-plane; o p -out-of-plane.

### 3.2. *Group vibrations :*

The $CH_3$ symmetric and asymmetric stretching vibrations appear around a fairly constant region and they are found to occur at 2878 $cm^{-1}$ and 2969 $cm^{-1}$ respectively, in the present case [12]. The $CH_2$ asymmetric stretching modes appear at about 2930 $cm^{-1}$ and for propranolol, it appears at 2928 $cm^{-1}$ [13,14]. All C–H stretching vibrations appear as a very strong and broad absorption centred at about 2900 $cm^{-1}$ in the IR spectrum. The $CH_3$ symmetric bending is sensitive to the atom adjacent to the $CH_3$ group and occurs at 1370 $cm^{-1}$. The $CH_2$ symmetric bending is placed at 1405 $cm^{-1}$. The $CH_3$ and $CH_2$ asymmetric deformation frequencies lie within the range and is assigned to the intense absorption at 1470 $cm^{-1}$ [12]. In Raman spectrum, the weak absorption at 1434 $cm^{-1}$ may be attributed to $CH_3$ asymmetric bending vibration. The $CH_3$ rocking vibration [13,15] is assigned to the 1080 $cm^{-1}$ absorption of strong intensity. The frequency at 1220 $cm^{-1}$ is assigned to $CH_2$ rocking vibration. The other group vibrations are the wagging and twisting modes. The methyl wagging is placed to 908 $cm^{-1}$ while the $CH_2$ twisting occurs as a weak Raman absorption at 1287 $cm^{-1}$ [16]. The C–$CH_3$ in-plane and C–$CH_3$ out-of-plane bending occur at 325 $cm^{-1}$ and 264 $cm^{-1}$ respectively.

The other vibrations for the molecule are the C–O stretching which occur at about 1159 $cm^{-1}$ [17] and C–N stretching at about 1186 $cm^{-1}$ [18] in both IR and Raman spectra. The N–H and O–H stretchings have been assigned to 3359 $cm^{-1}$ and 3295 $cm^{-1}$ respectively [19] while they give rise to a broad band of absorption in the IR spectrum of the molecule. The region between 1650 $cm^{-1}$ and 2500 $cm^{-1}$ is treated as due to overtones and combinations.

## 4. Conclusion

The infrared and Raman spectra for propranolol hydrochloride has been analysed assuming $C_s$ point group symmetry and the observed fundamentals have been assigned to different normal modes of vibration. The assignment of the fundamental frequencies is made on the basis of magnitude and relative intensities of the observed bands. A complete vibrational assignment has been made for the molecule.

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