Photoluminescence of 2-hydroxybiphenyl and its methyl derivative

K Kalaiyarasan, N Rajendiran & M Swaminathan*  
Department of Technology, Annamalai University,  
Annamalainagar 608 002

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The effect of solvents on the absorption and fluorescence spectra of 2-hydroxybiphenyl and 2-methoxybiphenyl has been investigated. In the ground state hydrogen acceptor interaction of 2-hydroxybiphenyl is more predominant whereas in the excited state its hydrogen donor interaction is more effective. Analysis of photoluminescence of 2-hydroxybiphenyl reveals its dual emission. The dual luminescence in polar solvents is explained by the formation of solute-solvent exciplex with the trans isomer of the compound.

Fluorescence spectroscopy provides a powerful methodology to study the changes that occur in the excited state of a molecule. Solvent spectral shifts in the fluorescence spectrum of a compound have been extensively utilized to draw conclusions about the nature of transition, site of solvent interaction, change in geometry and dual luminescence. The anomalous dual luminescence was first reported by Lippert for p-(dimethylamino)benzonitrile (DMABN) in solution. To account for the anomaly several models like twisted intramolecular charge transfer, formation of excimer and solute-solvent exciplex have been proposed. A dual fluorescence was observed for 2-hydroxybiphenyl during our study on hydroxybiphenyl derivatives. The present investigation was carried out to analyse the dual luminescence of 2-hydroxybiphenyl (POH). A comparative study of solvatochromic effects of 2-hydroxybiphenyl (POH) and 2-methoxybiphenyl (POM) have also been carried out to explain the specific hydrogen bonding interactions in 2-hydroxybiphenyl.

Experimental

2-Hydroxybiphenyl (Aldrich) was purified by recrystallisation from pet.-ether (60-80°C). 2-Methoxybiphenyl was prepared by methylation of POH. The purities of POH and POM were checked by obtaining identical fluorescence when excited at different wavelengths. Triply distilled water was used to prepare the aqueous solution. Spectrograde solvents (BDH) were used as received. Absorption spectra were recorded using a JASCO UNIDEC-650 spectrophotometer and fluorescence measurements were made using a JASCO FP-550 spectrofluorimeter. pH of solutions in the range 1-13 were measured on a Systronics 335 digital pH meter. Due to poor solubility of POH in water, a stock solution was prepared in methanol. Experimental solutions were prepared just before taking spectral measurements. The concentration of the solutions were of the order of $10^{-5}$-10^{-4} mol dm^{-3}.

Results and discussion

The absorption maxima, log ε and fluorescence maxima of POH and POM in solvents of different polarity and hydrogen bonding ability are compiled in Table I. There are two absorption bands in both the molecules. These bands are due to short axis ($\pi$-$\pi^*$) and long axis ($\pi$-$\pi^*$) polarised transitions. By comparing these two bands with those of biphenyl and 4-hydroxybiphenyl the short wavelength band is assigned according to piau's notation, as $L^\pi_a$ and the long wavelength band as $L^\pi_b$. Since these compounds are not planar in the ground state, both $L^\pi_a$ and $L^\pi_b$ bands are unaffected by solvent interaction.

The solvatochromic shifts in both the bands of POH and POM are in the same direction but the shifts are not regular according to polarity of solvents. When compared to cyclohexane the absorption maxima of POH and POM are red shifted in acetonitrile and methanol and blue shifted in water. The solvent molecule can interact with the solute molecule through three different ways (i) dispersive (ii) hydrogen acceptor solvent and (iii) hydrogen donor solvent interactions. In the case of a solute molecule with an

<table>
<thead>
<tr>
<th>Solvent</th>
<th>POH</th>
<th>POM</th>
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<tbody>
<tr>
<td></td>
<td>λ abs (log ε)</td>
<td>λ flu</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>283.0 (3.54)</td>
<td>322.0</td>
</tr>
<tr>
<td></td>
<td>244.0 (3.88)</td>
<td></td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>286.8 (3.71)</td>
<td>330.0</td>
</tr>
<tr>
<td></td>
<td>245.0 (4.08)</td>
<td>396.6</td>
</tr>
<tr>
<td>Methanol</td>
<td>286.5 (3.63)</td>
<td>332.0</td>
</tr>
<tr>
<td></td>
<td>245.0 (3.99)</td>
<td>398.0</td>
</tr>
<tr>
<td>Water</td>
<td>281.4 (3.68)</td>
<td>343.0</td>
</tr>
<tr>
<td></td>
<td>241.8 (4.04)</td>
<td>415.0</td>
</tr>
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</table>
electron-donating substituent and \( \pi-\pi^* \) as the lowest energy transition, the first two effects lead to a red shift whereas the last effect leads to a blue shift in absorption maxima\(^{10}\). If there is more than one effect, acting in opposite directions, some irregularities may arise\(^{11}\). The hydroxy group can act as a hydrogen acceptor as well as a hydrogen donor, resulting in a blue shift in the former case and a red shift in the latter. Acetonitrile is hydrogen accepting solvent whereas methanol and water can behave in both ways. It has been reported that hydrogen donating capability of water is more than that of methanol\(^{12}\). The observed solvatochromic shifts in POH indicate that first two effects are predominant in acetonitrile and methanol whereas the third effect is more operative in water. In POM, only the third effect is significant in water.

The fluorescence spectra of POH and POM in different solvents are displayed in Figs 1 and 2. Table 1 gives the fluorescence maxima of both the compounds in different solvents. In cyclohexane POH shows only one band but in other solvents it shows two fluorescence bands, one in the shorter wavelength region around 330 nm (Fluorescence Normal, FN) and the other in the longer wavelength region around 400 nm (Fluorescence Anomalous FA). In the case of POM only one fluorescence band is observed around 330 nm in all solvents. Analysis of the fluorescence maxima of POH in all the solvents shows that there is a regular bathochromic shift with increasing polarity and hydrogen bonding ability of solvents. This reveals that hydroxy group behaves like a hydrogen donor species due to increased charge transfer interaction with the ring in the excited state. A similar trend is observed in the fluorescence maxima of POM from cyclohexane to water. The shift is according to polarity of solvents. Since the polarities of methanol and acetonitrile are closer, the maxima observed in both the solvents are the same.

**Dual luminescence of 2-hydroxybiphenyl**

POH exhibits two fluorescence bands FN and FA in polar solvents. The intensity of longer wavelength band is more in water (Fig. 1). The Stokes shift for both short and long wavelength fluorescence maxima in different solvents are given in Table 2. The Stokes shifts are large even for FN band. The large Stokes shift and the absence of mirror image relationship show that the molecule undergoes geometry change in the excited state. This change is observed in biphenyl and its derivatives\(^{13}\). The dual fluorescence could be attributed to a variety of causes viz., twisted intra-
molecular charge transfer (TICT), formation of solute-solvent exciplexes, eximers etc. The dual emission by TICT was first observed in DMABN and recently reviewed in detail. In DMABN dual emission is reported to be due to the reversal of the states $L_1^a$ and $L_1^b$. To test this in POH we recorded the excitation spectra using the excitation wavelengths corresponding to $L_1^a$ and $L_1^b$ transitions. The same fluorescence spectrum was obtained. Furthermore there was no significant change in the maxima of FA with increase in polarity of solvents i.e., from methanol to water. POH is reported to exist as cis and trans-isomers in non-polar solvents.

In the ground state the percentage of cis is estimated to be ca 80-85%. In the excited state the percentage of cis isomer should be greater due to increased charge transfer interaction of the lone pair on the oxygen atom. The FN observed in cyclohexane is from the cis isomer. But in basic solvents like acetonitrile, methanol and water a hydrogen bonded exciplex is formed with trans isomer and this is in equilibrium with the cis isomer in the excited state. It is already reported that the compound also exists in trans form in basic solvents. To confirm the formation of exciplex both absorption and fluorescence spectra of the compound in cyclohexane with 1% water (v/v) were recorded and compared. There was no change in the absorption spectra in cyclohexane by the addition of water but FN and FA appeared in the fluorescence spectrum (Fig. 3).

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References