Exciplex formation with associated exciplex emission in diphenyl-hexatriene-tertiary amine systems in nonpolar solvents

Anupa Guha Majumder (nee Kar Purkayastha) & Benoy B Bhowmik*
Department of Chemistry, Jadavpur University, Calcutta 700 032
and
Sadhan Basu
Department of Chemistry, University College of Science, Calcutta 700 009

Received 12 March 1991; revised and accepted 21 July 1991

Diphenylhexatriene (DPH) forms exciplexes with N,N-diethylaniline and N,N-dimethylaniline with associated exciplex emissions. Excimer formation of DPH has not been observed. Using Onsager's reaction field concept the dipole moment of the exciplex has been calculated. It has been justified that the delocalised orbital in aromatic tertiary amine takes part in exciplex formation. The exciplex emission is sometimes suppressed in highly polar media.

Pyrene and anthracene in their excited states have been reported to form complexes with tertiary amines in nonpolar solvents. This complex formation is associated with structureless emission in the longer wavelength side of the hydrocarbon emission band in nonpolar solvents. The emission shows progressive shift towards longer wavelength with increasing dielectric constant of the medium. Such exciplexes have been detected in other systems as well, such as catacondensed aromatic hydrocarbons and tertiary amines. Basu has laid the condition for such complex formation with some theoretical justification in which he assumed that the orbital energy level of the donor tertiary amine should lie between the ground state and first excited state orbital energy of the acceptor hydrocarbon. From the energy consideration it was surmised that biphynylpolynes as acceptor and tertiary amines as donor are the systems of choice to study exciplex formation in nonpolar solvents and hence the following investigation has been carried out.

Experimental

1,6-Diphenyl-1,3,5-hexatriene (DPH) was a Sigma extrapure product. The tertiary amines used were N,N-diethylaniline and N,N-dimethylaniline (BDH) and were distilled before use. The other solvents were also purified following the recommended procedure.

Fluorescence measurements were made by Shimadzu Recording Spectrofluorophotometer (model RF-540).

Results and discussion

DPH is used extensively for fluidity probe. The intense absorption maximum (8,000 m² mol⁻¹) and the high fluorescence quantum yield (0.8 in hexane at 25°) facilitates detection of a fluorescence signal at DPH concentration as low as 10⁻⁸ mol dm⁻³ (ref.5). The well-separated absorption and emission bands reduce considerably both the possibility of excitation energy transfer from one DPH molecule to the other and the contribution of scattered excitation light to fluorescence signal.

At [DPH] = 1 x 10⁻⁶ mol dm⁻³ absorption spectrum of DPH exhibits absorptions at 334, 351 and 375 nm whereas it exhibits peaks in its emission spectrum at 404, 428 and 450 nm. As [DPH] is increased, the emission is quenched but the peaks of the emission spectrum remain unaltered at the same positions. Since no new radiation appears at longer wavelength on increasing [DPH], it is concluded that DPH does not form excimer. But fluorescence spectrum of DPH at [DPH] = 10⁻⁶ mol dm⁻³ and diethylaniline (10⁻¹ mol dm⁻³) in heptane does not exhibit three peaks of DPH, instead a new, broad, structureless quenched peak appears at 468 nm. This observation of fluorescence quenching accompanied by the appearance of a new fluorescence emission is attributed to an excited charge transfer complex or exciplex. The emissions of DPH-diethylaniline exciplex are observed in solvents such as chloroform, butyl acetate, ethyl acetate and methyl acetate. The emission shows progressive red shift and quenching as the dielectric constant of the medium increases. Following Onsager equation of liquid dielectrics the dipole moment of DPH-diethylaniline exciplex is estimated to be 8.92 Debye (Table 1).

With dimethylaniline also DPH exhibits exciplex emission at 476 nm in heptane. The catacondensed aromatic hydrocarbons form exciplexes also with aliphatic tertiary amines. But in the case of DPH no exciplex emission with aliphatic tertiary amines is noticed.

During exciplex formation of catacondensed aromatic hydrocarbon with tertiary amine it is assumed that the lone pair electrons at the nitrogen
**NOTES**

**Table 1—Determination of dipole moment of DPH-diethylaniline exciplex**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\varepsilon$ (dielectric constant)</th>
<th>$n$ (refractive index)</th>
<th>$\varepsilon - 1$</th>
<th>$n^2 - 1$</th>
<th>$\lambda_{\text{nm}}$</th>
<th>$h\Delta\nu$ (eV)</th>
<th>$\mu$ (dipole moment) (Debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heptane</td>
<td>1.93</td>
<td>1.388</td>
<td></td>
<td></td>
<td>468</td>
<td>0.2873</td>
<td>8.92</td>
</tr>
<tr>
<td>Chloroform</td>
<td>4.806</td>
<td>1.444</td>
<td>0.2075</td>
<td>0.2529</td>
<td>502</td>
<td>0.3495</td>
<td></td>
</tr>
<tr>
<td>Butyl acetate</td>
<td>5.01</td>
<td>1.392</td>
<td></td>
<td></td>
<td>510</td>
<td>0.3495</td>
<td></td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>6.02</td>
<td>1.370</td>
<td>0.3998</td>
<td>0.4325</td>
<td>526</td>
<td>0.4389</td>
<td></td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>6.68</td>
<td>1.362</td>
<td></td>
<td></td>
<td>526</td>
<td>0.4680</td>
<td></td>
</tr>
</tbody>
</table>

atom in tertiary amine participate in electron transfer process. Further, the exciplex emissions in presence of $n$-propanol and acetone are widely different although both the solvents have the same dielectric constant. This happens due to the fact that the hydroxyl group of propanol forms hydrogen bond with tertiary amine thereby stabilising the nonbonding electrons with consequent appearance of exciplex emission at lower wavelength than that of acetone which cannot form such hydrogen bond. In the case of diphenyl polyene the situation is different. It is observed that the exciplex emissions for $n$-propanol and acetone appear at the same wavelength. This observation suggests that the lone pair electrons do not participate in the electron transfer process of DPH-diethylaniline exciplex system. This may be due to the fact that the delocalised orbital in aromatic tertiary amines participate in exciplex formation since aromatic amines have the delocalised orbital. This also supports the fact that the aliphatic amines which have no such delocalised orbital do not form exciplex with DPH.

**References**