

ON THE SINGLET \rightarrow TRIPLET ABSORPTION IN
AROMATIC COMPOUNDS IN GASEOUS STATE

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Plate IX

ABSTRACT. The absorption spectra in the near ultraviolet region of benzene and *o*-bromotoluene in the vapour state at the respective saturation pressures at the room temperature with a path length of about 62 feet have been photographed and compared with the spectra due to the substances in the liquid state having equivalent path lengths. It has been observed that although benzene in the liquid state with a path length 1.2 cms shows considerable absorption in the 3300Å - 3400Å region due to singlet \rightarrow triplet transition, such absorption in the case of the vapour at 12 mm pressure, with a path length of 62 feet is very much less than that in the liquid. Similar results have been observed in the case of *o*-bromotoluene, the path length being 7 mm for the liquid and 62 feet for the vapour at 55 mm pressure. It has been pointed out that the singlet \rightarrow triplet absorption and the corresponding luminescence observed by previous workers in these cases are enhanced considerably in the state of aggregation of the molecules.

I N T R O D U C T I O N

The singlet \rightarrow triplet absorption in some aromatic liquids was first observed by Lewis and Kasha (1945). Kasha also observed later (Kasha, 1952) that this absorption is strengthened when a heavy substituent atom is introduced in the benzene molecule and also when the molecules are dissolved in a solvent, the molecules of which contain such heavy atoms. Sirkar and Biswas (1956) and Biswas (1956) observed that the relative intensities of the bands and their positions in the luminescence spectra of frozen solutions of certain disubstituted benzene compounds depend to some extent on the nature of the solvent. Later, Roy (1959) proved conclusively that the luminescence in such cases was produced after absorption in the process of singlet \rightarrow triplet transition. As it was suggested by Sirkar and Biswas (1956) and also by Biswas (1956) that the luminescence exhibited by the molecules in the solid state at low temperatures might be due to formation of small groups of molecules it would be of interest to find out whether the singlet \rightarrow triplet absorption is an intrinsic property of the individual molecules in the gaseous state or it is developed in the state of aggregation. It is difficult to make experimental arrangement for this purpose, because the life time of the

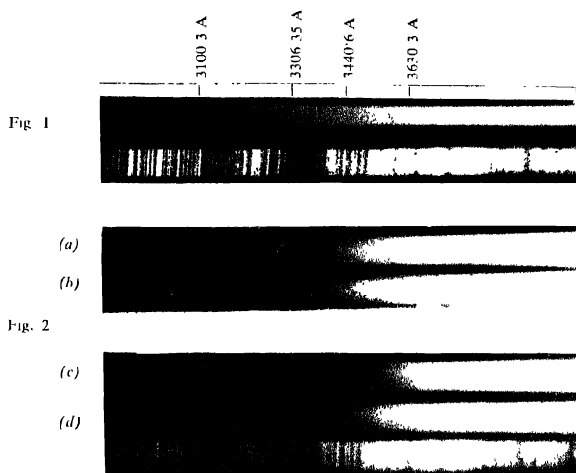
triplet state is large and consequently the absorption is very weak. However, the absorption is exhibited by some of these liquids even when the absorbing path is only about 5 cms. If the absorption could be detected in these cases using absorption cells of thickness about 1 cm, it would be possible to study the absorption in the vapour with equivalent path length.

An attempt has, therefore, been made to study the absorption spectra in the near ultraviolet region of vapours of benzene and *o*-bromotoluene at pressures 12 cm and 5.5 cm respectively, the absorbing path being 18.90 metres long in each case. The spectra due to the liquids of equivalent thickness have also been photographed under identical conditions and compared with those due to the vapours. The results have been discussed in the present paper.

EXPERIMENTAL

The absorbing path of the vapour about 18.90 metres long was obtained by making two cells of straight pyrex glass tubes each about 32 feet long, provided with quartz windows and placed side by side parallel to each other. The continuous radiation from a tungsten filament lamp in glass bulb was made parallel with a quartz lens and passed through one of the tubes. The rays being then reflected by two right angled quartz prisms, passed through the other tube and were finally focussed on the slit of the spectrograph with another quartz lens. The radiation emitted by the lamp was found to have wavelengths longer than 3000 Å and therefore the absorption due to singlet → singlet transition was not possible in this arrangement. A bulb of Pyrex glass containing the liquid was connected to each of the absorption cells through a greasless stopcock and a side tube. First, the long cells were evacuated and the spectrum of the incident radiation passing through the tubes was recorded. The short empty cell for the liquid was next placed in the path of the rays and the long absorption cells were filled with the vapour of the liquid at the saturation pressure which was measured with a differential manometer. The pressure was found to be 120 mm in the case of benzene and 55 mm in the other case. After photographing the absorption spectrum of the vapour on a photographic film the long cells were evacuated and the short cell was filled with the distilled liquid and the absorption spectrum of the liquid was photographed on the same film with the same exposure and under identical conditions as in the case of the vapour.

The liquids benzene and *o*-bromotoluene used in the investigation were of chemically pure quality and they were first fractionated and then distilled in vacuum before being introduced in the bulb mentioned above. The thickness of the cell for the liquid was 1.2 cm for benzene and 7 mm in the case of *o*-bromotoluene. The spectra were photographed with Hilger medium quartz spectrograph on Agfa Isopan films, the time of exposure being about 10 hours in each case.



Ultraviolet absorption spectra

Fig. 1. Absorber — evacuated cell, 18.90 metres long

- Fig. 2 (a) Absorber — benzene (liquid), 12 mm long cell
+ above evacuated cell
(b) Absorber — benzene vapour at 120 mm of Hg,
18.90 metres long cell
(c) Absorber — *o*-bromotoluene (liquid), 7.0 mm long cell
+ above evacuated cell
(d) Absorber — *o*-bromotoluene vapour at 55 mm of Hg,
18.90 metres long cell

RESULTS AND DISCUSSION

The spectrograms for benzene and *o*-bromotoluene are reproduced in Figs. 2(a), 2(b), 2(c) and 2(d) in Plate IX, the spectrum of the incident continuous radiation passing through the evacuated absorption tube being shown in Fig. 1. These spectra show that in the case of benzene in the vapour state (Fig. 2b) there is only a very weak absorption in the region 3400 Å-3300 Å, while in the spectrum due to the liquid of equivalent thickness (Fig. 2a) there is appreciable absorption in this region. In the case of *o*-bromotoluene in the vapour state Fig. 2(d), however, there is weak absorption even in the region 3600 Å-3400 Å and the absorption in this region is very much stronger in the spectrum due to the liquid Fig. 2(c). It is evident, therefore, that even in the vapour state the *o*-bromotoluene molecule shows much stronger absorption due to singlet→triplet transition than the benzene molecule and that such absorption increases enormously when the vapour is liquefied. Thus the substituent bromine atom in the *o*-bromotoluene molecule in the vapour state is responsible for the increase in the strength of singlet→triplet absorption and shift of the region of absorption towards red. When the vapour is liquefied the influence of intermolecular forces increases the strength of the absorption enormously in the case of *o*-bromotoluene, but only slightly in the case of benzene. If in the liquid state the dissipation of energy of the excited state by processes other than radiation would result in the shortening of the life-time of the excited state and consequent increase in the absorption such increase would be of the same order in both the liquids. The increase is, however, much larger in the case of *o*-bromotoluene than in the case of benzene. In the former case the molecule has not only a heavy atom but it also has a permanent electric moment. On comparing the luminescence exhibited by different disubstituted benzenes, it is found that the luminescence produced by chloro- and bromotoluenes is much stronger than that exhibited by dichloro- or dibromobenzenes. It appears, therefore, that not only the presence of heavy atoms but also the formation of groups of associated molecules may be partly responsible for the luminescence and absorption due to singlet→triplet transition.

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