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SOME SOLID MOLECULAR COMPLEXES OF I_2

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In water I_2 combines with methylene blue, thionine, para-rosaniline, crystal violet and acridine orange, and solid complexes precipitate out. The complex with methylene blue is 1 : 1 and shows a new absorption band in $CHCl_3$ at 365 nm. It appears to be of the electron donor-acceptor type: n (dye) $\rightarrow \sigma^*$ (I_2).

Of the large number of iodine complexes reported so far relatively few have been obtained in the solid state.[1)] Such solid complexes are usually prepared from solution by evaporating the solvent and thereby risking partial decomposition of the complex. Here we report the formation of some new complexes of iodine and a simple method for preparing them in the solid state by immediate precipitation. The second component in the complexes are the dye: methylene blue chloride (MB), Lauth's violet, crystal violet, para-rosaniline and acridine orange. Bromine also was found to form a complex with MB.

In this method a saturated aqueous solution of iodine is added dropwise to a dilute solution of the dye (10^{-4} M), until there is a slight excess of iodine. A precipitate is immediately formed, slowly flocculates and settles down. An excess of the dye seems to peptonize the solid. Alternatively, crystals of iodine can be added to the dye solution and when the solution acquires a faint tinge of yellowish brown color of aqueous iodine, the loose and light precipitate can be easily separated from iodine by decantation. This method was applied to mixtures of dyes and from the absorption spectra of the solution at different times it was found that different dyes go out of solution at different rates. It was possible to establish the following order: crystal violet > para-rosaniline > methylene blue > thionine > acridine orange. Of all the complexes prepared only the one with methylene blue (MBI_2) has been investigated. Methylene blue nitrate also forms a similar complex.

The Composition of the Complex MBI_2 This was determined by a simpler technique. The water insoluble complex is readily soluble in chloroform. A known weight of the complex, dissolved in $CHCl_3$ (10^{-4} M), is equilibrated with a concentrated KI solution upon which the dye remains in $CHCl_3$, presumably as the iodide salt which is sparingly soluble in water, and the iodine moves up into the aqueous layer. The top layer is analyzed volumetrically for iodine and the bottom layer colorimetrically (at λ_{max} = 645 nm) for the dye. The composition was computed to be 1 : 1.

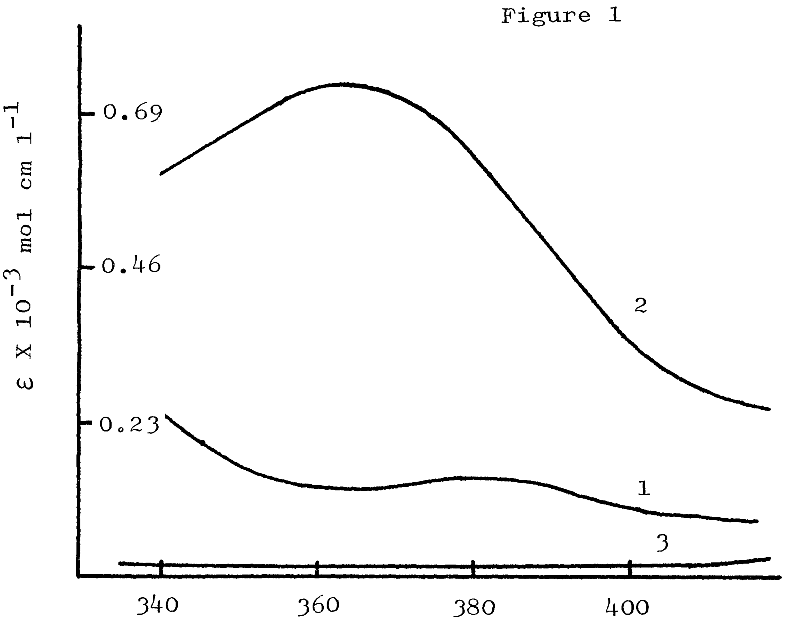
The method of analysis also establishes that the solid MBI_2 is a molecular complex with each component present in its molecular form.

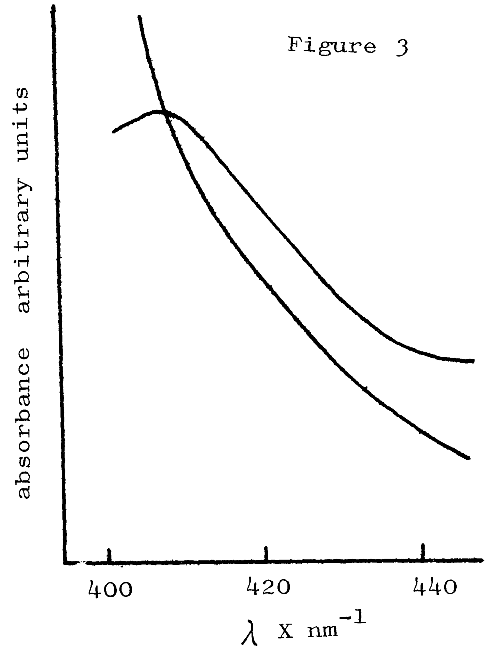
Charge Transfer Band Absorption spectra of the complex and its component (Fig. 1) show that although MB and I_2 absorb very little in this region the complex has a moderately strong absorption band at 365 nm (ϵ_{max} = $7x10^3$ l $mol^{-1}cm^{-1}$). The complex may therefore be regarded to be of the electron donor-acceptor (EDA) type.

The Nature of the Donor and the Acceptor The iodine absorption band (not shown) at 510 nm undergoes a hypochromic shift to 490 nm. This indicates, as Mulliken[2)] interpretes in terms of an exchange repulsion between the donor and the acceptor, that iodine is the electron acceptor, which of course is the case in all known EDA complexes of iodine. MB has an extended π-system as well as nonbonding electron pairs on the heterocyclic N and S atoms. So the dye possibly be a π-donor or an n-donor. However, the oxidized form of MB, unlike the parent compound phenothiazine and its derivertives such as leuco-methylene blue, is believed to be an acceptor.[3)] Photoreduction of MB in the presence of EDTA is explained by electron transfer to MB.[4)] The π-π* absorption band of MB at 645 nm in $CHCl_3$ (Fig. 2) is not displaced. From this it may be reasonable to infer that a π-electron of the conjugated system is not directly involved in the complex formation, and MB functions as an n-donor. The donated electron could be free from either N or S. Ordinarily N has higher ionization potential as well as greater electron affinity than S. But as Takahashi et al.[5)] calculated from the energy shift of sulfur K-line in the x-ray emission spectra of MB, there is net positive chrge (0.15 + 0.11) on the S atom which could plausibly arise from one of the canonical structures of the dye molecule. It would still be difficult to assign the donated electron preferentially to either N or S since there could be one canonical structure with positive charge on the N atom.

Triplet-Triplet Absorption Figure 3 shows that the triplet-triplet absorption band of solid MB obtained by steady illumination changes with complex formation. A somewhat similar shift of the triplet-triplet band of MB was noticed in solution with change of pH. A comparison of the two effect shows that protonation presumably of the pyridine-like nitrogen n-orbital, and electron transfer from the same orbital have oppotite effects on the triplet-triplet transition. This seems quite reasonable since protonation would concentrate the $(n)sp^2$ electron cloud around the N-H^+ axis and thus reduce the overlap of the $(n)sp^2$ and the triplet π^* orbitals. On the other hand, the n-σ^* electron transfer would reduce the repulsion between the N-C σ-bonding pairs and the lone pair and thus increase the π^*-$(n)sp^2$ overlap.

Solubility The observation that the complex is highly soluble in $CHCl_3$ and insoluble in water is in contrast with the behavior of the dye itself. This may be explained by a close association between Cl^- and the dye cation resulting from an increased positive charge on the dye caused by electron transfer.





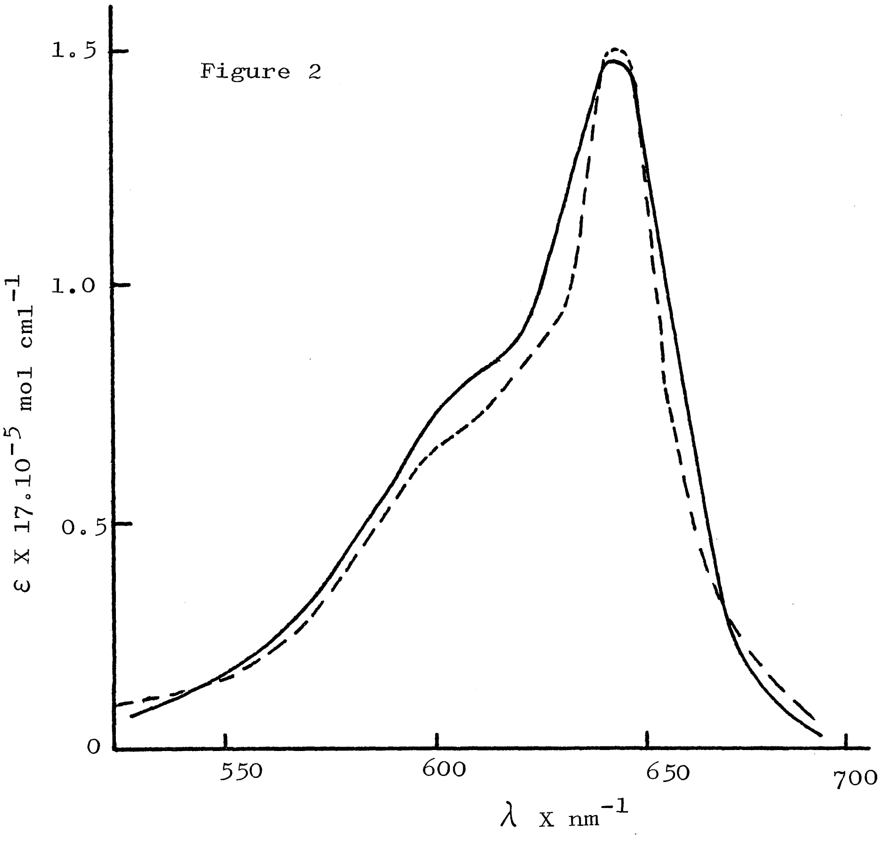


Fig. 1. Absorption spectra of methylene blue (curve 1), MBI_2 (curve 2), and I_2 (curve 3) in $CHCl_3$.

Fig. 2. Absorption spectra of MB and MBI_2 in $CHCl_3$.

Fig. 3. Triplet-triplet absorption spectra of solid MB (1) and MBI_2 (2).

REFERENCES

1) R. Foster, "Organic Charge Transfer Complexes", Academic Press, 1969, p. 216.
2) R. S. Mulliken, Recl. Trav. Chim. Pay-Bas. Belg., 75, 845(1956).
3) C. Bodea and I. Silberg, Adv. in Heterocyclic Chemistry, 9, 329(1968).
4) G. Oster and N. Wotherspoon, J. Amer. Chem. Soc., 79, 4836(1957).
5) Y. Takahashi, K. Yabe, and T. Sato, Bull. Chem. Soc. Japan, 42, 2707(1969).
6) S. Sato, M. Morita, and M. Koizumi, Bull. Chem. Soc. Japan, 37, 117(1964).
7) A. Knowles and S. Gurnani, Photochem. Photobiol., 16, 95(1972).

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