The Temperature Dependence of Absorption Spectra of Cation Radicals of Benzidine and *N, N, N,' N'*-Tetramethyl-benzidine and Their Dimerization in Solution

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Detailed spectroscopic studies of cation radicals of *p*-phenylenediamine and its methyl derivatives have already been reported,[1-4] but those of benzidines have not yet been obtained. In the present letter, the absorption spectra of the cation radicals of benzidine (I) and *N, N, N', N'*-tetramethyl-benzidine (II) are reported.

Bromides of radicals, which were obtained by oxidation of their parent bases by bromine, were used for this study. Alcoholic solutions of the two radicals were stable enough to obtain quantitative spectrophotometric data below 0°C, although they gradually decomposed at room temperature.

Spectra of the alcoholic solution of II are shown in Fig. 1. Spectra of the solution of I (not shown here) are very similar to those of II except that the A band of II is shifted towards longer wavelengths compared with the corresponding band of I. This red shift of II is perhaps due to the hyperconjugation effect of the methyl groups. Therefore, we suppose that the A band has a transition moment oriented towards the longer molecular axis.

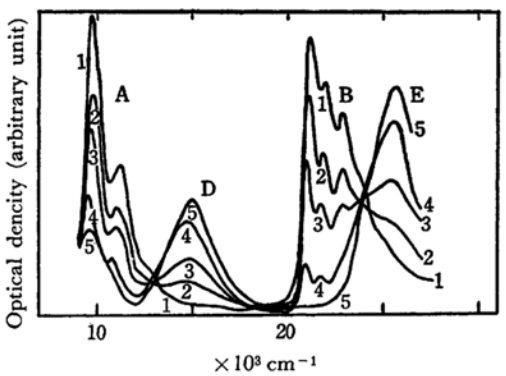

Fig. 1. Spectra of *N, N, N', N'*-tetramethyl-benzidine radical in ethanol.
Curve 1: 25°C, 2: −47°C, 3: −56°C, 4: −77°C, 5: −117°C

The temperature dependent spectra of II were analyzed by assuming an equilibrium $nR^+ \rightleftarrows R_n^{n+}$. Intensity data at each temperature are best fitted by assuming n values between 2.0 and 2.3. Therefore, it is concluded that the radicals form dimers as in the case of phenylenediamines at low temperature. The heat of dimerization of II is estimated to be 13 kcal/mol from the above analysis.

A similar analysis of I leads to the same conclusion, but the data contain greater experimental error. The heat of dimerization of I agreed with that of II within the error (±1 kcal/mol).

It is interesting to add that the heat of dimerization of tetramethyl-*p*-phenylenediamine radical (5 kcal/mol) is smaller than that of *p*-phenylenediamine (8 kcal/mol).

The spectra of solids of I and II are compared with those of their solutions at low temperature in Fig. 2. The solid spectra are very different from those of the solutions at room temperature (the monomer spectra), and have some resemblance to those at low temperature (the dimer spectra). The bands of the solids are, however, shifted towards the red. These suggest that the radicals in the solids interact strongly with each other and exist as dimers of some kind.

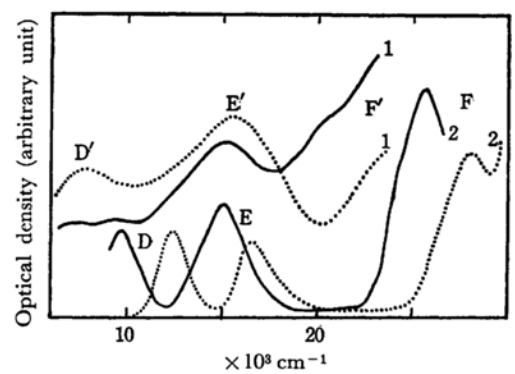

Fig. 2. Spectra of solids and low temperature solutions of benzidine cation radical (·····) and *N, N, N', N'*-tetramethyl-benzidine cation radical (——).
Curve 1: solids (25°C), 2: solutions (about −117°C)

More detailed experimental and theoretical research is now in progress in this laboratory.

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