Molecular Complex between Two Free Radicals. A Complex between the *p*-Phenylenediamine Cation Radical and the *N,N,N′,N′*-Tetramethyl-*p*-phenylenediamine Cation Radical

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Dimerizations of the cation radicals of *p*-phenylenediamine and its analogues[1-6] have already been studied by spectroscopic[1-4,6] and ESR[5] techniques. In the present communication, a spectroscopic study of a molecular complex formed between the cation radical of *p*-phenylenediamine (PD^+) and that of *N, N, N′, N′*-tetramethyl-*p*-phenylenediamine ($TMPD^+$) will be reported.

The temperature and the concentration dependence of the UV and visible spectra of solutions containing PD^+ and $TMPD^+$[*1] were determined by using a Cary Model 14 recording spectrophotometer. From the analyses of these results, it was concluded that a (1 : 1) molecular complex $(PD^+)_1(TMPD^+)_1$ is formed below −80°C. A typical run is shown in Fig. 1. The spectrum at room temperature is only a weighted sum of the spectra of PD^+ and $TMPD^+$. The spectrum at −195°C consists of three new bands (C, R′, and Y′) which are characteristic of the complex. The spectra in the intermediate-temperature range may be explained as sums of the absorption bands of PD^+, $TMPD^+$, $(PD^+)_2$, and the complex.[*2]

The spectrum of the present complex closely resembles those of the dimers of PD^+ and its methyl-derivatives.[1] The ν_{max} and the heat of complex formation (which was obtained from the temperature dependence of the equilibrium constant determined from the above spectra) of the present complex are compared with those for the above dimers in Table 1.

From these results, it may be considered that the present complex is formed by the pairing action of odd electrons in the PD^+ and the $TMPD^+$, and that the C band is due to a charge-transfer transition[7] between the covalent (PD^+-$TMPD^+$) and charge-transferred states (resonance between PD^{2+}-TMPD and PD-$TMPD^{2+}$).

More detailed research is now progress at this laboratory.

TABLE 1

Substance	ν_{max} (kK) of absorption C	R′	Y′	Heat of complex formation (or dimerization)
$(PD^+)_1(TMPD^+)_1$	14.7	24.0	34.8	*ca.* 6.0 kcal/mol
$(PD^+)_2$	16.5	27.4	36.0	8.0
$(DMPD^+)_2$	15.0	24.3	35.3	10
$(TMPD^+)_2$	13.1	19.7	32.1	5.0

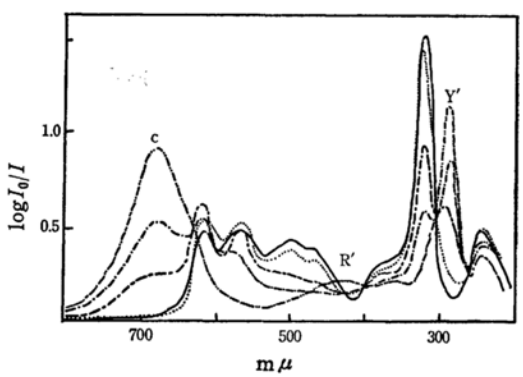

Fig. 1. Temperature dependent spectra of a solution containing PD^+ (0.347 mol/*l*) and $TMPD^+$ (0.430 mol/*l*). Solvent used was a ethanol-ethyl ether (2 : 1) mixture. Molar ratio $[PD^+] : [TMPD^+] = 0.807 : 1$.
—— 25°C, ····· −87.9°C, —·— −114.2°C, —·— −128.5°C, —··— −159.2°C

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*1 PD bromide and TMPD perchlorate were used.

*2 Amount of $(TMPD^+)_2$ was very small in these conditions.