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October 31, 1967

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Charge Transfer Complexes with Hexafluorobenzene and
Pentafluorobenzonitrile as Acceptor Components*

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October 31, 1967

Charge transfer associations are a well-established phenomena and a rather extensively investigated one also.¹ Since the acceptor component of such complexes normally does not exist as a liquid under standard conditions,² we wish to report on two organic liquids which function as acceptor components with suitable complimentary molecules.

As indicated in Figure 1 (the presence of an extended shoulder in the spectra of the mixture), pentafluorobenzonitrile (PFBN) complexes with N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD), with N,N-dimethylaniline (DMA), and with phenothiazine in cyclohexane. In addition, crystalline complexes of TMPN-PFBN and DMA-PFBN are obtained when the pure materials are mixed.

These two organic bases also form solid complexes with hexafluorobenzene (HFB) when the materials are mixed in the pure state in a ratio of 1:1. However, new absorption bands are not detected in the spectra (in cyclohexane solutions) of mixtures of TMPD or DMA with HFB. When HFB is used as a solvent for TMPD or DMA, the solutions are visibly yellow. However, with time a reaction occurs as evident by the formation of a black precipitate.

The solid complex formed between TMPD-PFBN, which is orange, was analyzed by a combination extraction and spectroscopic method and by vapor phase chromatography and found to contain a ratio of the two components of 1:1 which agrees with an elemental analysis of this complex.

Analysis of DMA-PFBN or DMA-HFB complexes were complicated by the presence of excesses of the liquid components on the crystalline complexes. When attempts are made to dry the crystals, the crystals dissociate as the excesses evaporate until the crystals and the two components totally disappear. The TMPD-HFB complex was not analyzed. The complex between phenothiazine and PFBN was not isolated as a crystalline material.

The association constants for the TMPD-PFBN and DMA-PFBN complexes were determined according to the method of Hildebrand and Benesi.³ The data obtained for these complexes, plotted according to the Hildebrand-Benesi equation, are shown in Figure 2. The association constants and extinction coefficients are given in Table I.

Although the NMR spectrum of the TMPD-PFBN complex suggested that free radicals were present in this complex (evidenced by line broadening compared to TMPD in CCl_4), no radical species could be detected by EPR in any of the complexes reported here; either in solution or in the solid complexes. Nor did illumination with ultra-violet or visible light produce a detectable level of paramagnetic species.

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2. G. Briegleb, Electron-Donator-Acceptor Komplexe, (Springer, Berlin, 1961).
3. H. Benesi and J. H. Hildebrand, J. Am. Chem. Soc. 70, 2832 (1948); 71, 2703 (1949).

TABLE I. Association constants and extinction coefficients for
TMPD-PFBN and DMA-PFBN complexes

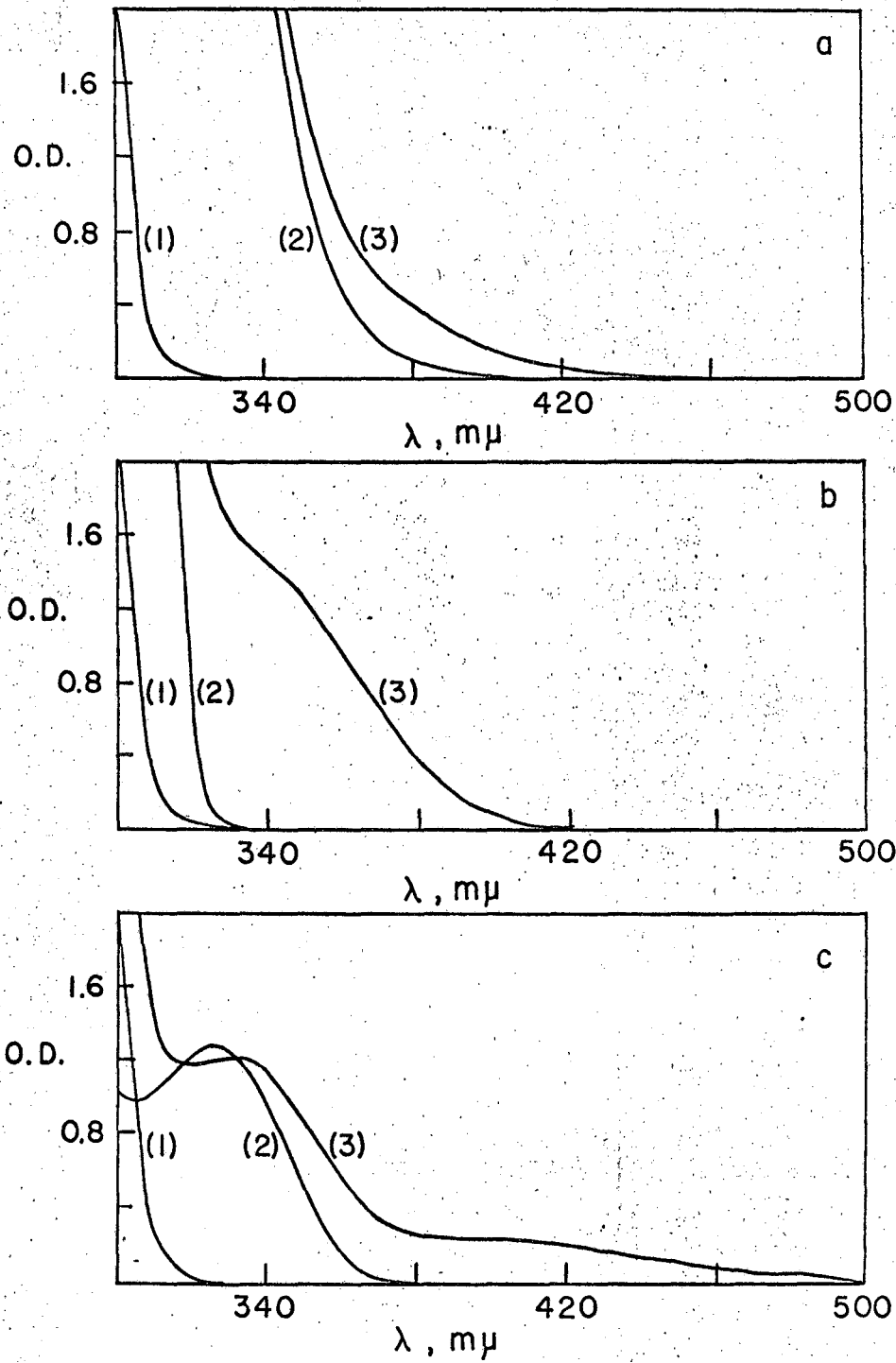
| Concentrations | | | K | | |
|-----------------------|-------------------------------|-------------------------------|------------|-----------|-------------|
| PFBN | TMPD | DMA | ($m\mu$) | (moles/l) | (1/mole cm) |
| 0.08 to 0.73 <u>M</u> | 5.0×10^{-4} <u>M</u> | 0 | 380 | 4.0 | 800 |
| " " " | " " | 0 | 400 | 4.1 | 700 |
| " " " | " " | 0 | 420 | 4.3 | 600 |
| ----- | | | | | |
| 0.07 to 0.66 <u>M</u> | 0 | 4.5×10^{-3} <u>M</u> | 340 | 2.7 | 500 |
| " " " | 0 | " " | 350 | 3.1 | 400 |
| " " " | 0 | " " | 360 | 3.1 | 310 |

The cell path length was 1 cm in all these experiments.

Figure Captions

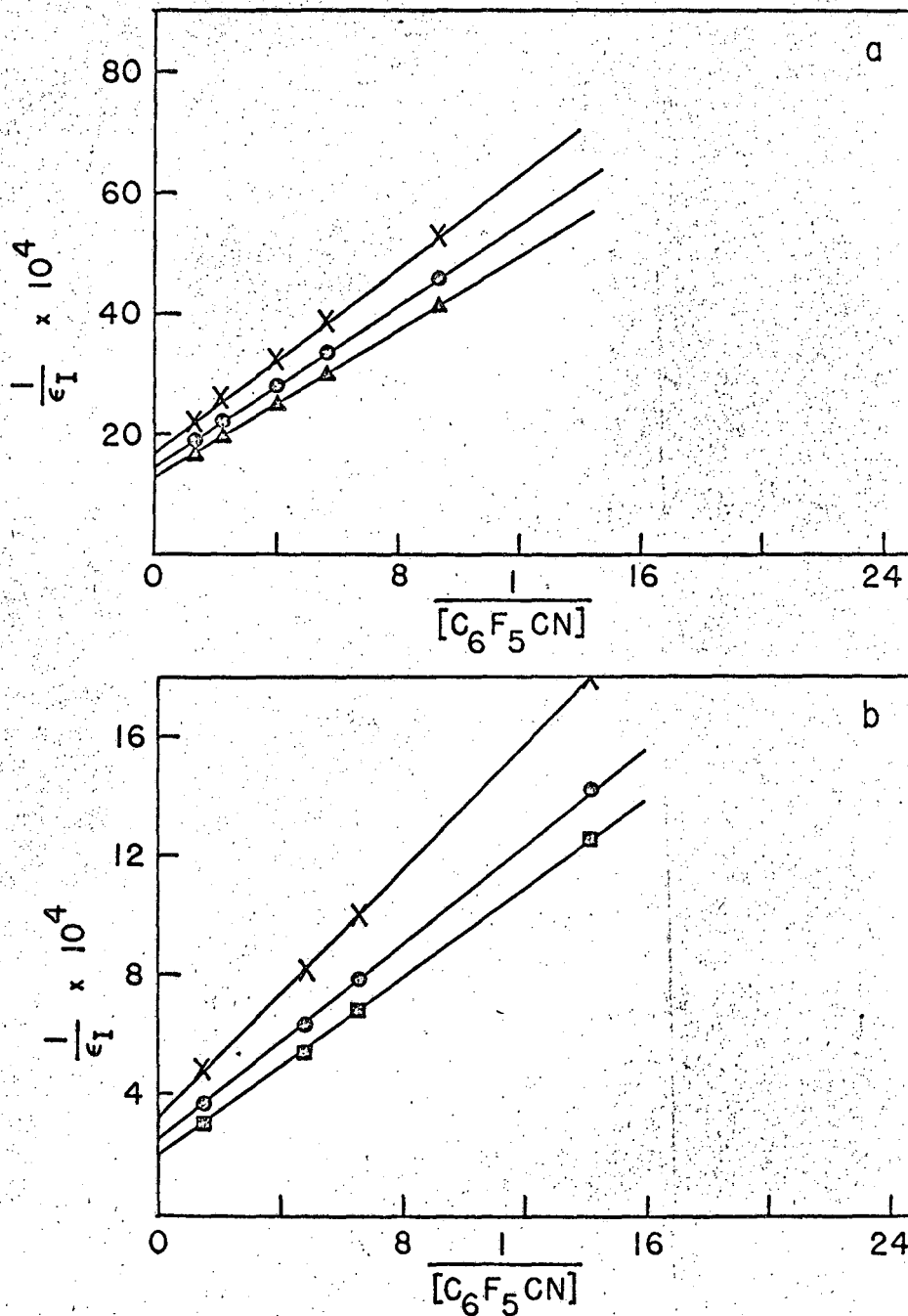
Figure 1. Optical spectra in cyclohexane in one cm cells. (a) 1. 0.74 M PFBN, 2. 1.3×10^{-3} M phenothiazine, 3. mixture of 1.3×10^{-3} M phenothiazine and 0.11 M PFBN. (b) 1. 0.74 M PFBN, 2. 4.5×10^{-3} M DMA, 3. mixture of 4.5×10^{-3} M DMA and 0.66 M PFBN. (c) 1. 0.74 M PFBN, 2. 5.0×10^{-4} M TMPD, 3. mixture of 5.0×10^{-4} M TMPD and 0.74 M PFBN.

Figure 2. Hildebrand-Benesi plots of charge transfer absorption. (a) TMPD-PFBN complex at 380 $m\mu$ (closed triangles), 400 $m\mu$ (closed circles), and 420 $m\mu$ (crosses). (b) DMA-PFBN complex at 340 $m\mu$ (closed squares), 350 $m\mu$ (closed circles) and 360 $m\mu$ (crosses).



XBL 679-6137

Fig. 1



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Fig. 2

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