

mean values were used in calculating f ; this increased 20% without increase in bandwidth. ΔH was between 2 and 7 kcal/mole at various pressures but the values are too approximate to establish any trends.

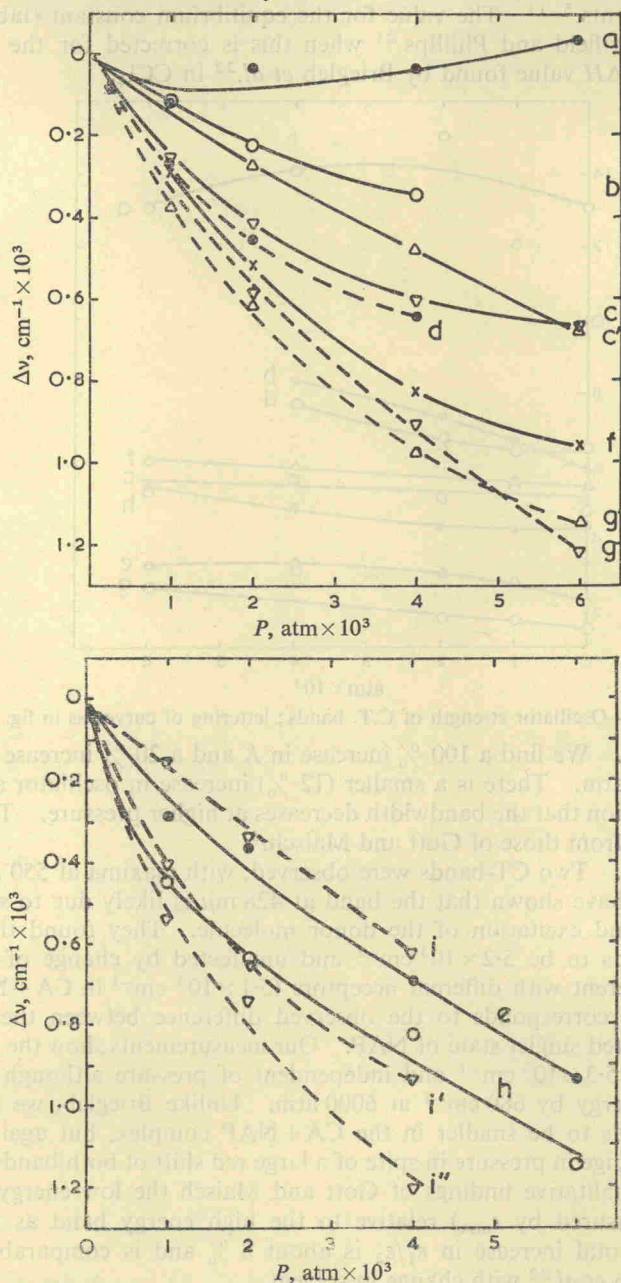


FIG. 3.—Pressure shift of C.T. absorption maxima. In methylene chloride except where indicated. (a) TCNE+HMB; (b) CA+HMB, (MCH); (c) and (c'), first and second max. of TCNE+NAP; (d) TNB+HMB (MCH); (e) CA+PYR; (f), TCNE+BEN; (g) and (g'), first and second max. of CA+NAP; (h), TNB+NAP, (i), (i'), (i'') TNB+ANT in CH_2Cl_2 , MCH, EtOH respectively.

TCNE+HMB. This system could not be measured in MCH because of the low solubility of TCNE in this solvent. The pressure shift of the CT-maximum in CH_2Cl_2 is unusual in going through a minimum and our observations confirm earlier measurements.^{5, 11} The value for the equilibrium constant (table 1) agrees with that¹⁰ of Merrifield and Phillips²¹ when this is corrected for the temperature difference by the ΔH value found by Briegleb *et al.*²² in CCl_4 .

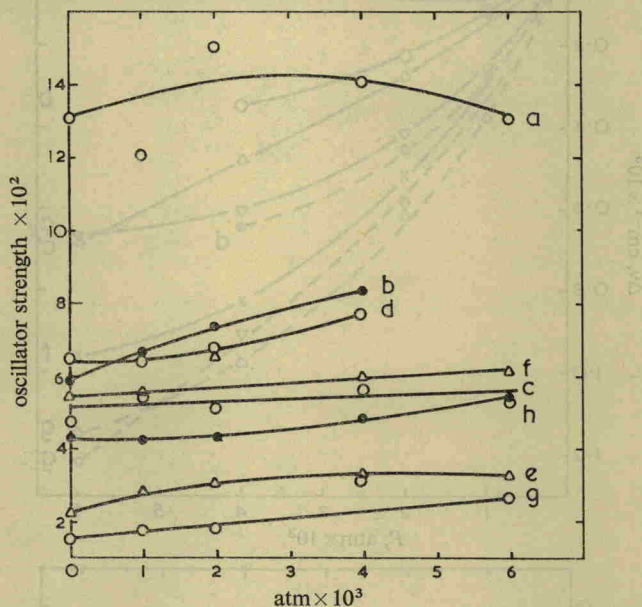


Fig. 4.—Oscillator strength of C.T. bands; lettering of curves as in fig. 3.

TCNE+BEN. We find a 100 % increase in K and a 20 % increase in ϵ for this complex at 6000 atm. There is a smaller (12 %) increase in oscillator strength and thus some indication that the bandwidth decreases at higher pressure. The quantitative results differ from those of Gott and Maisch.⁵

TCNE+NAP. Two CT-bands were observed, with maxima at 550 and 428 $m\mu$. Briegleb *et al.*²² have shown that the band at 428 $m\mu$ is likely due to simultaneous CT absorption and excitation of the donor molecule. They found the difference between the bands to be $5.2 \times 10^3 \text{ cm}^{-1}$ and unaffected by change of solvent and only slightly different with different acceptors ($5.1 \times 10^3 \text{ cm}^{-1}$ in CA+NAP). This energy difference corresponds to the observed difference between the lowest and the strongest excited singlet state of NAP. Our measurements show the gap between the bands to be $5.3 \times 10^3 \text{ cm}^{-1}$ and independent of pressure although both bands shift to lower energy by 680 cm^{-1} at 6000 atm. Unlike Briegleb, we find the gap between the bands to be smaller in the CA+NAP complex, but again to remain constant with change in pressure in spite of a large red shift of both bands. In agreement with the qualitative findings of Gott and Maisch the low energy band gains intensity (as measured by ϵ_{max}) relative to the high energy band as the pressure increases. The total increase in ϵ_1/ϵ_2 is about 8 % and is comparable with that found by Briegleb *et al.*²² with change in solvent.

TNB+NAP. The TNB absorption overlaps the CT bands, and even after correction for this only the low energy band could be measured. The correction usually was a large part of the measured optical density and the accuracy of the results, particularly those at low pressure, is low.