

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

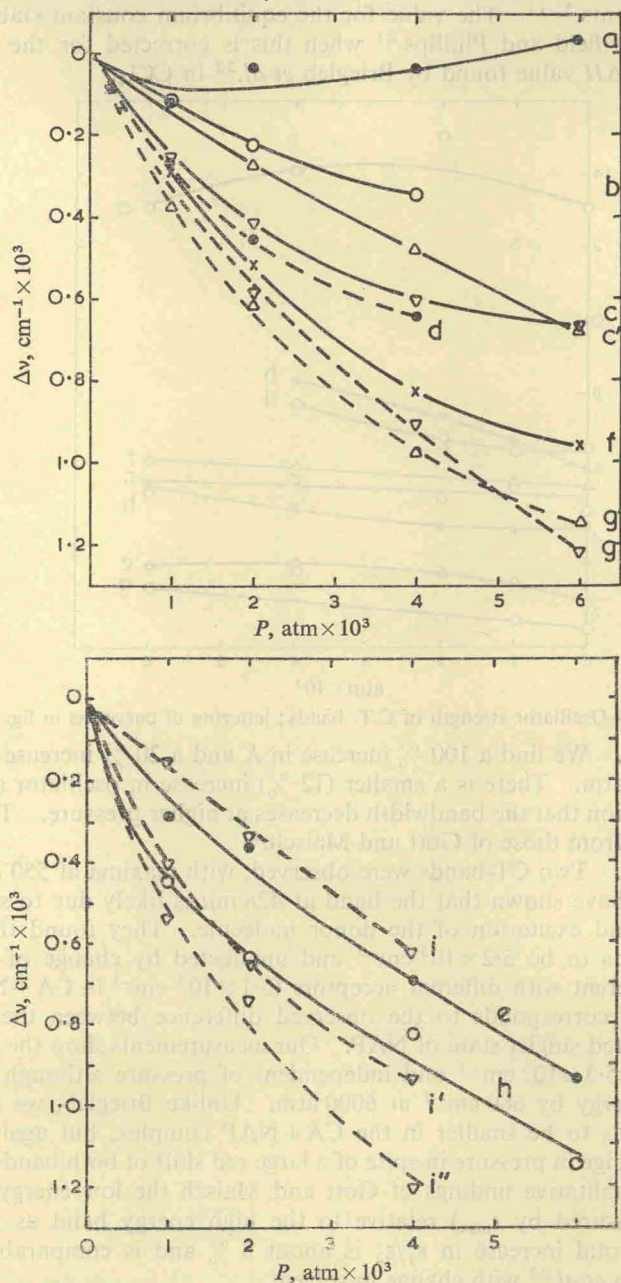


FIG. 3.—Pressure shift of C.T. absorption maxima. In methylene chloride except where indicated. (a) TCNE+HMB; (b) CA+HMB, (MCH); (c) and (c'), first and second max. of TCNE+NAP; (d) TNB+HMB (MCH); (e) CA+PYR; (f), TCNE+BEN; (g) and (g'), first and second max. of CA+NAP; (h), TNB+NAP, (i), (i'), (i'') TNB+ANT in  $\text{CH}_2\text{Cl}_2$ , 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  $\text{CH}_2\text{Cl}_2$  is unusual in going through a minimum and our observations confirm earlier measurements.<sup>5, 11</sup> The value for the equilibrium constant (table 1) agrees with that<sup>10</sup> of Merrifield and Phillips<sup>21</sup> when this is corrected for the temperature difference by the  $\Delta H$  value found by Briegleb *et al.*<sup>22</sup> in  $\text{CCl}_4$ .

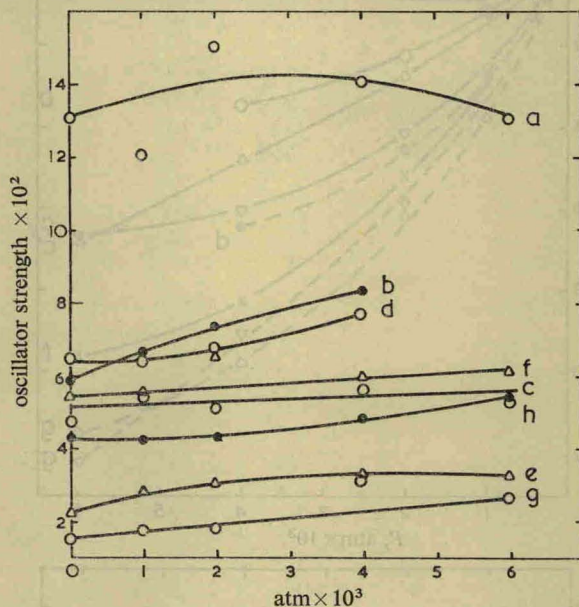


Fig. 4.—Oscillator strength of C.T. bands; lettering of curves as in fig. 3.

TCNE+BEN. We find a 100 % increase in  $K$  and a 20 % increase in  $\epsilon$  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.<sup>5</sup>

TCNE+NAP. Two CT-bands were observed, with maxima at 550 and 428  $m\mu$ . Briegleb *et al.*<sup>22</sup> 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  $680 \text{ cm}^{-1}$  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  $\epsilon_{\text{max}}$ ) relative to the high energy band as the pressure increases. The total increase in  $\epsilon_1/\epsilon_2$  is about 8 % and is comparable with that found by Briegleb *et al.*<sup>22</sup> 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.