are parallel to each other in a more or less symmetrical arrangement and the distance between the planes of the molecules is 3·45 Å. In CA + HMB the molecular planes are also parallel and the distance between them is 3·51 Å, but there is only incomplete overlap between the components. One can calculate the volume change associated with the formation of the complexes from their components by using Wallwork's distances and van der Waals radii [26] to calculate the van der Waals volumes of the separate components and the complexes. Using projected areas of the component molecules multiplied by the thickness of the molecules (thickness of HMB 4·0 Å, CA 3·6 Å, TNB and ANT 3·4 Å) one finds for TNB + ANT, $\Delta V = -3$ cm^3 mole^{-1} and for CA + HMB, $\Delta V = -13$ cm^3 mole^{-1}. The first is in exact agreement with the value found from the pressure dependence of the equilibrium constant, while the second is slightly more negative; this difference may be due to neglecting the incomplete overlap of CA and HMB in calculating the volume of the complex. The general agreement of ΔV calculated from the structure of the solid complex and the measurements in solution is consistent with the assumption that similar complexes are formed in the two cases. The magnitude of ΔV is connected with the magnitude of K, but exceptionally large values of ΔV can occur where steric effects prevent the formation of a strong complex (see PIC + ANT above).

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