

Molecular Complexes, 14. Isomeric Arene Complexes of Caffeine and 1,3,7,9-Tetramethyluric Acid Detected with Toluene. Polar Interactions Inverted with Hexafluorobenzene

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Stacking of an arene D on caffeine (**1**) near 7-Me and 8-H is known (^1H NMR shifts, CCl_4 , AUS concept) to yield the same association constant K for each signal of **1**. Toluene (**T**) and **1** now yielded the same K from 7-Me and 8-H while K from 1-Me (and 3-Me) is smaller indicating a minor stacking centre near N-1 that forms both **1T** and **1T₂**; this **1T₂** disturbs computations of K . The main stacking centre forms no **1T₂** since its **1T** is stabilized by dipole-dipole interaction. Diphenylmethane **Dp**, a substituted **T** that cannot form a dimer of type **T₂**, does not form **1Dp₂**. Ethyl of 1-ethyltheobromine (**2**) is proven to stand perpendicular so that the above minor complex can only arise on one face of **2** halving K_{minor} and making the disturbance of computations by **2T₂** insignificant; apart from this minor **2T** there are *cis-trans* isomers of the main complex. Stacking of **1** and **2** with larger arenes is discussed in terms of relative molecular sizes under consideration of the perpendicularly placed ethyl group of **2**. Stacking of D near N-3 and N-9 of 1,3,7,9-tetramethyluric acid (**4**) is known. **4** and **T** now provided $K = 0.218 \text{ l mol}^{-1}$ from 3-Me and 9-Me but $K = 0.157 \text{ l mol}^{-1}$ from 1-Me and 7-Me. This and the complex induced shifts IK indicate formation of stacking **4T** + **4T₂** and of two edge-on **4T** standing on 3-Me and 9-Me under dipole-dipole interaction with a neighbouring oxygen. The oxygens of **4** (and probably of **1**, too) form edge-on complexes with hexafluorobenzene; this underlines the importance of polar effects.

Key words: Arene Complexes in CCl_4 , Formation Constants, Topologies